INVESTIGATION ON TRANSPORT MECHANISMS AND INTERFACIAL PROPERTIES OF SOLAR CELLS BY SIMULATION

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INVESTIGATION ON TRANSPORT MECHANISMS AND INTERFACIAL PROPERTIES OF SOLAR CELLS BY SIMULATION

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Dissertation

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ABSTRACT

Understanding the charge transport mechanisms and interfacial properties of solar cells is a prerequisite to decipher the working mechanism and improve the performance of photovoltaic devices. In order to increase the power conversion efficiency of dye sensitized solar cells (DSSCs) and polymer-based hybrid photovoltaic, experimental approaches have been widely used to change the chemical recipe and morphology of photovoltaic components. The introduction of simulation approaches to experimental researchers provides new ground to analyze the laboratory results and guide in research directions for dye sensitized solar cells. As mainstream materials simulation techniques, molecular dynamics simulation, Monte Carlo simulation and quantum mechanical calculations can only investigate some components of organic photovoltaic cells rather than the device level. Therefore, advanced models to simulate the mechanisms and characteristics of organic solar cells at the device level are needed.

We propose a coarse grain model based on a molecular dynamics (MD) simulation protocol, to simulate the function and performance of dye sensitized solar cells at the nanoscale. In a multiscale, coarse-grain model for dye sensitized solar cells, the MD code LAMMPS is modified to represent the photovoltaic procedures in dye-sensitized solar cells. An approximate force field is developed to describe the interactions between the
different components of the dye sensitized solar cells, whereby electrons and holes are treated as explicit particles of low mass and all other components at a coarse-grain level. The model was employed to trace transport mechanisms of charge carriers, calculate the relation between current intensity and voltage, and explore the mobility of electrons. The model offers a path to simulate the charge generation and recombination processes and power conversion efficiencies of the dye sensitized solar cells by a MD simulation protocol at the device level. With this new model, we analyzed semi-quantitatively the main factors determining the current intensities and performances of dye sensitized solar cells. The simulation results show current-voltage curves that are similar to experimental results and the power conversion efficiencies of the coarse grain model can be related to real devices. The interpretation of length and time scales remains somewhat challenging as the light intensity was chosen higher than that in the solar spectrum to shorten simulation times. Nevertheless, this DSSCs coarse grain model is a promising method to study and potentially predict the performance of photovoltaic devices.

We also employ MD simulation approaches to explore the surface properties of core-shell cadmium sulfide nanoparticles immersed in semiconducting polymers. Investigation of the interfacial structure of surface-modified cadmium sulfide nanoparticles in contact with several substituted poly(phenylene ethynylene)s helped identify the preferred location of functional groups and the impact of cross-links between the polymer and the nanoparticle. Simulation results show that polymers with long alkyl side chains containing hydroxyl groups were the best candidates to approach the trimethoxysilyl shell of the cadmium sulfide nanoparticle surfaces and to form covalent links.
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CHAPTER I

BACKGROUND AND MOTIVATION

Energy is the significant source to fuel the increase of industry. Most of the traditional
energy is non-renewable resource. Energy issues become a new challenge for the
human being since by current energy consuming speed, the natural source only lasts
for less than one century. How to achieve sustainable energy supply without
consuming fossil fuels or reducing consumption become the main research topics for
the scientist all around the world.

Renewable energy comes from natural resources, such as sun irradiation, geothermal
heat and tides movement. For time being, solar radiation, along with secondary solar
powered resources, such as wind and wave power, hydroelectricity and biomass,
makes up the major part of renewable energy on earth. Although there are a lot of
hydroelectric power plants, wind power plants all over the world, only a minuscule
fraction of the available solar energy is exploited. Because the popularity of the
source depends on four dimensions: supply; storage; larger interconnections between
adjacent markets; demand-side management empowered through intelligent energy
networks including, for instance, smart grids.\footnote{1}
Solar photovoltaics (PVs) have proven to be a major technology to utilize the solar energy. Until recent years, PV products have been commercialized and enter into market in large scale. PV products can provide sustainable and clean electricity, which can contribute to global goal to cut emissions and mitigate climate change. Seeing the vast potential of the application of solar electricity by PVs, more and more countries develop new solar PVs technology and promote the use of PVs product as the implement for traditional energy.

The development of solar PVs has experienced three importance stages. Although there is no strict dividing line for the different stages of PV products, PV industry always classify the PV products to three generations. The first generation is made from basic crystalline silicon; the second generation introduced the thin film technology, including amorphous silicon, multi-junction thin silicon film, cadmium telluride (CdTe) thin film, copper, indium, gallium, selenide/sulphide (CIGS) and copper, indium, selenide/sulphide (CIS); the third generation includes organic PVs, dye-sensitized solar cells (DSSCs) and concentrator PVs.

Today about more than 95% percent of the solar electricity is produced by Si-based solar cell. Si-based solar cells, including mono- and multicrystalline Si-based solar cells, occupy about 90% of the market share. The photovoltaic industry has to depend on the needs of the semiconductor industry. The reason is that the products of the
The semiconductor industry offer a much larger value per area of the product than the solar cells. Thus semiconductor industry can afford to pay more budgets to the silicon manufacturers. In addition, the decrease of Si availability has pushed scientists to develop new thin film solar cells based on CIGS or CdTe to compete with the fast growth rate of traditional Si solar cells. But these new solar cells do not increase obviously in their market share. Therefore, the research on cheap and reliable alternatives to Si-based cells is necessary.

The race to develop cost-effective solar cells has boosted a lot of innovation. As a result, more and more smart products come into market. DSSC is one of the most advanced solar cells, with wonderful efficiency as much as 11%, a level believed high enough for commercial use. DSSCs are based on TiO₂, a kind of non-toxic semiconductors, which can be sensitized with some organic dye. In contrast to conventional Si-based photovoltaic devices, DSSC converts light energy to electricity on a molecular level, similar to natural photosynthesis. It's the first example of an artificial "molecular machine" in a commercial application.

Since the 1970's, attempts had been made to design a solar cell by the idea of photosynthesis. In the early attempts, a layer of chlorophyll was employed to cover crystals of titanium dioxide. However, the electrons were not easy to move across the layer of pigment. Thus for the solar cells fabricated in this method, the power
efficiency was about 0.01%. Until in 1988 at École Polytechnique Fédérale de Lausanne in Switzerland, Prof. Michael Grätzel used nanotechnology and then overcame this problem. Instead of choosing a single bulk TiO₂ semiconductor, he investigated on small particles, about twenty nanometers in diameter, coated with an extremely thin layer of pigments. So the effective surface area available for absorbing the light could be increased several times by this method. The improvement in the light harvesting of the cell and conversion efficiencies of 7% trigged extensive research activities on this cell concept.

It is more than 20 years since the introduction of the concept of Grätzel solar cell. Although the power conversion efficiency of DSSC is almost doubled in the previous 20 years, it cannot beat traditional inorganic solar cells. In order to break the bottleneck of power conversion efficiency, some new ideas and innovative concepts have been proposed. Some are available for the commercial implementation of the DSSC. Today enterprisers and scientists work together to improve the performances and reduce the cost of DSSCs. In future DSSCs can give us more clean energy and become more and more popular.
CHAPTER II

INTRODUCTION OF DYЕ SENSITIZED SOLAR CELLS AND CADMIUM SULFIDE-BASED SOLAR CELLS

This chapter targets to review the structure, working mechanism and problems of current DSSC. We start from the working principle of DSSC, which explains how the device performs step by step. Then we list some issues and practice problems in most DSSCs, from which the industrial requirement and commercial requirement of solar cells. In the last part, we focus on the major components of DSSC. Their functions, performances, improvement solutions have been discussed in details. At the mean time, the features and applications of cadmium sulfide-based solar cells are also introduced.

2.1 Historical developments of DSSCs

In retrospect, the ancestor of modern DSSC is the chlorophyll sensitized zinc oxide cell in 1972. By injecting the charge of exited dye molecules into ZnO -- a kind of wide gap semiconductor, photons can be converted into an electric current. In the following years, Matsumura et al.\textsuperscript{15} and Alonso et al.\textsuperscript{16} started to use sintered ZnO as
the electrodes for solar devices to increase the performances. The technique issue is the low efficiency of solar cell since only a small dram of the incident light can be absorbed by a monolayer of dye molecules on the flat electrode surface, even as low as less than 1%. In 1985, Desilvestro, Grätzel, Augustynski and their cooperators used dye-sensitized fractal-type TiO$_2$ electrodes with high surface area$^{17}$. New findings of Grätzel in 1991 introduced the nanoparticulate porous TiO$_2$ to academic community and increase the light harvesting efficiency to almost 7.1%$^{2}$. These significant improvements triggered a new boom in developing advanced solar cells. In 1993, N3 black dye was introduced by Nazeeruzzin for DSSCs with efficiency as much as 10.3%$^{18}$. Solaronix, a Swiss company started to sell the materials for DSSCs at the end of 1990s: titania pastes, dyes, staining additives, electrolytes, ionic liquids, electrode materials and sealing materials. This promotes the research on DSSCs because more and more scientists make use of nanostructure titania and ruthenium dye as to develop new DSSCs. In the following 10 years, a great number of materials, including dyes, electrodes, electrolytes have been tested and tried to increase the efficiency and stability. In 2001, Nazeeruzzin found that DSSC using “black dye” can reach the efficiency as high as 10.4%$^{19}$. After that, black dye has attracted a lot of attentions. In 2005, Wang utilized black dye to make the DSSC with 10.5% efficiency$^{20}$. At the same year, a new dye called N719 was synthesized and applied to DSSCs. Nazeeruzzin reported the efficiency with 11.2% can be achieved by using dye N719$^{21}$. In 2006, Chiba has reported a DSSC with black dye can reach the efficacy of
11.1% 22. During the last 5 years, the appearance of new ruthenium complexes furnished with an antenna function, such as dye Z991 and C101, have increased the efficiency of DSSCs. These dyes have higher extinction coefficients and their spectral response is shifted to the red 23. In 2011, the efficacy has reached as much as 12.3% 24, which is about 5% increase compared to the work which of 20 years ago. PV community believes that the theoretical limit for DSSCs efficiency could be 30% and there is still a lot of space to increase. However, the mechanisms of DSSCs are not unlocked completely by now. So how to increase the efficiency becomes a major challenge for the materials scientist. In order to solve these issues, the working principles of DSSCs have to be analyzed first.

2.2 Working principles and mechanisms of DSSCs

We choose classical DSSCs as our discussion objective. The components include TiO2 as semiconductor, dye as sensitizer, I-/I3− as electrolytes. The schematic diagram of DSSC working principle is shown in Figure 2.1. The working principle of the DSSCs includes six steps.
Figure 2.1 Schematic of working principle of DSSC. The number indicates the basic electron transfer processes. At the internal of the DSSC, the arrows represent the moving direction of electrons between different energy level. VB means valence band, CB means conduction band. Number represents different reaction.

Reaction 1. Electrons Excitation

The ruthenium dye (sensitizer), as the primary absorber of sunlight, can be excited by visible radiation. When the sensitizer adsorbs a photon, an electron will be excited from ground state S to a higher energy level state $S^*$. If the onset of the adsorption for the dyes is about 750 nm wavelength, the photon energy corresponds to 1.72eV. The lifetime of the exciting procedure is at nanosecond timescale and the typical value for
ruthenium-complexes used in DSSCs is 20~60ns \(^{25}\). Generally speaking, the excited state could be deactivated at high iodine concentration environments \(^{26}\).

Reaction 2. Electrons Injection

Electrons can be injected from the excited ruthenium complexes into the conduction band of the TiO\(_2\) to generate free charge carriers. The timescale of this procedure is in the femtosecond range. After the injection reaction takes place, the energy level of dye can be increased as high as 0.2 eV ~ 0.3 eV above the energy level of TiO\(_2\) conduction band. At the mean time, the oxidized sensitizer molecules will be reduced by electrons in conduction band as back reaction, which occurs much slower than injection, as low as \(\mu s \sim ms\) timescale. This huge difference results to the efficient charge separation in solar cell. The reduction reaction corresponds to the reaction 0 in Figure 2.1.

Reaction 3. Transportation through mesoporous TiO\(_2\) layers

After injected into the conduction band of TiO\(_2\), electrons will percolate through the nanoporous TiO\(_2\) layer containing spherical anatase particles to the conductive support. This charge transport phenomenon is highly efficient. The diameter of spherical anatase is about 20 nm and the thickness of the TiO\(_2\) layer is about 10 \(\mu m\). The charge transport reaction is labeled as 3 in Figure 2.1. By now, the charge transport phenomena are still under debate. One popular view for the electrons transportation in the TiO\(_2\) layer is that, the main transport mechanism is diffusion.
Once electrons arrive at the anode, they will pass through external load to reach the cathode. During their movement, electron flow performs work. In order to get the maximum power, external load has to be adjusted.

Reaction 4. Oxidized dyes regeneration

During the regeneration reaction, as the electron donor, the iodide can reduce the oxidized dye $S^+$ to its ground state $S$. Timescale of regeneration of the oxidized dye is in microsecond range. This stage has two steps:

$$2I^- + S^+ \rightarrow I_2^- + S \quad (2.1)$$
$$2I_2^- \rightarrow I^- + I_3^- \quad (2.2)$$

Reaction 5. Electrons recombination with oxidized dyes

After injected in to the conducting band of TiO$_2$, some electrons will recombine with acceptors in oxidized sensitizer, with time scale from microsecond to millisecond.

Reaction 6. Electrons recombination with electrolytes

Some electrons will recombine with the acceptors in the $I/I_3^-$ electrolyte with time scale at centisecond.
Reaction 7. Electrons reduction in cathode

After reaching the cathode via external load, electrons are then transferred to triiodide to yield iodide. Iodide/iodine redox couple is also called hole conducting medium. Generally platinum is employed as the catalyst in the procedure of reduction.

$$I_3^- + 2e^- \xrightleftharpoons{\kappa} 3I^- \quad (2.3)$$

The performance of DSSC depends on the efficiency, which depends on the different rate constants for iodine reductions at anode and cathode.

2.3 Major components of DSSCs

The major components include Anode, Sensitizer, Electrolytes and Cathode. FTO/ITO glass and TiO$_2$ constitute Anode; FTO/ITO – coated glass constitutes Cathode.

2.3.1 Titanium dioxide

In 1991, the application of mesoporous TiO$_2$ electrodes was found to improve the performances of DSSCs. In the following 30 years, different nanostructured metal oxide electrodes has been tried and tested, including ZnO, SnO$_2$, Nb$_2$O$_5$ and so one.

Today, nanoporous anatase TiO$_2$ has been chosen as the standard semiconductor in the first generation of commercial DSSC for its excellent performance. Titanium dioxide, also known as titania, is a kind of non-toxic inorganic semiconductor with wide band
gap and chemical stability. In our life, this kind of materials can be found in wall paint, pigment and tooth paste. As a photo-catalyst, it can also be used in anti-foggy coating on the surface of glass to split water since it will be excited with UV-irradiation. It has no photo-degradation phenomena upon excitation compared with other semiconductors, which have similar band gap. In DSSCs, TiO₂ plays an important role during the charge transfer. In nature, titanium dioxide exists in three forms: anatase, brookite and rutile. Anatase TiO₂ is the first choice as TiO₂ electrodes used in DSSCs because of higher band gap. Rutile TiO₂ has the highest thermodynamic stability in three structures.

For conventional solid-state semiconductor, a solar cell is made up from two types of doped crystals: n-type semiconductor, which provides extra free electrons and p-type semiconductor which provides extra hole. When these two types of semiconductor contacted, extra in n-type semiconductor will flow in p-type semiconductor. As the flow across the boundary, a new Fermi level will form, which results in p-n junction. When sunlight strikes the bound electron in n-type semiconductor, the photon will be excited and jump from valence band into conduction band. When there is a load, the electrons will move out of the n-type side into p-type side and lose energy via the external circuit, and back to the n-type where they can re-combine again with the hole in valence band. In this procedure, electrical current is created by sunlight.
For DSSC, the semiconductor (TiO₂) is used only for charge transport. While the sensitizer (dye) provides photoelectrons, rather than traditional solar cell, where the silicon is the source of photoelectrons and also provides the electric field to separate the charges and generate the current. Today, TiO₂ is still one of the most popular electrodes used for DSSCs. In recent years, a lot of progress is made on modifying its morphologies.

2.3.2 Sensitizer (Dye)

In DSSC the photoelectrons are provided by the sensitizer (photosensitive dye), which can be divided into metal complex, metal-free organic dyes. Ruthenium-complex is the most popular metal complex sensitizer used in DSSCs because of its unbeatable efficiency and stability. Other metal ions, such as Os, Pt, Cu, Fe and Re, have also been investigated to construct the metal complex sensitizers. A lot of significant dyes have been introduced in the CHAPTER 2.1, where we can see that dye is developing synchronously with the efficiency improvements of DSSCs. In Table 2.1, more ruthenium-complexes are listed.
Table 2.1  Major sensitizers used in DSSCs

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<th>Dye</th>
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<th>Wavelength for test (nm)</th>
<th>Power Efficiency</th>
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<td>N3</td>
<td>1993</td>
<td>14.2</td>
<td>534</td>
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<tr>
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<td>2003</td>
<td>11.1</td>
<td>525</td>
<td>7.3</td>
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<td>Z910</td>
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<td>16.9</td>
<td>543</td>
<td>10.2</td>
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<td>Z955</td>
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<td>519</td>
<td>8.0</td>
<td>Ref [31]</td>
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<td>N719</td>
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<td>N/A</td>
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<td>N621</td>
<td>2005</td>
<td>N/A</td>
<td>N/A</td>
<td>9.6</td>
<td>Ref [32]</td>
</tr>
<tr>
<td>K19</td>
<td>2005</td>
<td>18.2</td>
<td>543</td>
<td>7.0</td>
<td>Ref [33]</td>
</tr>
<tr>
<td>N945</td>
<td>2006</td>
<td>18.9</td>
<td>550</td>
<td>9.6</td>
<td>Ref [34]</td>
</tr>
<tr>
<td>K73</td>
<td>2006</td>
<td>18.0</td>
<td>545</td>
<td>9.0</td>
<td>Ref [35]</td>
</tr>
<tr>
<td>Black Dye</td>
<td>2006</td>
<td>N/A</td>
<td>610</td>
<td>10.8</td>
<td>Ref [36]</td>
</tr>
<tr>
<td>(N749)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Chemical structure of N3](image1.png)  
![Chemical structure of N712](image2.png)
Figure 2.2 Illustration of the chemical structures of mainstream ruthenium-dye used in DSSC devices
In order to achieve higher efficiency, the development of new dye is necessary and urgent. During the developments of new dye, the new products should consider four important factors: (1) Absorption spectrum; (2) Energy level of ground and exited state; (3) Charge injection and recombination rate; (4) Stability.

Absorption spectrum is the first factor considered by chemists. Wider absorption spectrum is what we are seeking for, since wider wave range means more photons to absorb. DSSC uses a wider range of the light spectrum than traditional solar cells, giving it the excellence ability to generate power from all kinds of visible light sources, not only at the range of sunlight, but also at relatively low levels of light intensity. Now the dye can not only absorb the spectrum of visible length, but also cover the near infrared. If chemists can synthesis novel dyes which can absorb waves at infrared range, the short circuit current can expect to enhance significantly.

Energy level is another important factor. After the dye is excited by the strike of sunlight, the ideal energy level of exited state should match to the low edge of conduction band of anatase TiO₂ to minimize energetic losses during electron transfer. Generally, energy level of the exited dye is 0.2 ~ 0.3 eV above the edge of conduction band, which can result to efficient charge injection. However, when a dye attached the surface of TiO₂, its energy level will change a bit. So the real condition is more complex.
Charge injection and recombination rate should never be neglected. In order to guarantee the efficient charge injection, the back reaction of a conduction band electron to the oxidized dye should be much slower than the reduction of the oxidized dye by the electrolyte. As a result, when the regeneration rate is a hundred times faster than recombination rate, it can ensure 99% injection yield.  

![Dynamic Competition](image)

Figure 2.3 Time scale of electron injection, transport, interfacial recombination and dye regeneration (Reference Source: [27] Journal of the American Chemical Society 1993, 115 (14), 6382~6390)

Stability is also very important. It includes three aspects: thermal stable, chemical stable and photostable, which decide the life span of PV devices. Photobleaching makes dye loss its function. An ideal dye may function 20 years or longer.
2.3.3 Electrolytes

During the early stage, liquid electrolytes are used to PV devices. Chemical stability, solubility and viscosity are most important three effects to be considered during the development of liquid redox electrolytes for DSSCs. In order to overcome the electrolyte leak problems in DSSCs, developing nonvolatile electrolyte become a good method. So later on, gel/polymer electrolytes, even solid electrolytes are applied to improve the performances.

Iodine based electrolytes are commonly used in DSSCs. In order to achieve high efficiency, chemists always change the solvents and additives. For the stability of electrolytes, it can be enhanced by the reduction of vapor pressure of solvent and the improvement of TiO₂-dye surface. High viscosity electrolytes generally have low leak risk. Triiodide is chosen as solute and solvent has a lot of choices, such as acetonitrile, propionitrile, methoxypropionitrile and so on. At the same time, other additives should also be added to increase electrolyte performance.

Ionic liquids, which have high conductivity and impressive vapor pressure at room temperature, can be used to prepare non-volatile iodide electrolytes. Today ionic liquids become more and more popular and gradually replace traditional organic solvent. The chemical reaction of ionic liquids is:

\[
S^+ + 2I^- \rightarrow S^- + I_2^2 \]

(2.4)
Here listed some commercial ionic liquids which are been commonly used in the industry. For the detail, see Table 2.2

Table 2.2  Major ionic liquids used in DSSCs

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Chemical Name</th>
<th>Molecular Formula</th>
<th>Formula Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMPII</td>
<td>1,2-dimethyl-3-propylimidazolium iodide</td>
<td>C₈H₁₅N₂I</td>
<td>266.00 g/mol</td>
</tr>
<tr>
<td>PMII</td>
<td>1-methyl-3-propylimidazolium iodide</td>
<td>C₇H₁₃N₂I</td>
<td>252.00 g/mol</td>
</tr>
<tr>
<td>HMII</td>
<td>3-hexyl-1-methylimidazolium iodide</td>
<td>C₁₀H₁₉N₂I</td>
<td>294.00 g/mol</td>
</tr>
<tr>
<td>DMHII</td>
<td>3-hexyl-1,2-dimethylimidazolium iodide</td>
<td>C₁₁H₂₁N₂I</td>
<td>308.00 g/mol</td>
</tr>
<tr>
<td>EMII</td>
<td>3-ethyl-1-methylimidazolium iodide</td>
<td>C₆H₁₁N₂I</td>
<td>238.07 g/mol</td>
</tr>
<tr>
<td>EMIDCA</td>
<td>3-ethyl-1-methylimidazolium dicyanamide</td>
<td>C₈H₁₁N₅</td>
<td>177.21 g/mol</td>
</tr>
</tbody>
</table>

Except for using ionic liquid, another method to overcome the volatile issue is to use solid organic hole conductors, which includes conducting polymer and molecular hole conductors.

2.3.4 Cathodes

Platinum is the preferred materials for DSSCs. Other materials, such as carbon\textsuperscript{38}, cobalt sulfide\textsuperscript{39} have also been investigated for counter electrodes.
2.4 Current Issues and key problems of DSSCs

It is nearly 20 years since the announcement of the sensitized electrochemical photovoltaic device with a conversion of 7.1% in 1991. Scientists make use of varieties of methods to improve the performance of DSSC, including the change of substrate roughness, the development of new dye and new electrolyte. Now the efficiency has increased significantly and the cost has decreased a lot.

2.4.1 Efficiency

For time being, the highest efficiency for a DSSC is 12.3%. Although it has exceeded the amorphous Si solar cell, there is still a huge distance when compared with multicrystalline Si solar cell.

The global efficiency depends on incident photon-to-electron conversion efficiency (IPCE) and quantum efficiency (QE). IPCE and QE indicates the ratio of the total number of incident photons on a solar cell, to the total number of generated charge carriers, specifically, IPCE is a measure of the internal efficiency while QE is a measure of the external efficiency. Both IPCE and QE measurements are very important at the stage of materials research and cell structure design, because the spectral distribution of sunlight should match the spectral response of the solar cell to ensure the highest power conversion efficiency during the generation of charge carrier.
The power of a solar cell device depends on the product of current and voltage. We can use short circuit current $J_{sc}$, open circuit voltage $V_{oc}$ and fill factor FF to evaluate the key performance of a DSSC. The typical value of $J_{sc}$ is 20.5 mA/cm$^2$; the difference between the redox potential of electrolyte and the Fermi level of the TiO$_2$ decides the maximum output voltage of a DSSC. The typical value of $V_{oc}$ is 0.72V under normal solar illumination condition\textsuperscript{42}. Fill factor in the context of solar cell technology is defined as the ratio of the maximum obtainable power, $(J_{mp} \times V_{mp})$ to the theoretical power, $(J_{sc} \times V_{oc})$. For commercial solar cells, the typical value of fill factor is larger than 0.70. $V_{mp}$ is maximum power point voltage; $J_{mp}$ is maximum power point current. Consider the effect from FF, the peak power production efficiency of DSSCs is about 11%.

There are two ways to increase the efficiency. The first method is improving the open circuit potential $V_{oc}$. If chemists can develop a kind of new electrolyte with a higher oxidation potential, the chance of enhancing the open circuit potential is large. Co$^{II}$/Co$^{III}$ – redox couple had been tried and a high open circuit potential with 840 mV had been achieved \textsuperscript{43}. Organic hole conductor has higher open circuit potential, which give us more hope to us \textsuperscript{44}.

The other method is enhancing the short circuit current $J_{sc}$. The improvement of the absorption spectra of the dye can increase $J_{sc}$. The absorption spectrum of traditional
dye only covers the visible region for time being. If a new dye can extended to the near infrared (NIR), or infrared (IR), the enhancement of the short circuit current will be realized.

2.4.2 Stability

DSSC should have long term stability to guarantee the commercialization of it to be successful. The reliability of solar devices depends on the stability of DSSC. Today most DSSC manufacturers can provide their customers with about 20 year warranty which promises their product can maintain 80% ~ 90% performance level of the brand new one. The working environment of DSSC is variable since devices working outside. All the impacts from the cyclic changing temperature and its range, the exposure to humidity, the prolonged illumination, mechanical deformation, bacterial growth are the major factor every engineer should consider. The stability of DSSC can be divided into intrinsic stability and extrinsic stability.

The intrinsic stability of DSSC depends on the physical and chemical properties of components. We can use accelerated aging experiments to test the lifespan of components and intrinsic stability. The sensitizer, electrolyte and Pt-coated Cathode have thermal stable limit and they cannot work normally under the high temperature. In addition, the dyes also have photobleaching phenomena. Consider the factor from engineering application, the components will surfer stress from the deformation of the
solar cell, which also degrade their performance. In all, intrinsic problems will always obsess us since once a new potential replacement is developed, we should consider its intrinsic stability under the working condition.

The external stability is another conundrum for us. The stability of the sealant in DSSC is the major issue we should focus. Hotmelt foils are widely used for DSSC manufactures. The sealing ability weakened with the increase of the external pressure applied on the solar cell. Moreover, if the sealant is exposed to cyclic temperature change environment, it is much more vulnerable. Hotmelt foil is cheap and easy to process. Although the adhesion of the foil to the glass substrate is so limited, if the glass could be pretreated with metal oxide particles, the adhesion ability can be increased significantly. Despite some manufacture alleged that their products can work for 15 ~ 20 years, its reliability still needs time to validate them.

2.4.3 Scalability

The scalability of DSSC depends on the properties of glass substrates. We do not use silver fingers to collect current in DSSC because of the chemically aggressive electrolyte. As a result, the transparent conducting oxide (TCO) – coated glass becomes the best candidate materials for TiO₂ electrode. Fluorine tin oxide (FTO) – coated glass is chosen in the early stage. It is difficult to upscale the device since the sheet resistance of the FTO glass is about 10 Ω/square.
The conversion efficiency of a DSSC will decrease as the area of the cell increase. For example, the efficiency can reduce to 6.3% when the area enlarged from 1 cm\(^2\) to 26.5 cm\(^2\) \(^{48}\). The appearance of indium tin oxide (ITO) changed this. ITO is a kind of materials with high conductivity but low chemical stability, while FTO has relatively low conductivity and higher chemical stability. By the combination of ITO and FTO, the TCO glass sheet resistance can reduce to as low as 1.3 Ω/square \(^{46}\). However, the size of DSSC still cannot be made too large, which limits the power of DSSC.

2.5 Recent progress of DSSCs

In the recent five years, scientists all over the world are exploring new approaches to improve the performance of DSSC devices. The development of new sensitizer and TiO\(_2\) includes the most progress in recent years. Using nanostructured TiO\(_2\), such as nanorod, nanofibers and nanowires instead of traditional TiO\(_2\) has been tried and tested.\(^{49-55}\)

In order to reduce the cost of manufacturing nanostructured TiO\(_2\), electrospinning is a good solution for the mass production of one-dimensional TiO\(_2\) nanostructures, which is the key component to increase the performance of DSSC devices. In the Department of Polymer Engineering, University of Akron, Professor Mukerrem Cakmak introduced the electrospining to fabricate the TiO\(_2\) nanofibers. The fibers are collected on the surface of FTO plates to form the sintered porous TiO\(_2\) morphology.
Then the sintered TiO$_2$ nanofibers are coated with N719 ruthenium-dyes before sealing step. By now using this kind of approach to improve the morphology of TiO$_2$ is still going on.

2.6 Introduction of Cadmium Sulfide-based Solar Cells

Cadmium sulfide (CdS) is a kind of II-VI class semiconducting luminescent materials with wide forbidden band and direct transition band structure. CdS nanoparticles (NPs) can demonstrate quantum size effects at nanoscale. With its advantages of opto-electronic properties, CdS has more and more application in the field of LEDs, photovoltaic devices, sensors, infrared window materials, fluorescent labels materials and environment detection technology.$^{56,57}$

Because of the small size, CdS NPs have large surface energy, which make it easy to aggregate to form large clusters and lost the fundamental feathers and functions of CdS NPs. Thus the intergration of CdS NPs into polymer matrix is a good solution for this issue since it can not only increase the performances of polymer-based solar cells, but also utilize the opto-electronic properties of CdS and chemical properties of polymer. As a result, CdS NPs based polymeric materials are widely employed for hybrid solar cells.$^{58-64}$
CHAPTER III

MATERIAL SIMULATION MODELS AND METHODS

In this chapter, several simulation methods used in molecular modeling or materials calculation are introduced. This part starts from the basic concept of computer simulations. And then discuss three popular modeling approaches by simulation length scales: quantum mechanics calculation, classical molecular dynamics (MD) simulation, and coarse grain simulation.

3.1 Computer simulations bridge theories and experiments

With the development of computer technology and mathematical algorithm, more and more theoretical and experimental scientists utilize computers to study complex academic phenomenon, which promotes the progress and prosperity of computational materials science. A lot of puzzles, which are impossible to figure out due to the massive amounts of data, the complexity of the phenomenon and the limits of experimental conditions, could been solved by computer simulations. Computer simulation can test theories, model the real process and design experiment devices. (See Figure 3.1)
Figure 3.1 The Relations for theories, simulations and experiments for the scientific researchers.

Today computational materials science has become an important branch of materials science since it can promote the communications between experimental researches on materials and computational work on both existing and new, advanced materials and their applications. With the increasing speed and available of parallel processors and distributed computing, calculating the properties of materials, even with very huge and complex system, also becomes available.
But how do we describe real material with a simple model and which approach will give us the desired results efficiently?

The simulation methods to study materials can divide into quantum mechanics method, molecular dynamics (MD) method, mesoscale dynamics method, finite element analysis (FEA) method and engineering design method by length scale. (See Figure 3.2) Different method has its own features and application area.

Figure 3.2 Schematic of multi-scale modeling approaches. X-axis represents length scale, Y-axis represents time scale.
3.2 Introduction of computational materials sciences

After the rapid development of quantum mechanics theory in 20\textsuperscript{th} century, all the properties of molecules, such as structure, conformation, dipole moment, ionization, electron affinity and electron density, can be obtained from the quantum mechanics calculation. The results from quantum mechanical calculation are identical with the experimental ones. Moreover, by analyzing the results from quantum mechanics calculation, scientists can get the information that cannot be obtained from experiments directly, which promotes the understanding for practical problems.

Compared to experiments, material science research by computer has a lot of advantages: (1) low cost; (2) high safety; (3) available to study the ultrafast chemical reaction; (4) high accuracy; (5) deepen the understanding of problems. Based on the above reasons, quantum mechanical calculations for molecules attract more attention by chemistry community from 1970S. Analyzing the features of molecules by computer simulation has been a significant mean for synthesis chemists and drug design chemists. Using this method, Chemists can design the best reaction routes, predict the possibility of synthesis, evaluate the applicability of molecules to be synthesized, save more time and avoid the waste of materials.

In addition, molecules modeling have been applied to other complex large system, such as polymer and biomaterials. Today, computational techniques are believed to be the indispensable tools in the every aspect of chemistry. Moreover, the role of
computation is increasing rapidly as the improvement of methods and the development of the hardware of computers.

In quantum mechanics, all the behaviors of electrons can be described by their wavefunctions, which are the solutions of Schrödinger Equation.

\[ H\Psi = E\Psi \]  

(3.1)

Where \( H \) is Hamiltonian; \( \Psi \) is wavefunction; \( E \) is energy for a specific system.

Atoms or molecules have a lot of electrons. So it is not easy to get the accurate solutions of equation (3.1). The most fundamental method in quantum mechanical calculation is \textit{ab initio} calculation method, a molecular orbital calculational method, separating wavefunction of a system to the combination of wavefunction of atomic orbitals. These atomic orbitals can be extended by some specific mathematical function (for example, Gaussian Function). This method is accurate but slow, and there is a lot of limit to the system, generally the total atoms cannot exceed 100. In order to improve the calculation efficiency of quantum mechanical method, different methods have been proposed since 1960s, which simplify the calculation procedures. One method is called semi-empirical molecular orbital method, where some integral completed by computers, could be replaced by empirical parameters from experiments. The advantage of the semi-empirical molecular orbital method is that it can be used to calculate relatively larger molecules and in some condition, its
computational results are identical with ones from quantum mechanical computation. However, even with semi-empirical molecular orbital method and most advantaged computational techniques, such as parallel processors and new algorithm, the largest system applied to quantum computational method is still small, with total atom number less than 1000. Other approximation schemes have been developed, but none was very successful until the appearance of density functional theory (DFT). In 1964, Walter Kohn proved the idea that knowing the average density of electrons at all points in space is enough to uniquely determine the total energy, and therefore all the other properties of the system.\textsuperscript{65,66,67} In the late 1980s, physicists started to modify the Kohn-Sham density functional in ways that improved its accuracy. In 1992 Professor John Pople added density functional theory (DFT) - including the latest functionals - to his widely-used computational chemistry program GAUSSIAN. The program was already recognized as the principal tool to study materials structures and process of chemical reactions, at least for small molecules, but with the addition of DFT, chemists were immediately impressed with its accuracy and speed. In 1998, Kohn and Pople received the Nobel Prize in chemistry for their contributions to computational chemistry, which is now employed routinely as a tool by scientists in many fields.\textsuperscript{65}

In all, quantum mechanical computation can only be applied for small molecules, or a system with a few electrons. However, in nature and industry, a lot of systems such as
biological molecules (such as protein, nucleic acid, enzyme, amylose), polymers have a great number of atoms and electrons. In addition, for metal materials, polymeric materials, thickened solutions, nanoscale materials, scientists and researcher are not only interested in the properties of single molecule and the interaction in different molecules, but also wonder the specific properties of the whole system, the dynamic behaviors and thermodynamic properties. Faced with such a complex and large system, which a so many electrons, we cannot rely entirely on quantum mechanical computations. In 1960s, non-quantum mechanical computational methods are proposed to study materials.

Molecular mechanics (MM) simulation is an alternative approach which can be used to study a large system. It is also referred to as the potential energy or force field method. The Born-Oppenheimer approximation to the potential energy with respect to the nuclei, $E_p(X)$, can be imagined as the target function in molecular mechanics ($X$ represents the collective position vector for the nuclei). Movements of electrons are neglected for calculation. The force field of molecules contains a lot of parameters, which can be obtained by experimental results or quantum mechanical computation. Thus, based on molecular mechanics method, calculation on stable conformations, thermodynamic properties and vibration spectrums of larger and complex systems becomes possible. This method is much simpler, and the time needed to get the properties of molecules is reduced when compared with quantum mechanics. In some
conditions, the results obtained from molecular mechanics are very close to that from quantum mechanics, the time needed is much less. So molecular mechanics becomes an important mean to study drugs, biological macromolecules and clusters.

Monte Carlo (MC) simulation method is the earliest non quantum mechanical method used to study the large system. Monte Carlo simulation approach is based on the use of random numbers and the principle of probability statistics, to investigate problems. The most disadvantage of Monte Carlo simulation is that it can only get the statistical average of a specific system, without dynamic information of the system. So this kind of random motion based on computer, does not apply to the principle of motion in physics. In addition, the calculation speed of Monte Carlo simulation has no advantage compared to other non quantum mechanical computational methods. Thus after the prevalence of molecular dynamic simulation, Monte Carlo simulation method lost its competitive edge.

Molecular dynamics simulation, is the most widely used simulation method to study complex large systems. In 1970s, molecular modeling is characterized by the rapid development of molecular dynamics simulations, with a great number of force fields introduced to be used in biological molecular system, polymer, metal and nonmetal materials. Thus, the capability and accuracy to calculate the thermodynamic and spectrum properties are increased significantly. Compared to Monte Carlo simulation,
the motion of particles in molecular dynamics simulation has more reliable theoretical foundation. The advantages of molecular dynamics simulation include high accuracy, the access to system dynamic status and thermodynamic information. After continuous improvements, molecular dynamic simulation is already a mature discipline. With so many advantages, a lot of commercial simulation packages based on molecular dynamic simulation have been developed. Today these molecular dynamics simulation package has become an indispensable research tool, which can be found from research laboratories in schools, industries and hospitals. However, the molecular dynamics simulation package also has some limits. Mathematical integral methods are exploited, so molecular dynamics simulation can only apply to the motion of system in short time, rather than the motion with long time, such as protein folding. For the time being, scientists are trying their best to increase the computational capability and improve calculation algorithm, in order to make sure molecular dynamics simulation can be used to study the motion of system for longer time.

Brownian dynamics simulation is a mesoscopic method and it is similar to molecular dynamics simulation. It is a simplified version of Langevin dynamics. Brownian dynamics simulation can apply to the system of macromolecule solution. Based on Brownian motion equation, the motion trajectory of macromolecules and thermodynamic properties can be obtained. So Brownian dynamics simulation is used
for calculate the aqueous solution of biochemical molecules, such as polypeptide, protein, DNA and so on. The advantages of Brownian dynamics simulation is it can calculate the motion of macromolecules for long time, as much as nanoseconds. However, it also has disadvantage. In Brownian dynamics simulation, it assumes that the motions of solvent molecules can be treated as Brownian motion. This assumption is not correct in some condition.

Today, computational chemistry or physics community are focusing on combining the quantum mechanical computation with classical mechanical computation to arrive the desired accuracy and more application areas. In addition, using high performance workstation or PC cluster to increase calculation speed is another approach to improve computation capacity. We can expect that the role of computers in scientific research will be increasing and it will become an indispensable approach, as the improved computational capability and expanded computational system.

3.3 Force field methods and molecular dynamics

Force field methods, developed from 1960s, are frequently used to optimize molecular geometries and perform molecular dynamics right now. So the typical application targets for the force field methods are polymers of hundreds of thousands of atoms and biological macromolecules, such as proteins. In addition, this method can also be utilized to research the behavior of substances in gaseous, liquid
or solid states. A force field describes the interactions taking place inside the molecule and those between molecules as a simplified function. The fundamental hypothesis in the force field based model is that individual atoms or groups of atoms can be represented by electrically charged spherical objects that have a mass. Then chemical bonds within molecular can be defined as force applied on these spheres.

So we can view molecules as a bunch of spheres that are interlinked by springs that describe chemical bonds and other types of interaction. The molecule can rotate, vibrate and translates to assume favored conformation in space as a collective response to the inter- and intramolecular forces acting upon it. The force can expressed as a sum of harmonic-like term for bond-length and bond-angle deviations from reference equilibrium values; trigonometric torsional terms to account for internal rotation and nonbonded van der Waals and electrostatic potential. 68

Several kinds of different springs are linked to each sphere and their total effect determined the total force experienced by the sphere. This idea makes the computation faster than the method by quantum chemistry, but also ignores several chemically important properties, such as covalent bond.

The core of force field is the energy function expression and bond coefficients. 72, 73 Force field can be viewed as the basic functional expression of the potential energy
function. For different study objectives, force fields can be expressed with different forms, corresponding to different application areas and limits.

The total energy of a molecule can be divided into kinetic energy and potential energy. The potential energy $E_p$ can be expressed as the function of atomic position $E_p(X)$. For example, the vibration potential energy of a bi-atomic molecule AB, can be expressed by a function of the distance from A to B.

$$U(r) = \frac{1}{2} k(r - r_0)^2$$  \hspace{1cm} (3.2)

Figure 3.3 Schematic showing the mathematical expression of bond stretching potential.

In the expression above, $k_b$ represents the stiffness of the spring, $r$ is distance from atom A to atom B and $r_0$ describes the optimal bond length between the atoms.

Using this kind of simple mathematical form to express the potential function is called force field. Generally speaking, the total potential energy of every complex molecule can be expressed as the summation of potentials, which include non-bond potential $U_{nb}$, bond stretching potential $U_b$, angle bending potential $U_\theta$, torsion angle
potential $U_\phi$, out-of-plane bending potential $U_\chi$, cumbic interaction potential $U_{el}$.

$$U = U_{ab} + U_b + U_\phi + U_\theta + U_\chi + U_{el}$$  \hspace{1cm} (3.3)

In order to demonstrate the physical meaning of every potential term in the equation above, we choose CHARMM (Chemistry at Harvard Macromolecular Mechanics) force field as the example. Figure 3.4 demonstrates the bonded energy components terms which are implemented in the CHARMM force field.  

\[ U_{bond} = k_b (r-r_0)^2 \]

\[ U_{angle} = k_\theta (\Theta) \]

\[ U_{torsion} = | k_\phi | - k_\phi \cos(n\phi) \]

\[ U_{plane} = k_\chi (\chi-\chi_0)^2 \]

Figure 3.4 Schematic showing the expression of potential energy function terms in CHARMM force field  

39
The stretching vibration of a bond can be expressed as an ordinary spring:

\[ U_{\text{bond}} = k_b(r - r_0)^2 \]  

(3.4)

\( k_b \) represents the stiffness of the spring and \( r_0 \) describes the optimal bond length between the atoms. The function of expression is only to model the effects of covalent bonds on the molecular structure, rather than depict the bond effects based on the real physical atom level phenomena. The harmonic function is a good example for it can only apply to the equilibrium bond length at a close range.

A plane angle \( \chi \), for example, can be represented with the similar mathematical function as the bond length, but needs its own parameters. A periodic function is employed to express torsion around the bond.

Electrostatic and van der Waals forces should also be included during force field calculation. In order to get these forces, we have to know the van der Waals radius and electric charge, which are fixed for each atom. The electric potential between any two atoms is determined by the distance \( r_{ij} \), charges \( q_i, q_j \) and dielectric constant \( \varepsilon_0 \)

\[ U_{\text{electrostatic}} = \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}} \]  

(3.5)

The effects of molecular interactions resulted from atomic electron clouds on each other could be described by van der Waals forces. The force usually demonstrates repulsive interaction at short distance, while can exhibit attraction at longer distances.
Lennard-Jones potential is one of the frequently used potentials for van der Waals interactions:

\[ U_{vdw} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]  \hspace{1cm} (3.6)

Where \( r \) is the distance between the particles; \( \epsilon \) is the depth of the potential well; \( \sigma \) is the finite distance at which the inter-particle potential is zero.

Lennard-Jones form, also called 12-6 potential, is the most common expression of non-bond potential in force fields. In this form, the \( r^{-12} \) term is the repulsive term, and the \( r^{-6} \) term is the attractive term. When the value of \( r \) is very large, the potential will approach to zero, which represents that there are no non-bond effects between two atoms if their distance is long enough. Lennard-Jones form can also be expressed as

\[ U_{vdw} = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \]  \hspace{1cm} (3.7)

\( A_{ij} \) and \( B_{ij} \) are constants determined by van der Waals radii of interactive atoms.

Thus the total energy of the system can be computed as the sum of all potential energy terms:

\[ U_{total} = U_{bond} + U_{angle} + U_{tortion} + U_{electrostatic} + U_{vdw} \]

\[ = \sum k_b (r - r_0)^2 + \sum k_\theta (\theta - \theta_0)^2 + \sum \left[ k_\varphi \left| -k_\varphi \cos(n\varphi) \right| \right] \]

\[ + \sum k_\chi (\chi - \chi_0)^2 + \sum \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + \sum \left( \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \right) \]  \hspace{1cm} (3.8)
When the total energy is known, we can derive force experienced by an individual atom from the derivative of the atom’s potential energy.

Other force fields, such as CVFF (Consistent Valence Force Field), PCFF (Polymer Consistent Force Field) 75, AMBER (Assisted Model Building using Energy Refinement) 76, COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) 77, and UFF (Universal Force Field) 78-80, have different total energy expressions. However all the force fields have a common feature: They all include a set of parameters and the value of these parameters for each combination of atoms should be known first. This process is called force field parameterization 81-84. This is a complex process and it determines the accuracy and applicability of the force field. Although the same parameters can be employed to investigate a large group of similar molecules, there is no universal force field that can apply to all molecules.

The thermodynamics procedure is to let molecules find the confirmation with the energy as low as possible, which is also the hypothesis of the use of force field. Molecular mechanics (MM) is employed to change the conformation of molecules to arrive the most stable one corresponding to minimum energy 85-89. This procedure is called geometry optimization. Today the most popular optimization algorithms are steepest descent algorithm and conjugated gradient algorithm 90-92.
In the real world, both the molecules and internal structure will move. Vibrations, torsions and twists will happen together. The target of molecular dynamics is to describe thermal-kinetic motions. Thermal energy leads to the vibration of molecules, which cause the variance of molecular bond lengths, angles and torsions. In addition, the interactions between atoms that do not connected also take place.

It is more than 40 years since the development of molecular dynamics simulation in 1966. Today, a great number of MD simulation packages have been used all over the world. Some of them have graphic interface, powerful function, and they are easy for learners. However, the success or failure depends on a lot of factors, such as the force field choice, computational speed, algorithm and the rationality of initial structure.

The molecular dynamics simulation method is based on Newton’s second law. If a system has $N$ atoms or molecules, its total potential can be represented by the function of the atom position $U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n)$

Generally speaking, potential can be divided into intermolecular potential - nonbonded (van der Waals interaction) and intramolecular potential.

$$U = U_{vdW} + U_{\text{int}}$$  (3.9)

The van der Waals interaction can be represented as the sum of potential of atomic pairs.
where \( r_{ij} \) is the distance between the atom \( i \) and atom \( j \).

The intermolecular interaction can be represented as the sum of the potential of internal coordinates, such as bond strength, angle bending……

By classical mechanics, the force on the atom \( i \) can be obtained from the gradient of potential:

\[
\vec{F}_i = -\nabla_i U = -\left( \frac{\partial}{\partial x_i} + \frac{\partial}{\partial y_i} + \frac{\partial}{\partial z_i} \right) U
\] (3.11)

By the equation of motion,

\[
\ddot{a}_i = \frac{\vec{F}_i}{m_i}
\] (3.12)

Integration of the equations of motion then yields a trajectory which describes the positions, velocities and accelerations of particles as they vary with time.

\[
\frac{d^2}{dt^2} \vec{r}_i = \frac{d}{dt} \vec{v}_i = \vec{a}_i
\]

\[
\vec{v}_i = \vec{v}_i^0 + \ddot{a}_i t
\]

\[
\vec{r}_i = \vec{r}_i^0 + \vec{v}_i^0 t + \frac{1}{2} \ddot{a}_i t^2
\] (3.13)

where \( \vec{r} \) and \( \vec{v} \) are the position and velocity of particle. Superscript 0 represents the initial value.
From this trajectory, the average values of specific properties could be determined. So this method is deterministic: once the positions and velocities of each atom are known, the state of the whole system could be predicted at any time in the future or the past. For every time step, a new position and force of each atom can be calculated by Newtonian equation and force fields.

In summary, the fundamental principle of the molecular dynamics is Newton's laws of motion. Numerical methods will be employed to get the solution of (3.13) by computer. In order to describe the motions accurately, we should assign each atom its mass, charge and velocity. During molecular simulation, positions and velocities of atoms can be stored as data. This procedure likes a movie, from which we can see the evolvement of movements, conformations and vibrations. So this information can be employed to derive other properties, such as thermodynamic parameters, diffusion constants, viscosity and so on.

3.4 Coarse grain methods

Polymer and macro-molecules have posed a significant challenge to the community of theoretical physics and chemistry. Thus, coarse-grained models are emerging as a practical alternative to force field simulation or atomistic model for a large system \(^93\). Generally coarse-grained methods are used to a huge system consisting of more than thousands or even hundred of thousand of atoms when the relevant length, time scales
of the phenomenon under research are larger than the molecular scale and the details of motion of individual molecules have no necessary to know. A lot of models use coarse-grained method. The wormlike chain model is a good example for this method.\textsuperscript{94–96}

For the simulation size, the number of atoms is the most important limiting factor. By describing several atoms as one interaction point, the number of atoms can be reduced. In classical MD simulation, each atom has been assigned mass, charge, and other interaction parameters. In this approach the model is called all-atoms model. If a carbon atom, together with hydrogen atoms is considered as one interaction point in an alkane chain, this model is a type of coarse-gained model. For example, an octane molecule can be represented by eight points. In a large system, the efficiency of coarse-graining could be exhibited. If the number of the total particles could be reduced by a small amount, the advantage of coarse-gained will be obvious.

In polymer science, famous Rouse bead-spring modal is a coarse-grained model, which simplifies the movement of polymer chain. The bead-spring model can be used to describe the visco-elastic properties via Monte Carlo simulations. In the next chapter, the details of coarse-grained methods are introduced.
CHAPTER IV

COARSE GRAIN MODEL OF DYE SENSITIZED SOLAR CELLS

Computer simulation has demonstrated a great potential to study materials properties and become the third pillar to crack the complicated phenomena in nature. Computer power and recourses are boosted by the prosperity of the application of simulation techniques. With the increase in computer power and the introduction of smart algorithm, exploring more complex system becomes available, such as soft matter, tissues, as well as biological cells.

Photovoltaic devices also attract a lot of attentions by the simulation community. DSSCs are widely studied all over the world by experiments and simulation. A complete DSSC device is composed of electrodes, TiO$_2$, dye, electrolytes and so on. Every component is made up of more than one hundred atoms. Thus modeling the DSSC at device level poses a challenge for simulation community since quantum mechanical calculation and classical molecular dynamics simulation have difficulty to deal with a system with more than hundred thousands of atoms. The only solution is to simplify the system to reduce the freedom of atoms.
In this chapter, the model, principle and approach of coarse grain simulation are introduced through the study of DSSCs. By now, coarse grain method is the best solution to simulate the working mechanism of DSSC at device level. 97–104

4.1 Principles of coarse grain simulation method

The components of a DSSC involve multiple scales. It spans from electrons to polymers, which corresponds from micro to macro. At the same time, the time scale also spans a lot of order of magnitudes. For the polymer used in DSSCs, every single polymer chain is made up of more than ten thousands of atoms, which has a lot of length scales and time scales. It is a typical representation of multi-scale behavior. The length scale of structure change in polymer chain span from angstrom (the bond length of main chain) to nanometer (radius of gyration). The time scale the dynamics procedure in polymer span from femosecond (the local vibration of length and angle) to micro second (diffusion of polymer chain) or more. Under the current speed of computers, all atom molecular dynamics simulation can only describe the system with length scale no more than hundreds Å, and time scale no more than hundreds of nano seconds. As a result, all atoms molecular dynamics simulation cannot study phase behavior, state and properties of a system because it has too many freedoms. Thus, a coarse grain model has to be established since it can link the simulation from micro scale to meso scale, realize an effective molecular dynamics simulation at meso scale. In short, coarse graining operation of polymer chain is to describe the polymer as a
chain made up of beads which are connected by different springs, and use simple
experience potential or accurate potential to describe the effects between two beads.
With less freedoms and softer interactions, coarse grain model can reach the
simulation length scale of micron and time scale of micro second.

Here we choose polymer as the example, to demonstrate how coarse grain model are
chosen to study a large system. Today coarse grain model is used widely in polymer
science community. Generally speaking, different coarse grain models are needed to
study different problems. When focus on the universal behavior, we can choose coarse
graining operation based on the factors of length and volume. When focus on the
relationship between chemical structures of systems and material properties of
polymer, we need reasonable coarse grain rules to set up the model for the system. A
specific coarse grain model can be obtained from an all atom model. So the coarse
grain model reserves the necessary detail information of chemical structure, and the
established specific coarse grain model can describe the impacts of component of
system to performances of polymer quantitatively and imply the major impact factors.
Although the prediction to the performances of system from universal coarse grain
model is not as good as all atoms atomic model, it can also be used to study the
universal properties of polymer.
4.2 Set up coarse grain model of DSSCs

The goal of simulation is to obtain the relationship between current density and voltage and predict the power efficiency of DSSCs under working load. Today computer simulations are used to explore the interested properties of DSSCs. Quantum mechanical calculation and all atomic molecular dynamic simulation methods are all employed to study the electronic structure and thermodynamic properties of some components of DSSCs, such as TiO$_2$, ruthenium-dye, I$_3^-$, I/$I_3^-$ and I. The current behaviors of DSSC device have never been studied before from micro or meso aspects. Quantum mechanical calculation can explore the electron density of atoms or molecules, but cannot get the dynamic properties of electrons, which relate to the current of the device. Molecular dynamics simulation can study the dynamic properties of atoms of molecules, but cannot deal with electrons. Thus an innovational method is necessary to set up a new model which can study the length scale from angstrom to micron. Coarse grain model is a good solution to simulate the behaviors of electrons and macromolecules in the same working framework. In traditional coarse grain model, beads are the basic elements, which can represent atoms, molecules or groups. Here we introduce an assumption that the electron and hole can also be represented by beads. With this assumption, we can separate the DSSC to a lot of components beads by beads.
In CHAPTER II, we have introduced the components of DSSC and their functions and structures in devices. Based on these structures, we set the rules for coarse grain operation. The structure-based coarse grain operation begin with the mapping scheme, which can simplify the interactions and keep the chemical structure to all atom model as close as possible.

We choose standard DSSCs as the reference for mapping scheme. So the DSSCs include Platinum as electrodes, TiO$_2$ as semiconductor, ruthenium-dye as sensitizer, I$_2$, LiI, 3-Methoxypropionitrile (MePN), 1-Methyl-3-Propylimidazolium iodide (MPII), 4-tert-Butylpyridine (4TBP) as electrolytes and electron-hole pairs as the main parts contributing to the quantity of current. We divide all the components into two classes by their movements at working status. Electrodes, TiO$_2$, dyes are static parts in DSSCs because they do not move during working status. I$^–$/I$_3^–$, electrons, holes, poly(ethylene oxide)$_{10}$ will move when the devices are under working condition.

In DSSCs electrodes are made of platinum since it has a good performance to collect electrons. In devices, morphology of platinum is a thin film layer, which is deposited on the surface of glass. In order to form the layer morphology, we need a 2-D array of platinum to form one electrode.
During fabrication procedure, TiO$_2$ is formed at 450°C. So it is the static part. We choose TiO$_2$ cluster as a bead. The surface of electrodes will be deposited a lot of TiO$_2$ beads to form a porous layer of titanium dioxide nanoparticles.

Ruthenium-dye is made up of approximate 100 atoms. So we choose one ruthenium-dye molecule as a bead to decrease the freedom of the system. Ruthenium-dye molecules are attached on the surfaces of porous TiO$_2$. So in the coarse grain model, several ruthenium-dye beads will attach on the surface of one TiO$_2$ bead. The mass and volume of ruthenium-dye is larger compared with the volume of electrons. So the movements of ruthenium-dye can be neglected when it compared with the movement of electrons. Thus ruthenium-dye beads are treated as static ones.

The electrolytes include a lot of components, which will exist as the form of ions and molecules. The elements iodine will exist by the form of iodine and triiodine and iodine since there will be a reaction:

$$2I^- + S^+ \rightarrow I_2^- + S \quad (4.1)$$

$$2I_2^- \rightarrow I^- + I_3^- \quad (4.2)$$
However, the iodine is a transition state in the reaction and the amount of iodine is not much. So during the coarse grain model set up, we neglect the iodide and only consider the bead of iodine and triiodine. They are not neutral. So these two beads will be assigned the amount of -1 e charge.

1-Methyl-3-Propylimidazolium iodide (MPII) will exist as the form of MPI$^+$ and I$^-$ in electrolytes. So MPI$^+$ will be chosen as a type of bead with the charge amount of +1 for coarse grain model.

Lithium iodide will form positive lithium ions and negative iodide ion. So lithium ions will replaced by positive lithium bead with +1 charge amount in coarse grain model.

3-Methoxypropionitrile (MePN) and 4-tert-Butylpyridine (4TBP) are neutral so they are treated as a neutral bead with no charge respectively.

In our coarse grain framework, poly(ethylene oxide) is the most complex bead. Poly(ethylene oxide)$_{10}$ is composed of ethylene oxide monomers. Every monomer is treated as a bead. There will a bond between two ethylene oxide monomer beads. So a polymer chain can be formed by connecting beads together.
How to deal with electrons and holes is another issue. Although electrons have never been treated as a particle in traditional molecular modeling, such as DFT calculation and molecular dynamics simulation, the dynamic behavior and trajectory of electrons can treat an electron as a bead from Newtonian mechanics or classical mechanics views.

Hole is more abstract than electron. It is the mathematical and conceptual opposite of an electron. This concept is useful in solid state physics, where it is the absence of an electron from a full electron shell, and can be used to conceptualize the complex interactions of the electrons within a nearly full system. In the DSSC coarse grain model, we assume that electron-hole pairs can be excited under sunshine. Based on the assumption, we introduce the hole beads which corresponding the electron beads in coarse grain model.

Here we have assigned 11 different kinds of beads for a DSSC coarse grain model and the main components in a DSSC have been covered. The next step is to choose a good algorithm to determine the simulation framework.

4.3 Algorithm and tools to realize DSSC coarse grain model

Coarse grain model can be executed via two simulation methods-molecular dynamics simulation and Monte Carlo simulation. It is called coarse-grained molecular
dynamics (CGMD) method and coarse-grained Monte Carlo (CGMC) method respectively. In CHAPTER 3.2, we have introduced and compared these two methods. For DSSC coarse grain simulation, we choose CGMD as the algorithm framework.

Molecular dynamics based coarse grain simulation on DSSC can be realized on standard molecular dynamics simulation package by replacing the all atoms force field with coarse grain force field. In addition to setting up coarse grain model, we also need to simulate the complex dynamics procedure in DSSC device, such as pair excitation, charge recombination, charge collection and so on. These complex procedures can be realized by programming.

Considering the above requirements, we compared a lot of standard molecular dynamics simulation packages. Finally, we find simulation package LAMMPS is the best candidate. Here we introduce some features of LAMMPS.

4.4 Introduction of Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)

LAMMPS is distributed as an open source code under the terms of the General Public License (GPL). It is a kind of classical molecular dynamics code developed by United States Department of Energy and Sandia National Laboratories. As the name implies, it's designed to run fine on parallel machines, but it also runs well on single-processor
desktop machines$^{105-109}$. LAMMPS has potentials for soft materials (bio-molecules; polymers) and solid-state materials (metals, semiconductors) and coarse-grain systems. It can be employed to model atoms or, more generically, as a parallel particle simulator at the continuum or mesoscale levels.

LAMMPS executes by reading the commands from an input script (text file), one line at a time. Once the input script ends, LAMMPS exits. Each command causes LAMMPS to take some actions. It can set internal variables, read in files, or run simulations.

With LAMMPS as the simulation platform, the complex chemical reactions can be separated into a lot of simple procedures, which can be translated to input script and be executed by computer line by line. By programming the input script for LAMMPS, the whole chemical reactions can be realized and visualized on computers.

As an open source code, we also have considered modifying the code to realize DSSC coarse grain. However, DSSC includes so many components, which means we have to define the every component of DSSC first to simulate the reaction procedures. As a result, it is impossible for modify or implement the universal code to realize such a complex code. Thus we choose to program the reaction procedures by writing the input script.
4.5 Determine the size of coarse grain model

The length scale of DSSC devices should also be an important factor to be considered because choosing a reasonable model size can reduce the freedoms and consume less calculation resources.

The thickness of most DSSC devices is around 5 to 20 micron. However, it is not easy to set up a DSSC model at length as much as micron scale since molecule dynamics simulation package are usually deal with a system from angstrom to less than hundred nanometer. So setting up a model with a reasonable size relates the calculation cost. The model can use periodic boundary condition (BC) to extend the size at the XY plane. For Z direction, we set the distance of two electrodes to be 10 nanometers. Although in coarse grain model, the thickness of DSSC is much shorter than real devices, the size of model is large enough for us to run simulation and explore the behaviors of different beads.

After the distance of two electrodes is determined, we set the size of model to $10 \times 10 \times 20$ nanometers. In the model size at z direction is about two times as much as the distance of two electrodes. This is because the coarse model uses boundary condition and there should be enough vacuum space between two electrodes to offset interaction effects from different grids (see Figure 4.1)
Figure 4.1 Illustration of DSSC coarse-grain model. Except for electron and hole, there are nine different beads representing nine fundamental components in the DSSC.

The model is set up by the software Accelrys® Materials Studio. Platinum electrode is constructed by a layer of 20 × 20 beads. TiO₂ and ruthenium-dye beads are distributed evenly at the space between two electrodes and their positions are fixed. Four ruthenium-dye beads are attached on the surface of every TiO₂ bead. All the electrolytes beads will be placed at the space between two electrodes randomly.
4.6 Force field development for DSSC coarse grain model

The coarse grain force field development is to obtain the interaction effects between beads. If include electron and hole, coarse grain model has 11 kinds of bead. Only the poly(ethylene oxide) bead has bond and non-bonded parameters. Other beads only have non-bonded (van der Walls) parameters, which include the Coulomb and 6-12 Lennard-Jones potential. Coarse grain bead inherit the mass and charge of the group of atoms, so we do not need to worry about the Coulomb interaction. The main issue in non-bonded interaction parameters is to extract the value of the parameters of LJ interaction, such as sigma and epsilon, from all-atom model.

TiO$_2$ bead development references the all-atom model of anatase TiO$_2$ supercell. Considering that the size of coarse grain model, the diameter of TiO$_2$ bead is set to 10Å. We construct an all-atom TiO$_2$ supercell model with the size as large as a sphere with 10 Å diameter. The size of anatase TiO$_2$ primitive cell is $3.76 \times 3.76 \times 9.48$ Å$^3$, so nine anatase TiO$_2$ primitive cells can construct one TiO$_2$ supercell with volume close to a sphere with 10 Å diameter. See (Figure 4.2)
Figure 4.2 Illustration of the 3D structure of TiO$_2$ supercell (3 × 3 × 1) model. The model is created by Materials Studio program. Grey spheres represent titanium atoms and red spheres represent oxygen atoms.

The size of 3D supercell model is 11.28 × 11.29 × 9.49 Å$^3$. The mass can be calculated by the totally weight of all atom model, which is made up of 72 oxygen atoms and 36 titian atoms. So the mass of bead is 2880. The value of sigma is decided by radius of gyration of the groups of atoms represented by the CG bead. (See Figure 4.3). The diagonal of supercell is:

$$d = \sqrt{11.28^2 + 11.28^2 + 9.49^2} = 18.62 \text{ Å} \quad (4.3)$$
Figure 4.3 Illustration of the diagonal length of 3D structure of TiO$_2$ supercell (3 × 3 × 1) model. The testing result shows that the diagonal length is 18.618 Å.

Figure 4.4 Illustration of the radius of gyration of the groups of atoms represented by TiO$_2$ bead. The TiO$_2$ supper cell can be contained in a sphere with the radius of 12.5 Å.
Generally speaking, the value of sigma is approximately more than the diagonal. So we estimate the sigma value to 25 Å. The value of epsilon could be obtained by the morphology of TiO₂. So we get the value of epsilon to 1.1 Kcal/mol.

N719 has a very complex chemical structure. By transforming to a coarse bead, the freedom degree is decreased significantly. The coarse grain force field development of ruthenium-dye N719 follows the same procedures as TiO₂ beads development. We start form an all atom model of N719. (See Figure 4.5)

By summing all the atoms up, we can get that the mass of dye bead is 1187. The sigma value is estimated from the radius of gyration of the whole dye molecules. After the molecule ruthenium-dye N719 is constructed by Accelrys® Materials Studio, structure optimization, based on molecular mechanics, will change the initial structure of ruthenium-dye N719 until it is total relaxed. Then the optimized ruthenium-dye N719 is placed in a cubic box. We decrease the size and volume of cubic box as much as possible. The value of sigma is decided by radius of gyration of the groups of atoms represented by the CG bead. (See Figure 4.6)
Figure 4.5 Illustration of the 3D atomic model of ruthenium dye N719 (Di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) ). The model is drawn by Materials Studio Program. Different kind of atoms is represented by different colors.
Figure 4.6 Illustration of the radius of gyration of the ruthenium dye N719 molecule.

By this approach, we find that ruthenium-N719 can be contained in a box with size $12.5 \times 12.5 \times 12.5 \text{ Å}^3$. The dye is relaxed at vacuum condition, so we estimate the value of sigma to be 20 Å. For the epsilon, we use the same strategy as TiO$_2$. Finally we choose the value of epsilon to 2.0 Kcal/mol Å$^2$.

1-methyl-3-propylimidazolium iodide is called PMII. It is a room temperature liquid organic iodide salt used to prepare triiodide based electrolytes such as employed in dye solar cells. In the DSSC electrolyte, it exits as the form PMI$^+$. The all atom model of PMI$^+$ is demonstrated in Figure 4.7
Figure 4.7 Illustration of the 3D structure of all atom model of dye PMI$^+$. The white one represents hydrogen atom, the blue one represents nitrogen atom, the grey one represents carbon atom.

Figure 4.8 Illustration of the 3D all atom model of PMI$^+$ in a box with $10 \times 10 \times 10$ Å$^3$. PMI$^+$ can be contained in a sphere with the radius of 5.0 Å.
After structure optimized, PMI$^+$ is placed in a box with size of $10 \times 10 \times 10 \text{ Å}^3$ (See Figure 4.8). So the cut off radius in LJ model should be longer than edge. By empirical estimation, the value of sigma is estimated to 14 Å. The value of epsilon is estimated by the density of PMII in room temperature. We choose epsilon at 1.0 Kcal/mol Å$^2$.

3-methoxypropionitrile (MePN) is used as the solvent for I$^-$/I$_3^-$ and PMII in the electrolyte of DSSC. The structure and 3D model can be found in Figure 4.9. The size of MePN is measured by a cubic box. It can be contained in a box with $8.6 \times 8.6 \times 8.6$ Å$^3$

![Figure 4.9 Illustration of the 3D all atom model of 3-methoxypropionitrile (MePN). The white one represents hydrogen atom, the blue one represents nitrogen atom, the grey one represents carbon atom, the red one represents oxygen atom.](image)
Figure 4.10 Illustration of the 3D atomic model of 3-methoxypropionitrile (MePN) in a box with $8.6 \times 8.6 \times 8.6$ Å³. MePN can be contained in a sphere with the radius of 4.3 Å

4-tert-butylpyridine (4-TBP) is the commonly used additive for DSSCs since it can block the reaction of TiO2 electrons with electrolyte. The 3D structure is shown in the Figure 4.11. 4-tert-butylpyridine can be contained in a box with $7.0 \times 7.0 \times 7.0$ Å³. Thus we set the value of sigma to be 8 Å. By comparing the density of 4-tert-butylpyridine, the value of epsilon is set to 1.1 Kcal/mol Å²
Figure 4.11 Illustration of the 3D atomic model of 4-tert-butylpyridine (4-TBP). The white one represents hydrogen atom, the blue one represents nitrogen atom, the grey one represents carbon atom.

Figure 4.12 Illustration of the 3D atomic model of 4-tert-butylpyridine (4-TBP) in a box with 7.0×7.0×7.0 Å³. 4-TBP can be contained in a sphere with the radius of 3.6 Å.
Iodide (I\(^-\)) and triiodide (I\(_3\)\(^-\)) will keep a dynamic equilibrium during working status. The force field development of I\(^-\) bead reference the force field of iodine in PCFF (polymer consistent force field) since the difference between I\(^-\) and iodine is only an electron. So the value of sigma is set to 4.8 Å and the value of epsilon is set to 0.4 Kcal/mol Å\(^2\).

I\(_3\)\(^-\) is a polyatomic anion composed of three iodine atoms. It is always found in aqueous solution of iodine and iodide salts. I\(_3\)\(^-\) is not stable at room temperature and it follows an endergonic equilibrium:

\[
I_2 + I^- \leftrightarrow I_3^- \quad (4.4)
\]

In the ionic compounds, the bond lengths and angles of I\(_3\)\(^-\) depend on the nature of the cation. So we use different strategy to get the value of sigma. Exploring the electron density of I\(_3\)\(^-\) can help us get the approximate value of sigma. In Lars Kloø’s paper “On the Intra- and Intermolecular Bonding in Polyiodides” \(^{110}\), the Figure 6 demonstrates the electron density of I\(_3\)\(^-\) with different I\(^-\) and I\(_2\) distance. We found that electron density covered an area less than 14 \times 10 Å\(^2\). Thus we set the value of sigma to 10 Å.

For the value of epsilon, it references the epsilon value of iodide. Triiodide has more atoms and electrons so its epsilon value should be a bit larger than iodide. Thus the epsilon value of triiodide is set to 0.5 Kcal/mol Å\(^2\).
In PCFF, the non-bond parameter of lithium is 3.25 Å for sigma and 0.70 Kcal/Mol Å² for epsilon respectively. So for lithium ion in coarse grain model, the non-bond parameters use the same value as lithium atom.

The force field parameters of electron and hole are not easy to estimate because no one has developed electron force field for MD simulation before. The mass of electron is $9.10938188 \times 10^{-31}$ kilograms, which is about 0.0005 time of the mass of hydrogen. So in the coarse grain force field, the mass of electron is set to 0.005 and sigma value of electron is estimated to be 0.001 Å. The epsilon value of electron is not easy to be estimated since it is much abstract than the effective distance. It has to be tested and adjusted by the behavior of electron during MD simulation.

Although hole does not exist since it is only the physics concept, we assume it has the same basic properties as electron during force field development. So the mass, LJ parameters are set as same as electron.

The force field of Poly (ethylene oxide)$_{10}$ (called PEO$_{10}$) is the most complex parts since it includes bond and angle parameters. In coarse grain model, poly (ethylene oxide)$_{10}$ is employed to increase the stability of device. So the task of force field development is to determine the parameters of bond, angle, and non-bond. In our coarse grain force field, the bond and angle potential has the form of
\[ U(r) = k_b (r - r_0)^2 \]  
(4.5)

\[ U(\theta) = k_\theta [\cos(\theta) - \cos(\theta_0)]^2 \]  
(4.6)

\( k_b \) is the prefactor of bond potential; \( r_0 \) reflects the equilibrium distance between two poly (ethylene oxide) monomer; \( k_\theta \) is a prefactor of angle potential; \( \theta_0 \) is the equilibrium value of angle.

By MD simulation test, the value of \( k_b \) is set to 50 Kcal/mol·Å²; \( r_0 \) is set to 3.3 Å; \( k_\theta \) is set to 10 Kcal/mol, \( \theta_0 \) is set to 130°. For the non-bonded parameters setting, the value of sigma is set to 4.3 Å, a bit larger than \( r_0 \). The value of epsilon is set to 0.1 Kcal/mol Å².

By now, all the non-bond force field parameters of coarse grain beads have been set, except for electron/hole. Table 4.1 below listed all the beads:
### Table 4.1 Non-bond force field parameters used in DSSC coarse grain model

<table>
<thead>
<tr>
<th>Beads</th>
<th>Mass (Å)</th>
<th>Pair Coefficient (Å, Kcal/Mol Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>2880.0</td>
<td>25.000 0.700</td>
</tr>
<tr>
<td>Ruthenium-dye (N719)</td>
<td>1187.7</td>
<td>20.000 2.000</td>
</tr>
<tr>
<td>I⁻</td>
<td>126.9</td>
<td>4.800 0.400</td>
</tr>
<tr>
<td>I₃⁻</td>
<td>380.7</td>
<td>10.000 0.500</td>
</tr>
<tr>
<td>Li⁺</td>
<td>6.9</td>
<td>3.250 0.700</td>
</tr>
<tr>
<td>1-methyl-3-propylimidazolium (PMI⁺)</td>
<td>125.2</td>
<td>14.000 3.500</td>
</tr>
<tr>
<td>3-methoxypropionitrile (MePN)</td>
<td>85.1</td>
<td>12.000 3.300</td>
</tr>
<tr>
<td>Pt (collection electrode)</td>
<td>195.0</td>
<td>2.900 9.140</td>
</tr>
<tr>
<td>Poly(ethylene oxide)₁₀ (PEO₁₀)</td>
<td>440.0</td>
<td>4.300 0.810</td>
</tr>
<tr>
<td>4-tert-butylpyridine (4TBP)</td>
<td>135.2</td>
<td>8.000 3.050</td>
</tr>
<tr>
<td>Electrons</td>
<td>0.005</td>
<td>0.001 0.001</td>
</tr>
<tr>
<td>Holes</td>
<td>0.005</td>
<td>0.001 0.001</td>
</tr>
</tbody>
</table>

#### 4.7 DSSC reaction process simulation

After all the force field parameters have been set, the next step is to design a suitable reaction process to simulate the working principles in DSSCs. In the Chapter 2.2, the main working principle of DSSC devices has been introduced. Our research is performed on computers. Thus we have to change the reaction process to algorithm flow chart which can be executed by computers. (See Figure 4.13)
Our target is to get the current intensity of the device, which relates to the total number of the collected electron or holes in electrodes. Electrons and holes come from the photons, which is generated under sunshine. So the current intensity is determined by the intensity of sunshine. The light intensity can be reflected by the frequency of inserted hole-electron pairs. As a result, the frequency of inserted hole-electron pairs becomes one of the main input variables for the simulation.

In the model, the Pt electrode beads, TiO\textsubscript{2} beads and ruthenium-dye beads are fixed in the coarse grain model. Li, I\textsubscript{3}\textsuperscript{-}, MePN, PMI\textsuperscript{+}, 4TBP beads are placed randomly in the coarse grain model. The concentration of every component in electrolyte reference the most commonly used recipe in experiments.\textsuperscript{111–120} We have converted the recipe to the number of every bead, which can be found in Table 4.2
Figure 4.13. Algorithm flow chart of coarse grain model for DSSC reaction process
Table 4.2  The type and number of beads in DSSCs coarse grain model

<table>
<thead>
<tr>
<th>Beads</th>
<th>Number</th>
<th>Position of beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>25</td>
<td>Fixed</td>
</tr>
<tr>
<td>Ruthenium-Dye  (N719)</td>
<td>100</td>
<td>Fixed</td>
</tr>
<tr>
<td>I⁻</td>
<td>360</td>
<td>Moveable</td>
</tr>
<tr>
<td>I₃⁻</td>
<td>60</td>
<td>Moveable</td>
</tr>
<tr>
<td>Li⁺</td>
<td>60</td>
<td>Movable</td>
</tr>
<tr>
<td>1-methyl-3-propylimidazolium (PMI⁺)</td>
<td>360</td>
<td>Movable</td>
</tr>
<tr>
<td>3-methoxypropionitrile (MePN)</td>
<td>690</td>
<td>Movable</td>
</tr>
<tr>
<td>Pt (collection electrode)</td>
<td>2601</td>
<td>Fixed</td>
</tr>
<tr>
<td>Poly(ethylene oxide)₁₀  (PEO₁₀)</td>
<td>5</td>
<td>Movable</td>
</tr>
<tr>
<td>4-tert- butylpyridine (4TBP)</td>
<td>60</td>
<td>Movable</td>
</tr>
<tr>
<td>Electrons</td>
<td>Increase</td>
<td>Inserted in specific region</td>
</tr>
<tr>
<td>Holes</td>
<td>Increase</td>
<td>Inserted in specific region</td>
</tr>
</tbody>
</table>

Hole-electron pairs will be inserted to a specific region which is close to the surface of TiO₂ beads.

Once the hole-electron pairs are inserted in to DSSC model, they will be separated and move randomly until they arrive at electrodes. For electrons, most of them will move towards anion to contribute as current, the rest of them will recombine with the holes in electrolyte or in cation; for holes, most of them will move towards cation to contribute as the current, the rest of them will recombine with electrons in electrolyte or in anion. All these processes are realized by program, which runs on LAMMPS.
At the same time, we also have to consider the workfunction of anatase TiO\textsubscript{2} because in real device, electron will be injected into the prosperous anatase TiO\textsubscript{2}. The workfunction of anatae TiO\textsubscript{2} is not unique and its value is in the range from 4.5eV to 5.0 eV.

By definition, the workfunction is the minimum energy needed to remove one electron from the specific surface of a metal. In order to generate the equivalent effects for the electron injection process, some positive charges will be placed at the surface of the cation and negative charge will be placed at the surface of anion. When electrons move forward to the surface of TiO\textsubscript{2}, it need to do some work to overcome electronic field, which is equivalent to the energy needed for electron to be injected into TiO\textsubscript{2}. Right now we estimate how much charges are needed to placed at the surface of electrodes. The work of the moving electron in an electronic field can be expressed as:

\[
E = \frac{1}{2} V Q
\]

(4.7)

Where \( V \) is the applied voltage between two electrodes, \( Q \) is the charge amount.

If we assume that the work is equivalent to workfunction, we will have the relation below:

\[
W_{\text{function}} = \frac{1}{2} V Q
\]

(4.8)
If the value of workfunction is chosen as 4.9 eV and $V$ use the typical value of open voltage of DSSCs ($0.7 \, V$), we can obtain the value of $Q$ based on the above formula.

$$4.9eV = \frac{1}{2} \times 0.7V \times Q$$  

$$\Rightarrow Q = 14e$$  

(4.9)

So 14 e positive charge and 14 e negative charge has to be specified at the surface of two electrodes. In order to generate an even electronic field and simplify model, 100 positive charges are distributed evenly on the surface of cation and 100 negative charges are distributed evenly on the surface of anion. (See Figure 4.14)

If the total charge is 14 e, it means that every charge has 0.14 e. This case corresponds to the minimum voltage condition of DSSC; if there is no charge on the surface of electrodes, it corresponds to the $0.7 \, V$ (open-circuit voltage) condition. So we can tune the voltage of the DSSC by adjusting the amount of charge. The voltage will decrease as the increase of charge. For example, 12 e charge amount corresponds to 0.1 $V$ and 10 e charge amount corresponds to 0.2 $V$. 
Figure 4.14 Schematic illustration of the DSSCs coarse graining model

(A) demonstrates the components in DSSC solar cell model. (B) shows the charge distribution on the surface of electrodes in DSSC coarse grain model.
4.8 The development of DCSC (*DSSC Coarse-grain model Simulation Code*)

The algorithm flow chart of coarse grain model (Figure 4.14) for the DSSC reaction process could be realized by programming. So the next step is to develop simulation code, which can run on LAMMPS.

LAMMPS needs two input files to run: one is the structure file, which includes the information of the topology of simulation model, the parameters of force fields; the other is the script file, which includes commands to be executed one by one by computers. So the main work of the development of DCSC is to write the input script file and debug it.
CHAPTER V

SIMULATION RESULTS OF THE DYE SENSITIZED SOLAR CELLS COARSE GRAIN MODEL

5.1 Simulation parameters settings

After the accomplishment of simulation code and coarse grain force field development, we can run the code on LAMMPS. Our simulation has some difference from the traditional MD simulation, so we have to highlight two assumptions of DSSC coarse grain simulation:

(1) Electrons and holes are treated as the general atoms for MD simulation. So the force field concept of electrons and holes are introduced and their forms are same to general atoms.

(2) The total number of particles (include atoms, electrons and holes) will vary with the time. The whole procedure can be divided into a lot of sub-procedures during the whole simulation. Although in the whole procedure, the total number is not constant, in every sub-procedure, the total particle number keeps the same. So in every sub-procedure, the system can be consider as a NVT ensemble.
(3) The open-circuit voltage of the DSSC is assumed to be $0.7 \, V$. This value corresponds to the workfunction of TiO$_2$, which is 4.9 eV.

In the DCSC program, a lot of variables are defined first as the input parameters determining the performance of DSSC devices. These input parameters include temperatures, hole-electron pairs inserted time interval $t_i$, charge amount in electrodes, recombination cutoff distance $d_r$.

In the coarse grain simulation, we use the PCFF coarse grain force field, which is developed by ourselves and introduced in Chapter 4.6. DSSC model uses periodic boundary condition and the temperature is set at 298.15K.

5.2 Current-Voltage ($I$-$V$) curve calculation

In $I$-$V$ curve calculation, we explore the relation between voltage and current density. Simulation step length is set to 1 femtosecond and simulation time lasts for 10000 steps. Hole-electron inserting frequency varies from 10 hole-electron pair / femtosecond to 100 hole-electron pair / femtosecond, which can help us analyze the impacts of light intensity to the performance of DSSCs.

Different recombination distances has been tried to see the impacts to the current intensity. The distance of recombination varies from 1.5 Å to 2.5 Å. All the simulation
results of DSSC coarse grain model are shown in Figure 5.1, Figure 5.2 and Figure 5.3.

Figure 5.1 is the simulation results of DSSCs coarse grain model with different light intensity, at 1.5 Å recombination distance. The graphic demonstrated that the current density will decrease with the increase inserting time interval, which coincides with our expectation. The red curve represents the highest light intensity, which corresponds to 1 hole-electron pair per 10 femosecond insert rate. The orange curve has the second highest light intensity and its current density is only low to the red curve. The green, blue and violet curves represent inserting 1 pair per 50 femosecond, per 75 femosecond and per 100 femosecond respectively.

All these curves pass through the point (0.7, 0) in coordinate, which is called open circuit voltage point, because it relates with the workfuction of TiO₂. The DSSC coarse grain model has the assumption at the device has the 0.7 V open circuit voltage.
Figure 5.1 Simulation results of the relation between current density and voltage with the recombination distance at 1.5 Å. \( t \) is the time interval to insert hole-electron pairs.

Figure 5.2 Simulation results of the relation between current density and voltage with the recombination distance at 2.0 Å. \( t \) is the time interval to insert hole-electron pairs.
Figure 5.3 Simulation results of the relation between current density and voltage with the recombination distance at 2.5 Å. \( t \) is the time interval to insert hole-electron pairs.

Figure 5.2 and Figure 5.3 demonstrate the same trend as Figure 5.1: larger insert time interval has small value of current density. The light intensities we used in simulation are much larger than experiments. If we choose the same light intensity as experiments, a much longer simulation time is needed because of the longer time interval in real device.

Under the same light intensity, the longer recombination distance will have lower current density. For example, if we compare the current density at 1 pair / 10 femosecond inserting rate, we find the order is \( I_{R=1.5} > I_{R=2.0} > I_{R=2.5} \). Longer
recombination distance means that the opportunity for holes and electrons to absorb each other is increased. If more holes and electrons are recombinated, less holes and electrons will contribute to valid current, which results the small value of current density.

We do not try the larger recombination distance because at angstrom scale, it is already very large to electrons. In experiments, it is not easy to get the real recombination distance when a hole meets an electron. So from our DSSC model, simulation results reflect the trend and help us analyze the impacts of recombination to real devices.

5.3 Power conversion efficiency calculation

In order to calculate the power conversion efficiency of DSSCs, we have to get the input power and output power of PV devices first. The input power of DSSCs can be estimated from the calculation of sun light radiation power. The output power of DSSCs can be calculated from the simulation results of voltage and current density.

At 1.5 AM solar spectrum, the power density is about 1000 W/m². In order to estimate the energy of photons, we assume the wavelength of light to be 400 nm. So the energy of every photon is:

\[
E = \frac{hv}{\lambda} = \frac{6.62 \times 10^{-34} \text{J} \cdot \text{s} \times 3 \times 10^{-8} \text{m/s}}{400 \times 10^{-9} \text{m}} \approx 5 \times 10^{-19} \text{J} \tag{5.1}
\]
In the area of $100 \times 100 \, \text{Å}^2$, the number of photons is:

$$\frac{1000 j/m^2 \times 10^{-16} m^2}{5 \times 10^{-9} j} \approx 2 \times 10^5$$

(5.2)

The time interval to insert one hole-electron pair is

$$\Delta t = \frac{1}{2 \times 10^5} = 5 \times 10^{-6} \, \text{s} = 5 \times 10^9 \, \text{fs}$$

(5.3)

If the sunlight power is inversely proportional to photon time interval, then the power of light can be calculated at different time interval value. See Table 5.1 below

<table>
<thead>
<tr>
<th>Time interval for every two</th>
<th>Power density of sunlight</th>
</tr>
</thead>
<tbody>
<tr>
<td>photons (fs)</td>
<td>(W/cm$^2$)</td>
</tr>
<tr>
<td>10</td>
<td>$5.00 \times 10^7$</td>
</tr>
<tr>
<td>25</td>
<td>$2.00 \times 10^7$</td>
</tr>
<tr>
<td>50</td>
<td>$1.00 \times 10^7$</td>
</tr>
<tr>
<td>75</td>
<td>$6.67 \times 10^6$</td>
</tr>
<tr>
<td>100</td>
<td>$5.00 \times 10^6$</td>
</tr>
</tbody>
</table>

In photovoltaic community, researchers care more about the power conversion efficiency (PCE) since it is the standard parameter to compare. For the power conversion efficiency test, the device will be measured at AM1.5, which corresponds the light intensity at 1000 W/m$^2$ as the standard light intensity. While our simulation results of power conversion efficiency is at higher light intensity.
In order to get the value of power conversion efficiencies of DSSCs, we have to calculate the fill factor (FF) first. Fill factor can be obtained via the formula below:

$$\text{FF} = \frac{P_{\text{OPT}}}{P_{\text{theory}}} = \frac{I_{\text{OPT}} \times V_{\text{OPT}}}{I_{\text{SC}} \times V_{\text{OC}}}$$  \hspace{1cm} (5.4)

Where $I_{\text{OPT}}$ is the current at the maximum power point; $V_{\text{OPT}}$ is the voltage at the maximum power point; $I_{\text{SC}}$ is the current of short circuit; $V_{\text{OC}}$ is the voltage of open circuit.

Fill factor is a significant parameter, which reflects the performance of solar cells. Once the fill factor is available, we can get the value of power conversion efficiency by the formula below:

$$\eta = \frac{P_{\text{OPT}}}{P_{\text{Sun}}} = \frac{I_{\text{OPT}} \times V_{\text{OPT}}}{P_{\text{Sun}}} = \frac{FF \times V_{\text{OC}} \times I_{\text{SC}}}{P_{\text{Sun}}}$$  \hspace{1cm} (5.5)

where $P_{\text{Sun}}$ is the power of Sun. The heat is absorbed by solar devices.

Our simulation has used different recombination distance to see the change of power conversion efficiency. The table below is the simulation results from DSSC coarse grain model.
Table 5.2 Fill factor and power conversion efficiency of DSSC with the recombination distance at 1.5Å

<table>
<thead>
<tr>
<th>Electron-Hole Pairs Inserting Gap (fs)</th>
<th>Fill Factor</th>
<th>$V_{oc}$ (Voltage)</th>
<th>$I_{sc}$ (Amp/cm²)</th>
<th>$P_{opt}$ (W/cm²)</th>
<th>$P_{Sun}$ (W/cm²)</th>
<th>Power Conversion Efficiency(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.739</td>
<td>0.7</td>
<td>$4.71\times10^6$</td>
<td>$2.44\times10^6$</td>
<td>$5.00\times10^7$</td>
<td>4.875</td>
</tr>
<tr>
<td>25</td>
<td>0.702</td>
<td>0.7</td>
<td>$2.32\times10^6$</td>
<td>$1.14\times10^6$</td>
<td>$2.00\times10^7$</td>
<td>5.700</td>
</tr>
<tr>
<td>50</td>
<td>0.744</td>
<td>0.7</td>
<td>$1.50\times10^6$</td>
<td>$7.81\times10^5$</td>
<td>$1.00\times10^7$</td>
<td>7.813</td>
</tr>
<tr>
<td>75</td>
<td>0.704</td>
<td>0.7</td>
<td>$1.22\times10^6$</td>
<td>$6.78\times10^5$</td>
<td>$6.67\times10^6$</td>
<td>9.019</td>
</tr>
<tr>
<td>100</td>
<td>0.680</td>
<td>0.7</td>
<td>$1.16\times10^6$</td>
<td>$5.00\times10^5$</td>
<td>$5.00\times10^6$</td>
<td>11.050</td>
</tr>
</tbody>
</table>

Table 5.3 Fill factor and power conversion efficiency of DSSC with the recombination distance at 2.0Å

<table>
<thead>
<tr>
<th>Electron-Hole Pairs Inserting Gap (fs)</th>
<th>Fill Factor</th>
<th>$V_{oc}$ (Voltage)</th>
<th>$I_{sc}$ (Amp/cm²)</th>
<th>$P_{opt}$ (W/cm²)</th>
<th>$P_{Sun}$ (W/cm²)</th>
<th>Power Conversion Efficiency(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.662</td>
<td>0.7</td>
<td>$4.48\times10^6$</td>
<td>$2.07\times10^6$</td>
<td>$5.00\times10^7$</td>
<td>4.148</td>
</tr>
<tr>
<td>25</td>
<td>0.664</td>
<td>0.7</td>
<td>$2.29\times10^6$</td>
<td>$1.06\times10^6$</td>
<td>$2.00\times10^7$</td>
<td>5.319</td>
</tr>
<tr>
<td>50</td>
<td>0.627</td>
<td>0.7</td>
<td>$1.44\times10^6$</td>
<td>$6.33\times10^5$</td>
<td>$1.00\times10^7$</td>
<td>6.325</td>
</tr>
<tr>
<td>75</td>
<td>0.527</td>
<td>0.7</td>
<td>$1.22\times10^6$</td>
<td>$4.50\times10^5$</td>
<td>$6.67\times10^6$</td>
<td>6.750</td>
</tr>
<tr>
<td>100</td>
<td>0.520</td>
<td>0.7</td>
<td>$1.10\times10^6$</td>
<td>$4.04\times10^5$</td>
<td>$5.00\times10^6$</td>
<td>8.085</td>
</tr>
</tbody>
</table>
Table 5.4 Fill factor and power conversion efficiency of DSSC with the recombination distance at 2.5Å

<table>
<thead>
<tr>
<th>Electron-Hole Pairs Inserting Gap (fs)</th>
<th>Fill Factor</th>
<th>Voc (Voltage)</th>
<th>Isc (Amp/cm²)</th>
<th>Popt (W/cm²)</th>
<th>Psun (W/cm²)</th>
<th>Power Conversion Efficiency(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.645</td>
<td>0.7</td>
<td>4.20×10⁶</td>
<td>1.90×10⁶</td>
<td>5.00×10⁷</td>
<td>3.795</td>
</tr>
<tr>
<td>25</td>
<td>0.557</td>
<td>0.7</td>
<td>2.40×10⁶</td>
<td>9.35×10⁵</td>
<td>2.00×10⁷</td>
<td>4.675</td>
</tr>
<tr>
<td>50</td>
<td>0.493</td>
<td>0.7</td>
<td>1.52×10⁶</td>
<td>5.25×10⁵</td>
<td>1.00×10⁷</td>
<td>5.250</td>
</tr>
<tr>
<td>75</td>
<td>0.505</td>
<td>0.7</td>
<td>1.30×10⁶</td>
<td>4.60×10⁵</td>
<td>6.67×10⁶</td>
<td>6.900</td>
</tr>
<tr>
<td>100</td>
<td>0.593</td>
<td>0.7</td>
<td>9.70×10⁵</td>
<td>4.03×10⁵</td>
<td>5.00×10⁶</td>
<td>8.050</td>
</tr>
</tbody>
</table>

The power conversion efficiency can be plotted in a graphic to make the comparison easily.

![Simulation Results of DSSCs Power Conversion Efficiency](image)

Figure 5.4 Illustration of the simulation results of DSSCs power conversion efficiency with the different recombination distances and pair-hole inserting rating.
In Figure 5.4, X axis represents the value of the time interval to insert every hole-electron pair, Y axis represents the recombination distance, Z axis represents the power conversion efficiency of devices.

Based on the simulation results of power efficiency, we found all the power efficiencies are located at the range from 0 to 11%, which coincides with the experiments and real devices.

When compared with the high light intensity and low light intensity, the low light intensity is easily to reach the high efficiency. In high light intensity, a great number of holes and electrons will be generated. The density of particles between two electrodes is relatively high and holes and electrons will move strongly. The opportunity for holes to meet electrons, or the opportunity for electrons to meet holes is high compare with low particle density. Thus a lot of hole and electrons will lose in recombination before they arrive at electrodes. While at low light intensity, the movements of holes and electrons are not as strong as the case of high intensity. Once a hole-electron pair is inserted, the time interval for the next hole-electron pair is longer compared to high light intensity. Some holes electrons may have reached their destination as the contribution of current before the next hole-electrons are inserted.
At the same light intensity, shorter recombination distance will result to higher power efficiency. This trend is also easy to understand. Shorter recombination distance will results to the fewer recombination number. So the number of holes and electrons contribute to the current will be more, and it results to higher current density.

5.4 Trajectory analysis and electrons/holes diffusion coefficients calculation

The transport mechanism of electrons in DSSCs is a current hot topic for photovoltaic research community, and it is still under debate. Scientists have used varieties of experimental methods to characterize the transport processes to get the value of electron diffusion coefficient $D_n$.\textsuperscript{121} Intensity modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS)\textsuperscript{122–125}, electrochemical impedance spectroscopy (EIS)\textsuperscript{126–127} and the open-circuit voltage decay (OCVD) technique\textsuperscript{128} are widely used to explore the kinetics of electron’s behavior. Theoretical study on the transport mechanism of electrons in DSSCs has proposed several models to explain the transport phenomena. In 2004, Bisquert and Vikhrenko had introduced a multiple-trapping model to explain electron’s transport mechanism in DSSCs.\textsuperscript{129}

Here we applied molecular dynamics simulation approach to trace the trajectory of electrons and holes when the photovoltaic device is at the working condition. The trajectory of electrons and holes could be obtained by connecting the coordinates of moving particles step by step in 3-dimension space. The diffusion coefficient of
electrons and holes could be obtained by calculating the mean square displacement during molecular dynamics simulations. However, the ensemble used in simulation for trajectory and mean square displacement is different from one used for $I-V$ curve. During the trajectory and mean square displacement calculation, we use traditional molecular dynamics simulation and keep the total particle number constant. While in $I-V$ curve calculation, the total particle number will vary as time.

For trajectory calculation, we insert more than 50 pairs of electrons and holes in DSSCs coarse grain model and trace the coordinates of electron and holes in the first 35 fs, with 1fs as time step. In the Figure 5.5 and Figure 5.6 below, the trajectory of electrons and holes are demonstrated in 3-dimension coordinate, which corresponding the internal space in DSSC coarse grain model. The size of the model is $100 \times 100 \times 200 \ \text{Å}^3$ and the electrodes are located at the plane of Z=50 Å and Z=150 Å. So electrons and holes can move in the space between two electrodes, which means the scope of Z direction is limited between 50 Å to 150 Å. For X and Y direction, there is no limit because the coarse grain model uses periodic boundary condition. In the Figure 5.5 and Figure 5.6, we only select several particles’ trajectory instead of all one. During the MD trajectory calculation, there is no absorption or recombination since the software materials studio can only visualize the system with constant total particles number.
In Figure 5.5 and Figure 5.6, the trajectories curves of electrons and holes are demonstrated. We can found that electrons and hole will move along curved path, rather than straight line, which means that when particle are moving in the DSSC, they will receive varieties of force impacts, including coulomb interactions and van der Waals interactions. So when electrons or holes approach other beads, their velocity and moving direction will change until arriving at electrodes.

Figure 5.5 Illustration of the trajectories of single hole in the DSSC Coarse Grain model. Cathode is at the upside, with Z=150 Å, Anode is at the downside, with Z=50 Å
Figure 5.6 Illustration of the trajectories of single electron in the DSSC Coarse Grain model. Cathode is at the upside, with Z=150Å, Anode is at the downside, with Z=50Å.

When the photovoltaic is at working status, the mobility of electrons and holes can reflect and determine the performances of the device. Single-particle tracking can provide a lot of useful information on the behavior of individual molecules. In molecular dynamic based coarse grain simulation, all electrons and holes will be treated as molecules. So it makes the tracking the behaviors of electrons or holes available. In our study, we choose a widely used method – Means Square Displacement (MSD) analysis to study the mobility of charge carriers – electrons and
holes. The Mean Square Displacement is defined as:

\[ MDS = \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle \]  \hspace{1cm} (5.6)  

where \( \vec{r}(0) \) is the displacement of particles at time 0; \( \vec{r}(t) \) is the displacement of particles at time \( t \), the bracket means that the value of MDS is a average number over the number of total particles.

Figure 5.7 is the simulation results of mean square displacement of holes and electrons in DSSCs coarse grain model. We trace the electrons and holes in the first 35 fs this is because for a longer time, some electrons and holes may be absorbed by electrons. After getting the MDS, we can calculate the diffusion coefficient by the Einstein Relation below:

\[ \lim_{t \to \infty} \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle = 6D \]  \hspace{1cm} (5.7)  

where \( D \) is the diffusion coefficient of the moving particles.

So we can get the value of diffusion coefficient by calculating the slope of mean square displacement over time via the formula below:

\[ D = \frac{MSD}{6t} \]  \hspace{1cm} (5.8)
Figure 5.7 Illustration of the simulation results of mean square displacement (MSD) of electrons and holes in the DSSC coarse grain model.

In Figure 5.7, red curve and green curve represent the MSD of electrons and holes respectively. Two curves are very close, which combines with our expectation. In order to ease the estimation of the value of diffusion coefficient, blue line has been added as a reference line. Based on the blue line, at the time from 17 fs to 35 fs, the mean square displacement has increase from 3000 Å² to 21000 Å². Thus the slope of MSD over time can be calculated through the formula below:

\[
Slope = \frac{21000 - 3000}{6 \times (35 - 17)} \, \text{Å}^2/\text{fs} \\
= \frac{18000 \times 10^{-20}}{6 \times 18 \times 10^{-15}} \frac{m^2}{s} = \frac{10^{-17}}{6 \times 10^{-15}} \frac{m^2}{s} \approx 1.667 \times 10^{-3} \frac{m^2}{s} = 16.67 \text{cm}^2/\text{s}
\]  

(5.9)
Thus the value of diffusion coefficient $D_n$ of electrons and holes is about 16.67 cm$^2$/s in DSSC coarse grain model.

In order to evaluate the degree of our simulation result of diffusion coefficient, we have to compare it with the experimental results of the diffusion coefficient of electrons. Although a lot of paper has the testing results of the diffusion coefficient of electrons in DSSCs, most of these data were tested under the condition of AM1.5$^{121,130-133}$ and the typical value of the diffusion coefficient is about 10$^{-5}$ cm$^2$/S.$^{121}$ While Oekermann et al had explored the relation between diffusion coefficient and light intensity (photon density).$^{125}$ His experimental results demonstrate that base 10 logarithm of light intensity is linear to the base 10 logarithm of electron’s diffusion coefficient. So when the light intensity is increased 100 times, the diffusion coefficient will increase approximately 10 times. However, in the experimental testing, the light intensity is only as high as 10$^{16}$ /cm$^2$ S. Here we assume that the relation between diffusion coefficient and light intensity at normal light intensity, can apply to the case of high light intensity, even as high as 10$^{31}$ /cm$^2$ S, then the value of diffusion coefficient at high can be inferred. Thus if the light intensity increases from 10$^{15}$ /cm$^2$S to 10$^{31}$ /cm$^2$S, the diffusion coefficient will increase from 10$^{-7}$ cm$^2$/S to 10 cm$^2$/S, which is close to 16.67 cm$^2$/S, the simulation result of our coarse grain DSSCs model.
Although the experimental data of diffusion coefficient of electrons at high light intensity is rare, we can still compare the simulation results to experimental data indirectly since the experimental data at high light intensity could be predicted by the trend extrapolation approach based on the current available relation between light intensity and diffusion coefficient. From the analysis and comparison above, we can make a conclusion that the DSSC coarse grain model can be used to calculate the diffusion coefficient of electrons and our simulation approach to investigate the mobility of electron and hole is creditable, which verifies the validity of the ideas and mechanisms behind DSSC coarse grain model.
CHAPTER VI

ATOMISTIC SIMULATION MODEL OF SURFACE-MODIFIED CADMIUM SULFIDE NANOPARTICLES AND SUBSTITUTED POLY(PHENYLENE ETHynyene)S

The main components of cadmium sulfide based-hybrid photovoltaic devices include three components: semiconducting nanoparticles, capping agents and polymers. 3-(trimethoxysilyl)propyl methacrylate (MPTS) has been used widely as a kind of capping agent to tailor the surface of CdS NPs.\textsuperscript{134–139} In order to get the polymer based CdS NPs, the first step is to synthesize CdS NPs, which can be obtained via the route below:

\[
\begin{align*}
CdSO_4 + (NH_4)_2S + Thioglycerol & \rightarrow CdS - Thioglycerol + NH_4^+ + SO_4^{2-} \\
\end{align*}
\]  \hspace{1cm} (6.1)

The second step is to cap the CdS NPs with 3-mercaptopropyltrimethoxysilane. The last step is to integrate MPTS-modified CdS NPs into polymer matrix. The polymer is provided by CIQA and its chemical structure is demonstrated in Figure 1 (We call it polymer \textbf{P0}). For the experiments, 70mg MPTS-modified CdS NPs (See Figure 6.1) can react with 100 mg polymer \textbf{P0} to form 50 mg polymer based CdS NPs (See
The hydroxyl group in polymer P0 will react with hydrogen ion, and a new bond will form at the surfaces of MPTS-modified CdS NPs. The product is called with CdS nanoparticle NP1.

Figure 6.1  Schematic showing the structure of MPTS-modified CdS nanoparticles

Figure 6.2  Schematic showing the CdS nanoparticle NP1. New bond is formed after CdS NP reacts with polymer P0.

However, the traditional characterization method has difficulty to verify the new bond formed between MPTS-modified CdS NPs and polymer. So simulation methods are introduced to study this problem.
The MPTS-modified CdS NPs has a net formula $C_{306}H_{765}O_{153}Si_{51}S_{79}Cd_{79}$ and the whole particle is neutral. The diameter of the pure CdS NPs sphere is about 20Å. After capped with MPTS, the diameter will increase to about 27 Å. (Figure 6.3)

![Figure 6.3 Illustration of the structure of MPTS-modified CdS nanoparticles](image)

In order to investigate the MPTS-modified CdS NPs in contact with several substituted poly(phenylene ethynylene)s, and to identify the preferred location of functional groups and the impact of covalent bonds between the polymer $P0$ and the nanoparticle, we introduce oligomer $P1$, oligomer $P2$, oligomer $P3$ and oligomer $P4$. (Figure 6.5) The difference among these oligomers lies in the side chains and functional group. Compared with oligomer $P1$, oligomer $P2$ has no hydroxyl group.
at the side chains; oligomer $P_3$ has short side chains; oligomer $P_4$ has short side chains and no carbonyl group. By comparing these four polymers, we can analyze the roles of these functional group and long chains during the reaction to MPTS-modified CdS nanoparticles. **NP1** is the product of the MPTS-modified CdS nanoparticles reacting with polymer $P_0$. (Figure 6.4)

![Figure 6.4 Schematic showing the chemical structure of polymer $P_0$](image)

Software Accelrys® Materials Studio is used to set up 5 systems below: (Figure 6.5)

(A) 2 CdS NPs + 20 oligomer $P_1$;  
(B) 2 CdS NPs + 20 oligomer $P_2$;  
(C) 2 CdS NPs + 20 oligomer $P_3$;  
(D) 2 CdS NPs + 20 oligomer $P_4$;  
(E) 2 NP1.

![Oligomer $P_1$](image) ![Oligomer $P_2$](image)
For the CdS NPs, the charge of cadmium is set to +1e and the charge of sulfide is set to -1e. While at the surface of CdS NPs, there are a lot of sulfide atoms which can react with capping agents. For the sulfide atom which links with MPTS, the charge is set to -1.065e.

For the oligomers P1 ~ P4, the charge amounts of the carbon atoms at the backbone are set the same. At the backbone of oligomers, there are 33 carbon atoms. (Figure 6.6)

We use number to mark every carbon atom. The charge amount of every carbon atom can be found from Table 6.1

Figure 6.6 Schematic showing the chemical structure of the backbone of oligomers P1, P2, P3 and P4.
Table 6.1 Charge distribution of carbon atom in oligomer backbone

<table>
<thead>
<tr>
<th>Charge</th>
<th>Carbon Atom Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.0852</td>
<td>C2, C5, C6, C9, C10, C13, C14, C17, C18, C21, C22, C25, C26, C29, C30</td>
</tr>
<tr>
<td>-0.0852</td>
<td>C3, C4, C7, C8, C11, C12, C15, C16, C19, C20, C23, C24, C27, C28</td>
</tr>
<tr>
<td>-0.1268</td>
<td>C1</td>
</tr>
<tr>
<td>-0.0400</td>
<td>C32</td>
</tr>
<tr>
<td>-0.1190</td>
<td>C33</td>
</tr>
</tbody>
</table>

Molecular dynamic simulation method is adopted to study the above five systems. We choose LAMMPS simulation package\textsuperscript{140} and Polymer Consistent Force Field (PCFF)\textsuperscript{141} as our simulation tools. All the MD simulations use NVT ensemble and the size of MD simulation box is set to 68\times68\times80 \AA\textsuperscript{3}. After setting up by the Materials Studio, the structures of all the systems are optimized to make sure the total energy of the system can be minimized.

From this step, all the cadmium atoms and sulfide atoms are fixed during minimization and molecular dynamic running. After the minimization, we increase the temperature of the system and then anneal to 298.15K, to form the initial structure, for the next step. The final step is to run dynamic simulation with 1 femtosecond as time step, and the running last as long as 10 nanoseconds.
CHAPTER VII

CADMIUM SULFIDE NANOPARTICLE INTERFACIAL STRUCTURE

SIMULATION RESULT AND DISCUSSION

The target of MD simulation is to locate which functional group in the oligomer $P_1$ can form the covalence bond with the trimethoxysilyl shell of the nanoparticle surface. After MD simulations, we can analyze the results from the aspects of specific functional groups, oligomer backbone and oligomer side chain that we are interested. Statistical approaches are introduced to investigate and compare the properties of these four oligomers.

7.1 Morphology of Oligomers after MD Simulation

After 10 ns MD simulation, the structure, position and morphology of oligomers are demonstrated at Figure 7.1. The Figure shows that the backbone of oligomer is straight and not easy to bent, which coincides with the expectation since with the triple carbon bond, the oligomer can keep straight. From Figure 7.1 it is also found that there are a lot of long chains wrapping the surface of CdS nanoparticles.
Figure 7.1 Snapshots of the morphology after 10 ns MD simulation. The left column is the side view of the system and the right column is the front view of the system.
The components of four systems are shown below:

(A) Two CdS Nanoparticles+Oligomer $\textbf{P1}$; (B) Two CdS Nanoparticles+Oligomer $\textbf{P2}$; 
(C) Two CdS Nanoparticles+Oligomer $\textbf{P3}$; (D) Two CdS Nanoparticles+Oligomer $\textbf{P4}$.

7.2 Radial distribution function

Radial distribution function, also called pair correlation function, describes how density varies as a function of distance from a reference particle. Our study is interested in how many functional groups distribute on the surface of core-shell CdS nanoparticles. So we choose a cadmium atom, which is at the center of CdS nanoparticles, as the reference particle. At the side chain of oligomer $\textbf{P1}$, there are two kinds of functional group: hydroxyl group and carbonyl group. Several useful radial distribution functions are plotted in Figure 7.2.
Figure 7.2  The radial distribution functions (RDF) of oxygen atoms from hydroxyl group of oligomers P1, P3 and P4
Figure 7.2 is the radical distribution function for oxygen atoms from hydroxyl group. It shows every curve has two major peaks. The first peak of oligomer P1 is located at approximately 9.75 Å; while the first peaks of oligomer P3 and P4 are located at approximately 10.0 Å. The second peaks of three oligomers are all located at 12.0 Å. It means that most oxygen atoms from hydroxyl group will distribute at the position around 9.5 ~10.0 Å and 12.0 Å area from the center of CdS NPs. The simulation results meet with our expectation, since the radius of CdS NP is about 10 Å.

All the peaks appearing at the space with 2 Å above the surface of CdS NP, supports the evidence that hydroxyl group tends to contact with the trimethoxysilyl shell of the nanoparticle surface and aggregate there. The first peak position shows that the position of oligomer P1’s hydroxyl group will be closer than that from oligomer P3 and P4, which demonstrates that oligomer P1 is easier than oligomer P3 and P4, to form covalence bond at the surface of CdS nanoparticle.
Figure 7.3 The radial distribution functions (RDF) of oxygen atoms from carbonyl group of oligomers P1, P2, P3 and CdS Nanoparticle NP1
Figure 7.3 is the radial distribution function of oxygen atoms from carbonyl group, which shows that all carbonyl groups only appear as far as 12.5 Å from the center of CdS NP, even farther than the second peaks position of hydroxyl group. So based on Figure 7.3, we also found that all the peaks are located at the 17.5 Å from the center of a CdS NP. Considering that carbonyl group and hydroxyl group are connected by carbon chain. So it can be inferred that hydroxyl group likes to contact the MPTS-modified CdS NPs surface, and carbonyl group has no tends to contact the MPTS-modified CdS NPs surface.

7.3 Backbone carbon end-to-end distance of oligomers

In order to compare the main chain of oligomer $P_1$ to $P_4$, we have to define the backbone carbon end-to-end distance of oligomer. In the 3D model, carbon end-to-end distance of the main chain of oligomer is defined as $h$. (Figure 7.4)
For oligomer P_1–P_4, we define the distance between C1 and C33 as the backbone carbon end-to-end distance of oligomer. By analyzing the output and trajectory files of LAMMPS, we can get the 20 backbone carbon end-to-end distance of every oligomer. So totally there are 80 backbone carbon end-to-end distances, which are listed with ascending order at Table 7.1.
Table 7.1 Backbone carbon end-to-end distance $h$ of oligomer P1, P2, P3 and P4

Unit: Å

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Oligomer P1</th>
<th>Oligomer P2</th>
<th>Oligomer P3</th>
<th>Oligomer P4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.41±3.99</td>
<td>41.65 ± 3.65</td>
<td>23.47 ± 5.14</td>
<td>36.58 ± 6.23</td>
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<td>2</td>
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<td>42.98 ± 2.51</td>
<td>27.04 ± 3.49</td>
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<td>3</td>
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<td>44.34 ± 2.60</td>
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<td>43.36 ± 2.58</td>
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<td>4</td>
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<td>7</td>
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<td>47.75 ± 1.97</td>
<td>50.80 ± 1.37</td>
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<tr>
<td>Average</td>
<td>45.39±2.44</td>
<td>47.60 ± 2.22</td>
<td>38.50 ± 3.03</td>
<td>46.30 ± 2.86</td>
</tr>
</tbody>
</table>
Figure 7.5 Average value of backbone carbon end-to-end distance and error of oligomer P1, P2, P3 and P4

By comparing the data above, it is easily to get the conclusion that the average value of backbone carbon end-to-end distance of oligomers has the order of $h_{P3} < h_{P1} < h_{P4} < h_{P2}$. (See Figure 7.5) backbone carbon end-to-end distance can reflect the bending degree of oligomer main chain. Oligomer P2 is the only one which has no hydroxyl group. So without hydroxyl group, the oligomer chain is easy to keep straight, which is coincidence with our expectation. During the analysis for radical distribution function, we have found the hydroxyl group has the trend to contact with the trimethoxysilyl shell of the CdS NPs surface. So when the hydroxyl group moves toward the surface of CdS NPs, the backbone is easily to bend. This is why oligomer P2, without hydroxyl group, has the longest backbone length.
7.4 Impacts from the side chains of oligomers

Oligomer \textbf{P1} and \textbf{P2} has a long side chain, while oligomer \textbf{P3} and \textbf{P4} has a short side chain. These difference impact the movement of these four oligomers during MD simulation. From the trajectory of oligomer, we find oligomer \textbf{P3} and \textbf{P4} has higher mobility, compared with oligomer \textbf{P1} and \textbf{P2}, which have long side chains. The function of a long side chain is same as a claw. It can help the oligomers wrap the aspheric surface of MPTS-modified CdS NPs. This is also supported by the data of backbone length of oligomers. It shows that errors of backbone length of oligomer \textbf{P1} and \textbf{P2} is shorter than oligomer \textbf{P3} and \textbf{P4}. Because oligomer \textbf{P1} and \textbf{P2} has long side chain, it can help the oligomers stick around the surface easily. With the low mobility of the oligomer, the extension degree of backbone can be reduced and the distance error of average value of backbone carbon end-to-end also be decreased.

7.5 Bond formed at the surface of CdS Nanoparticles

Condensation reaction between hydroxyl group and hydrogen can form the new CdS NPs, which are covered with polymer chains. After forming the covalence bond, carbonyl group is the only functional group in new CdS nanoparticle \textbf{NP1}. We compare the radial distribution function of carbonyl group of oligomer \textbf{P1} and \textbf{NP1} in Figure 7.3 We found that the position of the first peak of carbonyl group of \textbf{P1} is almost same as the \textbf{NP1}, which show that the behavior of carbonyl group stays same, whether the covalence bond is formed or not.
CHAPTER VIII

CONCLUSIONS

The development of extensions of molecular dynamics (MD) algorithms to simulate dynamic photovoltaic processes in dye-sensitized solar cells (DSSCs) using a multiscale model is a new development in the photovoltaic community to understand the performance of devices. The mechanism of charge transport, I-V curves, and power conversion efficiency (PCE) can be explored for a variety of operating conditions and chemical compositions, and enriches the portfolio of techniques to study DSSCs and their work mechanisms. By virtue of computer platforms and theoretical study, guidance toward improvement in the efficiency can be obtained.

Force fields for electron and holes, coarse grain models of the components in a solar cell, and molecular dynamics simulation methods are combined to realize the simulation of I-V curve and power conversion efficiency. To our knowledge, it is the first time to obtain I-V curves by simulation using models at the mesoscopic scale near device level. We also include recombination effects in an initially simple way that can be elaborated for specific systems and refined information on electronic
structure. Electrical engineers, optical engineers in the photovoltaic community, and specialists in molecular simulation can understand the model with relative ease. It does not require very specialized knowledge of chemistry or material science to be applied as it relies on classical mechanics in its basic form.

By exploring the transport properties and dynamic behaviors of electrons and holes in a model of a DSSC at a coarse grain level, we obtained sample trajectories of charge carriers, I-V curves, and power conversion efficiency for different intensity of light and recombination properties. The results demonstrate that I-V curves are in good agreement with experimentally observed shapes and show the expected dependence on external light intensity and recombination affinity of holes and electrons. Higher light intensity will generate higher current density, which is same as the trend of real DSSCs devices. In addition, the results show that shorter recombination distance will also generate higher current density. Also there is no experiment studying the relation between recombination distances with device performances, computer simulation has predicted this trend, which may become a solid proof for the study of recombination.

With the assistance from computers, the simulation of the photovoltaic process of DSSC devices at multiple length scales has thus become available and visualization tools can represent the critical processes that remain elusive by use of current laboratory instrumentation.
The model for the simulation of solar cells and its simulation code still contains weaknesses that benefit from further interpretation and improvements. Major limitations are access to realistic length and time scales. The current length scale of 10 nm in the model is still much smaller than for DSSC devices. Time scales have been limited in the range of hundred picoseconds due to the compute intensity. We therefore assumed a light intensity a billion times higher than the AM 1.5 solar spectrum to create enough current density for the simulation of I-V curves in the model. However, this assumption can be justified in the simulation by use of a thermostat that eliminates heat generation as a side effect, which would normally occur in a real system due to adsorption across the wide range of the visible spectrum (e.g. IR) and frequent recombination. The extrapolated dynamics for larger time scales and the actual AM 1.5 solar spectrum is projected to be similar, i.e., when the time interval for electron-hole insertion is increased from femtoseconds to microseconds, as the lifetime of many electrons and holes will remain in the femtosecond range. In addition, the interpretation of length scales and tuning of intermolecular interactions for specific systems is flexible in a certain range. The code currently runs on single processor and could be parallelized in the future for higher efficiency. A technical issue is also breaking of certain bonds (code stops) due to overlap of charge carriers with atoms or beads of other components in the course of the simulation. These challenges can be addressed in further work.
In addition, classical MD simulation methods are also used to explore the dynamic behaviors of several substituted poly(phenylene ethynylene)s at the surfaces of MPTS-modified CdS NPs. Substituted poly(phenylene ethynylene)s with different functional groups demonstrate varieties of behaviors when they approach to the surfaces of the trimethoxysilyl shell of the CdS nanoparticles, which is in coordination with our expectation. Large scale molecular dynamic simulation provides enough data for the statistical analysis on the distribution of functional groups, which makes the simulation results reliable enough.

Based on the above simulation results, we explain the how the hydroxyl group of polymer P0 is located as the candidate with the highest possibility to react with MPTS-modified CdS NPs to form covalence bonds. First we use statistical approaches to demonstrate how the hydroxyl group from the substituted poly(phenylene ethynylene)s, has the high trends to contact with the trimethoxysilyl shell of the nanoparticle surfaces. While other function groups cannot attach on the surfaces of the CdS NPs, as close as hydroxyl group under the same external environments. The statistical results describe the equilibrium distance from the surface to varieties of functional groups, which give us a clear comparison between different substituted poly(phenylene ethynylene)s. These results tell us that substituted poly(phenylene ethynylene)s with hydroxyl group, rather than carbonyl, is easier to carry condensation reactions to link with the CdS NPs surfaces. Secondly, the
measurement of the backbone carbon end-to-end distance of several oligomers also support that an oligomer with hydroxyl group is easy to bend, which confirm that an oligomer without hydroxyl group has no trend to contact the CdS NPs surfaces. The side chains also play a role of reducing the mobility of oligomers when they are attached on the surfaces of CdS NPs. On the basis of the observation of this study, we propose hydroxyl group has the highest possibility to react with the hydrogen atoms from the 3-mercaptopropyltrimethoxysilane, the capping agent for core-shell CdS NPs, to form covalence bonds at the surface. Thus substituted poly(phenylene ethynylene)s with hydroxyl groups and long side chains is the best candidate to anchor on the surfaces of MPTS-modified CdS NPs.
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