EMULSION POLYMERIZED MONODISPERSE SILICA-POLYMER CORE-SHELL NANOPARTICLES FOR ANTIREFLECTIVE COATINGS

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EMULSION POLYMERIZED MONODISPERSE SILICA-POLYMER CORE-SHELL
NANOPARTICLES FOR ANTIREFLECTIVE COATINGS

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ABSTRACT

Anti-reflective coatings (AR coatings) can improve the transmission of the light to provide a valuable property with highly effective reflectance and glare reducing. Hence, they are widely used in various optical and opto-electrical equipments. Over the year, extensive research in optical and biological reflectance minimization has contributed to the enhancement of AR coatings in a major way as well as the emergence of nanotechnology in the world of physical and chemical sciences.

In core-shell nanoparticles, the core is composed of inorganic nanoparticle which is covered by inorganic or organic materials, like some organic compounds or polymers with special groups, as the shell. We can endow these core-shell nanoparticles with diverse controllable properties as used in polymers by designing the shell with appropriate groups for covering a core.

In this thesis, it was a study about the feasibility of using core-shell nanoparticles to get anti-reflectivity in coatings. The synthesis for a kind of core-shell structure particles was a two steps method including the synthesis of the MPS-silica as the seed by grafting MPS onto the TEOS spherical oligomer and then grafting the TFEMA to provide the fluorinated alkyl group which could also polymerize to be PTFEMA onto the seed through the reaction with the olefin double bond brought by the MPS on the surface of
the MPS-silica through emulsion polymerization to cover a polymer shell onto the silica core. The investigation about the situation of application was done by studying the light transmittance of the coating formed with the core-shell particles synthesized before by UV-Vis. And it was proved that the silica-polymer core-shell nanoparticles can realize a transmittance increasing for preparing AR coatings. Other characterizations have been done with the seed MPS-silica and the core-shell PTFEMA-silica and also the coating, such as TEM, DLS, solid state $^{13}$C and solid state $^{29}$Si NMR, TGA, SEM.
DEDICATION

Dedicated to my parents; Jincheng Geng, and Ming Yan, for their unconditional love ever since I was born. I cannot survive till now without them.
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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction of Anti-reflective coatings

Anti-reflective coatings (AR coatings) are widely used in various optical and optoelectrical equipments like display screens, windows, optical filters, solar cells, and photodetectors. In the field of physical sciences, Lord Rayleigh (John Strutt) construed the idea of anti-reflective coatings incidentally after he observed the transmittance increasing of a glass with tarnishing. This set in motion to the approaches to achieve anti-reflectivity by changing the refractive index step by step. However, the first anti-reflective coatings were produced by Fraunhofer in 1817. He noticed that etching a surface in an atmosphere of sulphur and nitric acid vapors could help to reduce the reflection. Since the demand of optical and opto-electronic equipments is growing in diverse areas from the daily electronic products to the exploration in space, how to maximize light collection efficiency also has caused concern infinitely. Like for solar cells, silicon nitride or titanium dioxide coatings of nanometer scales realize the reflectance reduction. In addition, to increase light coupled into the cell with textured front surface is used especially in mono-crystalline silicon. Moreover, as the world pays more attention on alternative sources of energy where solar takes over an important place. But reflection losses in the conventional photovoltaic modules because of low conversion
efficiency come out as a major block. As reported that a normal solar panel can always absorb nearly 25% of the incident solar radiation, which means, a third of the incident radiation has been reflected which directly reduces the overall efficiency. A large amount of anti-reflective coatings have been manufactured commercially to overcome these issues and used to get an improvement in overall efficiency which always reduces obviously by durability, debonding and high cost issues, like in optical equipments especially cameras and eye glasses. The results are indeed paid attention which has led to product manufacturers of LCDs, cathode ray tubes and aerospace sensors and to take stock AR coatings to better the performance of their products as well.

1.1.1 Principles

Reflection, as an optical phenomenon, is brought about by the light’s travelling through the medium. Refractive index \((n)\), as a parameter, is always used here to characterized the medium (glass, water, air, etc) optically. It represents the speed of light in the medium with regard to that in vacuum. Thus, if there is a change happening to the refractive index (RI) as light travels, an optical disturbance will come into eyes. The basic theory for generating AR coatings by using the interference effect has been well known for many years till now which is mainly explained by the Fresnel equation (1-1). Reflectance, \(R\), helps to measure the fraction of incident light which is reflected at the interface. And the rest transmitted (refracted) is measured by transmittance, \(T\). The simplest case to obtain anti-reflective property (a thin film) on a substrate material (glass) follows quarter-wave rule which is shown in equation (1-2) and (1-3) derived from the equation (1-1). And make a deal to follow the assumptions:
1. The reflected waves have the same intensity and one reflected wave per interface.

2. Other optical interactions such as scattering, absorption etc. are negligible.

Figure 1-1 Light travelling through a single layer film on substrate ($n_s > n$)

Therefore, it’s obvious from Figure 1-1 that if the two reflected waves, $R_1$ and $R_2$, can cancel each other by a destructive interference, there would be no reflection. Then, Anti-reflection can be realized by the two essential criteria:\n
1. The reflected waves should be $\pi$ radians out of phase or has a phase difference, $\delta$, which is $n\pi/2$.

2. The thickness of the film ($d$) should be an odd number of times of $\lambda/4$. The $\lambda$ means the wavelength of the incident light.

According to Fresnel’s equation, the minimum reflection of a coated surface can be depicted:
\[ R_m = \left( \frac{n_1^2 - n_0 n_s}{n_1^2 + n_0 n_s} \right)^2 \]  

1-1

Where, \( n_1 \) – Refractive index of the film,

\( n_0 \) – Refractive index of the medium,

\( n_s \) – Refractive index of the substrate

To achieve zero reflectance, \( R_m \) should be set to zero. Then the refractive index of the film \( (n_1) \) comes out like equation (1-2). And \( d \) in equation (1-3) is the thickness of the film.

\[ n_1 = \sqrt{n_s \times n_0} \]  

1-2

\[ d = \frac{\lambda}{4n_1} \]  

1-3

From these relations above, if we chose the glass as the substrate, the air as the medium, then \( n_s \) is equal to 1.52 and \( n_0 \) is equal to 1. After the calculations with them into the equations above, we can get that \( n_1 \) must be 1.23 to attain zero reflection. It is absolutely unattainable because this value is so low that any ones of the homogeneous dielectric materials can’t have refractive indices as low as this one. Furthermore, the quarter-wave layer isn’t appropriate for all the wavelengths. As a result, multilayered AR coatings composed of at least four to six layers was most frequently adapted such as the AR layers on eyeglass which is designed for anti-reflectivity\(^5,6\). As shown in Figure 1-2, \( R_{ij} \) belongs to the reflected light from the interface between the adjacent layers \( i \) and \( j \) which is given by the equation (1-4)\(^7\).

\[ R_{ij} = |R_{ij}| \exp[-2(\delta_i + \delta_j)] \]  

1-4
Where, $|R_{mn}| = [(n_i - n_f)/(n_i + n_f)]$  

So, $R_{sum} = R_{01} + R_{12} + R_{23} + R_{34} + R_{4s}$

Equation (1-6) shows the $R_{sum}$ as the resultant reflection vector.

Where $R_{01} = |R_{01}|$

$R_{12} = |R_{12}| \exp[-2(\delta_1)]$

$R_{23} = |R_{23}| \exp[-2(\delta_1 + \delta_2)]$

$R_{34} = |R_{34}| \exp[-2(\delta_1 + \delta_2 + \delta_3)]$

$R_{4s} = |R_{4s}| \exp[-2(\delta_1 + \delta_2 + \delta_3 + \delta_4)]$
Then we can achieve an AR coating with the best anti-reflective properties through minimizing \( R_{\text{sum}} \) which can be attained by controlling \( R_l \) by the selection of the layer materials and the thickness of each layer of the film.

1.1.2 Approaches to attaining anti-reflection

According to interference layer concept, anti-reflection can be imparted in two ways which have been demonstrated by many researchers. Since, they found that imparting porosity to the film can lower the refractive index. Porous layer and patterned surface structure is the most widely explored approach in this background.\(^8,9\) It applies single layer with the refractive index varying gradually by lowering the volume fraction since porous layer, like porous silicon, is always a sponge like material with nanovoids to unity. It means that the refractive index can be lowered by increasing the proportion fraction of medium, like air. So, we can attain a layer with gradient refractive index by porous coatings or by periodic bumpy surface structures which mixes the low-index material with air to get a sub wavelength scale. It is the principle in this context as shown in Figure 1-3.
Figure 1-3 Schematic illustration of surfaces with varying refractive index: (a) porous coating, (b) periodic surface structure

The density and index of refraction in this type of material have a relation as shown in the equation below (1-12).

\[
\frac{n_p^2 - 1}{n^2 - 1} = \frac{d_p}{d} \quad 1-12
\]

Where, \( n \) - Index of the nonporous material,

\( d \) - Density of the nonporous material,

\( n_p \) - Index of the porous material,

\( d_p \) - Density of the porous material.

If in terms of porosity, Equation (1-12) can be written as the equation below (1-13),

\[
n_p^2 = n^2 \times (1 - \phi) + \phi \quad 1-13
\]

\( n_p, n \) and \( \phi \) are the effective refractive indices of porous film, pure film, and porosity. In this way, the best possible refractive index of the coating in accordance with the substrate can be regulated by changing the degree of the porosity in the coating.
1.1.3 Types of anti-reflective coatings (AR coatings)

Type I – based on the layer composition

Homogeneous AR coatings. As we have already discussed, the RI and thickness limit the refractive index \( n \) of a single homogeneous layer. The refractive index must be \( n = \sqrt{n_s \times n_0} \) and the thickness should equal to \( \lambda/4 \). If the substrate is put in air as the medium, \( n_0 \) is 1 and \( n \) mostly depends on \( n_s \). So, as the conclusion we got earlier, the \( n \) can be lowered by using a porous or pattern layer. In addition, multiple layers also help achieve zero reflectance at a certain wavelength. But the RI will not be strictly obeyed.

Inhomogeneous AR coatings. Inhomogeneous AR coatings base on the gradient refractive index approach to attain anti-reflectivity which has been discussed earlier.

1.2 Monodisperse Core-Shell Nanoparticles

1.2.1 Introduction

Nanomaterials are a field that takes a materials science based approach on nanotechnology. It is studied on the nanoscale which is one or more dimension in the nanometer scale range. The bulk materials of them are always endowed with novel properties depending on the design of the nanomaterials. In the wide range of nanotechnology areas, nanoparticles have been paid more attention by researchers on their synthesis, characterization, and applications since it lead to changes in the physical and chemical properties as microparticles changed to nanoparticles. At first, single nanoparticles were studied deal to its better properties than the bulk materials’. In the late
1980s, researchers found that in some cases heterogeneous, composite or sandwich colloidal semiconductor particles are more effective than the single particles and even develop more properties.\textsuperscript{11-13} As the synthesis of nanoparticles is complex, there are a lot of techniques available for producing diverse nanoparticles. These techniques can be divided into three classes: (i) condensation from vapor, (ii) synthesis by chemical reaction, and (iii) solid-state processes such as milling. Then, depending on the suitability of the applications, we can also synthesize hybrid or coated nanoparticles by using these techniques mentioned above. During more recently years, in the early 1990s, subsequently the “core-shell” came out as a new terminology since more concentric multilayer semiconductor nanoparticles had been produced to improve the property of more semiconductor materials. At the same time, the improvement in characterization techniques also helped to set up different core-shell nanostructures. For various properties, core-shell nanoparticles can be modified by tuning either the constituting materials or the ratio of the core to shell\textsuperscript{14}. Different materials chosen for either the core or the shell, sometimes, bring out properties quite different. So core-shell nanoparticles are highly functional. For example, after the shell materials coating on, the core particle’s properties, like decreasing reactivity and thermal stability, can be modified to different ones such as the dispersibility of the core particle increasing. And different materials employed together can lead to distinctive properties showed by the particles, finally, which maybe a way to help to meet the various application requirements about their bulk materials\textsuperscript{15, 16}. As the shell, it can endow the overall particle or even the bulk materials amount of properties by coating on the core particle such as stability, controlled release of the core, surface modification, increasing the functionality, and so on.
From Karele et al., the fact that core-shell nanoparticles are popular for devise applications has been demonstrated by many reports from different researchers. Such as biomedical\textsuperscript{17-20} and pharmaceutical applications,\textsuperscript{15} enhancing photoluminescence,\textsuperscript{21-23} catalysis,\textsuperscript{16, 24} creating photonic crystals,\textsuperscript{25} electronics,\textsuperscript{26-28} and so on. In the field of biomedical, such as for targeted drug delivery,\textsuperscript{19, 29-31} bioimaging,\textsuperscript{19, 29, 31-36} cell labeling,\textsuperscript{19, 37, 38} controlled drug release,\textsuperscript{29} and tissue engineering applications.\textsuperscript{39}

On the other hand, core-shell materials are also valuable for an economic point. For example, when we need to produce a precious material we can coat it with an inexpensive material to instead of amount of the precious material.

1.2.2 Classes of Core-Shell Nanoparticles

Based on the variety of the materials, single or multiple, nanoparticles can be classified into simple and core-shell or composite nanoparticles. Simple nanoparticles are based on a single material while core-shell and composite particles are made from two or more materials as their names. In general, the core-shell particles are composed of two materials: one for the core inside and one for the shell outside. From that broadly definition, amount of combinations of different materials as the core and shell can be consisted, for example, inorganic-inorganic, inorganic-organic, organic-inorganic, and organic-organic materials. It’s important to make sure about the end application since it determines the choice of the materials for the shell of the core-shell nanoparticle. Inorganic-organic core-shell nanoparticles will be introduced in detail for the purpose that we are working for a core-shell nanoparticle used into an antireflective coating.
1.2.2.1 Classified by the Structure of Core-Shell Nanoparticles

As shown in Figure 1-4 schematically, in general, the core-shell nanoparticles can be categorized into five classes. Concentric spherical core-shell nanoparticles which have a simple spherical core completely covered by a different material shell outside are more common than others (in Figure 1-4a). Core-shell nanoparticles are also classified through their different shapes since different properties can be endowed with materials from different shaped core-shell nanoparticles them using. As shown in Figure 1-4b, core-shell nanoparticles in different shape, nonspherical shape, are always made from a nonspherical core. The next, which is shown in Figure 1-4c, is one of multiple core core-shell nanoparticles. They are formed by coating a single shell materials onto many small cores put together. Another widely used type is nanoshells core-shell nanoparticles. They are formed by coating metal or dielectric core and shells onto each other in an A-B-A type as shown in Figure 1-4d, where dielectric spacer layers and metallic layers separate each other. They are also named as metallodielectric nanostructures or nanomatryushka and have an important application for the plasmonic property.\textsuperscript{40-43} There is also a kind of core-shell nanoparticles having a moveable core coated with a simple hollow shell outside as shown in Figure 1-4e. It is realized by coating a bilayer shell and removing the first layer of the shell through a feasible approach.
Figure 1-4 Classes of core-shell nanoparticles: (a) concentric spherical core-shell nanoparticles; (b) hexagonal core-shell nanoparticles; (c) multiple small core materials coated by single shell material; (d) nanomatryushka material; (e) movable core with in hollow shell material.

1.2.2.2 Inorganic-Organic Core-Shell Nanoparticles

The inorganic core are made of metal, metallic compound, metal oxide, or silica while the organic shell are generally a polymer shell or one made of some high density organic material. Inorganic-organic core-shell nanoparticles have many advantages. For example, core-shell structure can help to increase the oxidation stability of a metal core which will be oxidized to the metal oxide in a normal situation.\textsuperscript{44,45} In another case, for application in biological field, they improve the biocompatibility.\textsuperscript{46-49} The bulk materials of inorganic-polymer core-shell nanoparticles are broadly applied in additives, pigments, paints, and cosmetics. For many applications, the coated shell generally helps to stabilize the particle in their suspension media. And it’s the attractive and repulsive force between the particles controlling the stability of the suspension. Four different kinds of forces are shown as following: (i) Van der Waals forces, (ii) induced short-range isotropic
attractions, (iii) electrostatic repulsion, and (iv) steric repulsion. Then the aggregation of the nanoparticles can be avoided by tuning the synthesis media to find the electrostatic and steric repulsion forces suitable. For aqueous media, the particles’ stabilization is predominated by the electrostatic force while for organic media that’s predominated by the steric repulsion force. It’s hence necessary to find a simple shell of a suitable material to realize the control of these forces. The inorganic-organic core-shell nanoparticles can be widely categorized into two different types by distinguishing on the material properties of the core. The first one is magnetic-organic core-shell nanoparticles and the second one is nonmagnetic-organic core-shell nanoparticles.

Magnetic-Organic Core-Shell Nanoparticles are broadly used for magnetic recording, magnetic sealing, electromagnetic shielding, and also in biological field for specific drug targeting, magnetic cell separation and so on. It’s general to synthesize magnetic core particle by chemical processes which bring the advantages to obtain excellent crystallinity and magnetization. But to form bigger size particles, in the range of micrometers, is also a problem. As magnetic-organic core-shell nanoparticles are always used in an environment with high applied magnetic, the stability of them is very necessary. And it is realized by covering the magnetic cores with suitable organic materials to reduce the agglomeration to attain the particles with a higher stability in their suspension.

Nonmagnetic-Organic Core-Shell Nanoparticles are as important as the magnetic-organic ones because they are also broadly applied in a wide range of fields. This kind of particles can be classified into metal, metal oxide, and metal salt core particles covered
with various organic materials. Since the metal-organic core-shell nanoparticles have surfaces with amount of functional groups, they are easily modified for bioconjugation purposes\textsuperscript{55-57}. As an example, the distinctive optical properties including localized surface plasmon resonance of the nanoscale noble metals like Au and Ag lead to a considerable attention on them. For metal or metalloid oxide-organic core-shell nanoparticles the formation is easy by a chemical reaction. But it is difficult to attain the particles with smaller size in a dispersing media, because they highly tend to grow and easily in agglomeration. Coating the particles with a simple shell of polymer materials is an excellent method to solve that problem because the shell can be removed easily.\textsuperscript{58} Metal oxides, especially transition metal oxides coating on the organic materials can help them have excellent applications in a broad range of fields such as material additives,\textsuperscript{59-61} controlled release,\textsuperscript{62} catalysis,\textsuperscript{63} optics,\textsuperscript{64-66} and so on.
Figure 1-5 A schematic presentation of organic monolayer coatings on inorganic core particles. (a-COOH, b-OH)

As shown in Figure 1-5, for example, it can be a schematic view of a core-shell nanocomposite with a functionalized shell, (Ag or Au) or ZrO2 or stearate. The zigzag chains in the figure are the stearic acid chains. The presence of –OH groups indicate the presence of hydroxyl groups bounded on ZrO2. It is a liquid-like assembly owing to that there is no interaction between the chains. There are some common polymers always used as the organic shell materials for silica cores: polystyrene (PS), poly(methylmethacrylate) (PMMA), poly(vinyl chloride) (PVC), and poly(3-aminophenylboronic acid). As shown in Figure 1-6, it is the schematic diagram of a silica-polymer core-shell nanoparticle. Silica-polymer core-shell nanoparticles improve colloidal stability. They are important with a wide range of applications in electrical devices, material additives, controlled release, catalysis, sensors, and optical devices.
Figure 1-6 Schematic representation for the synthesis of silica-polymer core-shell particles by surface-initiated atom transfer radical polymerization.

Metal Chalcogenide or Metal Salt-Organic Core-Shell Nanoparticles are another kind of inorganic-organic core-shell nanoparticles. They also have attracted much attention for use in various applications in wide fields such as electronic devices, light-emitting devices, and chemical sensors. For example, the light-emitting properties of CdSe QDs are enhanced compared with naked QDs by coating polymer on them because on a higher current level the organic layer contributes more to the spectra than QDs. But these particles are difficult to be commercialized because the limited process ability of these polymer materials. As another example, a PMMA shell on CdS keeps the optical properties of the material away from environmental disturbance while simultaneously does not reduce the optical properties due to the transparency.

1.2.3 Approaches to Synthesize Core-Shell Nanoparticles

Core-shell nanoparticles are generally synthesized in two steps: the first one is synthesizing the core and the second one is to cover the shell onto the core. Depending on the availability of the core, the synthesis of core-shell nanoparticles is categorized into
two types. In the first method, the core particles are separately synthesized, and then will be purified and dried before suitable surface modification to coat the shell material onto them. In the second method, the core particles are synthesized in “situ” using suitable reactants along with a surface modifier and or a growth inhibitor. The shell coating onto the core is formed in “situ” by adding more reactants after the core is formed completely. In the external core synthesis, the advantage is that cores are available in pure form in which case there is less impurities on the core surface. However, the main problem of in “situ” synthesis is that there will be some impurities from the reaction media trapped on the interface between the core and shell. In the synthesis of core-shell particles, it is the most important to attain uniform coating and to tune the thickness of the shell. From many research reports, some of the diverse synthetic methods for core-shell particles are sol-gel condensation, micro emulsion, polymerization, precipitation, layer by layer adsorption techniques, and so on. But the proper control of the thickness or to getting uniform coating shell by these methods is still very difficult since there are many difficulties such as the core agglomeration in the reaction media, formation of shell material particles instead of the formation of shell covering the core, the shell coating onto the core unfinished, and controlling the reaction rate. Surface active agents and polymers are often used for the modification of the core surface to tune the surface selectivity and surface charge of the core particles to deposit the shell material onto the core surface to get the uniform and completely covering core-shell particles.
1.2.3.1 Synthesis of Organic Nanoparticles

Polymerization is the most broadly applicable approach to synthesize organic shell and can be categorized into addition polymerization and step polymerization. Based on the reaction with suitable initiator and the design of the reaction conditions, monomer molecules are combined to each other into 3-D networks during the polymerization. So, polymerization processes can be subdivided into bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization, due to their difference in the phase behavior.

Coating the polymer shell onto the inorganic core is generally realized “in situ”. According to the purpose to enhance the shell coated onto the inorganic core, the normal method is to modify the surface of the core by surfactants. Then, on the surface of the inorganic core, polymerization occurs such as bulk polymerization or solution polymerization. As an example, some silica-polymer composite nanoparticles are synthesized in those methods. In the bulk polymerization, the reactions of either monomers or polymers take place in the liquid phase. But the reaction in that method only proceeds in the liquid phase and requires a high temperature. The molecular weight and viscosity also increase progressively. In solution polymerization, there is also a disadvantage to remove the solvent so as to extract pure solid polymer. Another method, suspension polymerization is a reaction taking place in droplets. The monomers used in this method are soluble in their medium. A protective agent and a constant vigorous stirring are always used to keep the droplets in a suspended state. The next technique to talk about is emulsion polymerization where the monomer is general dispersed in water.
after a surfactant to achieve an emulsion. This method is broadly used in industry because it can form a stable suspension without continuous stirring. And compared with other methods mentioned above, the heat transfer efficiency of emulsion polymerization is higher while the viscosity changes less. But it is difficult to form a stable emulsion of the monomer water compound in the environment with a suitable emulsifier. And the surfactant is also hard to be removed completely. In the application for hydrophilic polymer coatings on inorganic particles, the main necessary is to improve the stability and biocompatibility of those inorganic particles. It can be attained by using an appropriate hydrophilic initiator during the polymerization. And the initiator may also help to modify the surface of the inorganic particles. The initiators used for different polymerization processes include hydrophilic inorganic compounds and hydrophobic compounds.

1.2.4 Characterization of Core-Shell Nanoparticles

After the synthesis of the core-shell nanoparticles, it’s important to do the measurement about the shape and properties of the particles such as size, thickness of the shell, elemental, optical properties, surface analysis, and thermal stability among others. Since the structure is special as coating shell materials onto the core surface, it is necessary to find a characterization technique suitable for both the core and shell. Generally, most characterizations used for core-shell nanoparticles are the same ones used for simple particles, but more than one technique is required for a complete report of a core-shell nanoparticle. The characterizations such as dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal
gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and UV-Vis spectroscopy are also classified depending on the techniques themselves and different instruments as following.

1.2.4.1 Microscopic Analysis

Microscopic analysis is reliable technique for the visualization of different types of nanoparticles. Scanning electron microscopy (SEM) is the most common one applied for size and shape analysis. The magnification of SEM is \(10^5\) - \(10^6\). But for core-shell nanoparticles it is necessary to distinguish the difference between core and shell which is difficult for SEM because it only works with surfaces. However, EDX, energy-dispersive X-ray spectroscopy, can be used with SEM together for the elemental analysis of the shell surface. In addition, field-emission SEM (FESEM) is recently useful for a higher magnification than normal SEM which can show the information about the shell surface, smooth or rough.

Compared with SEM, transmission electron microscopy (TEM) can provides more details such as confirmation of the core-shell structure formation, core size, the thickness of shell, lattice fringes of the shell material, and so on. The morphology of the particles can be easily measured from the contrast difference of different materials which form the core and the shell. High-resolution TEM (HR-TEM) is used for higher magnification reliable to see resolution at the molecular level.
1.2.4.2 Spectroscopic Analysis

For nanocrystal surface modification, optical properties are extremely sensitive since they can present some indirect information about the shell materials coated on the surface of the core. UV-Vis spectroscopy is a kind of spectroscopic technique that present an absorbance spectrum in its region by noting the energy absorption capacity. It’s a common spectroscopic technique for analyzing different types of nanoparticles. In the analysis of core-shell nanoparticles, UV-Vis is applied to analyze the difference between the spectra of core, shell, and core-shell material. In this approach, the intensity (absorbed or emitted light) and peak wavelengths will be different from the ones in coating.

Another important spectroscopic technique, X-ray photoelectron spectroscopy (XPS), is used to present surface information: chemical status, elemental composition, empirical formula, electronic state or binding modes of surface ligands, and depth analysis of atomic composition. But XPS requires an ultrahigh vacuum (UHV) chamber which means that the analysis can only reach a depth 10 nm from the particle surface.

1.2.4.3 Scattering Analysis

First, light, electron, neutron scattering is one of the major techniques for nanoparticle characterization in no matter the colloidal state or power form. Dynamic light scattering (DLS) is another major technique applied to measure direct particle size in nanoparticle suspensions. Sometimes it’s named as photo correlation spectroscopy or quasi-elastic light scattering. Then, the shell thickness can be measured by comparing the difference between the measurements of the size of the nanoparticles before and after coating the
Some indirect evidences can also be attained in the range of core surface modification, such as the hydrodynamic diameter of the particles, by measurement of the ζ potential of the core particles in the solution.\textsuperscript{97, 101}

For the characterization of synthesized crystalline materials, the technique extensively used is Power X-ray diffraction. The mainly applications are for the identification of unknown materials and to analyze the crystallographic structure, size, and preferred orientation in polycrystalline. For core-shell nanoparticles, it helps to prove the reveal of a complete uniform shell since the core material diffraction peak intensity will decrease as coating shell on it and completely disappear after a sufficient thickness of the shell is laid down.\textsuperscript{102-104}

1.2.4.4 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) is a technique used for characterization of the thermal stability. It is the measurement of weight loss. Differential thermal analysis (DTA) reveals a thermal profile as the temperature increasing.
CHAPTER II

EMULSION POLYMERIZED MONODISPERSE SILICA-POLYMER CORE-SHELL NANOPARTICLES FOR ANTIRELECTIVE COATINGS

2.1 Abstract

It’s an innovative idea that to apply monodisperse silica-polymer core-shell nanoparticles into coatings for an antireflective property. For preparing the monodisperse silica-polymer core-shell nanoparticles, silica nanoparticles grafted with 3-(trimethoxysilyl) propyl methacrylate (MPS, 98%) was employed as seeds in an emulsion polymerization. Since the core-shell nanoparticles should have a good migration towards coating-air interface, polyfluoroester grafted silica comes out as the final core-shell nanoparticles. The silica colloids can be driven to the interface between coating and air by the fluorinated alkyl group. In this project, the fluorinated alkyl group comes from 2, 2-Trifluoroethyl methacrylate (TFEMA, 99%). The monodispersity and diameters of the core-shell nanoparticles were found to depend on the size of the grafted silica nanoparticles, the MPS-silica. The size of the seed nanoparticles was controlled by changing the temperature set in the reaction for them. The amount of fluorinated alkyl groups was also varied for finding a perfect core-shell system of the silica colloids. In addition, the formation mechanism of the core-shell nanoparticles was verified. The seeds, MPS-silica, and the fluorosilica colloids, PTFEMA-silica, were characterized by TEM,
DLS, TGA, solid state $^{13}$C NMR and solid state $^{29}$Si NMR. The coatings were characterized by SEM and UV-Vis transmittance spectra.

2.2 Materials

For the preparation of the composite silica structure, the materials required are described as follows. Tetraethylorthosilane (TEOS, reagent grade, 98%), 3-(Trimethoxysilyl)propyl methacrylate (MPS, 98%), Sodium dodecylbenzenesulfonate (SDBS), Potassium persulfate (KPS), 2,2,2-Trifluoroethyl methacrylate (TFEMA, 99%), absolute ethanol were pure grade and absolute ammonium hydroxide were analytical grade and both of them were used as received. Deionized water was applied for all polymerization and treatment processes.

2.3 Instrumentation and Characterization

Dynamic Light Scattering, DLS also referred to as Photon Correlation Spectroscopy (PCS) or Quasi-elastic Light Scattering (QELS) was obtained on Brookhaven Research Goniometer and Laser Light Scattering System. It helped to calculate the average diameter of all the silica particles and investigated the monodispersity of them.

Transmission Electron Microscope (TEM, JEM 1200XII) was employed to observe the morphology and size of silica particles (preparation of sample: diluted solution in ethanol in certain proportionl was dropped on the surface of copper grid coated with carbon film, 400 Mesh Cu (Cu-400 Fc) pre-coated with Formvar carbon film, Pacific Grid Tech, and was dried before the characterization). Solid state $^{13}$C NMR and $^{29}$Si NMR were recorded on a Geminin-400 spectrometer (Varian) at room temperature. Thermal gravimetric
analysis (TGA) (TA Instruments Q50 Thermogravimetric Analyzer) is a technique used for characterization of the thermal stability. It is the measurement of weight loss. TA Instruments Q50 Thermogravimetric Analyzer Field Emission Scanning Electron Microscope (SEM, JEOL JSM-7401F) was used to study the distribution and morphology of silica particles on the coating-air interface. UV-Vis transmittance was obtained by HP Agilent 8453 UV/Vis spectrophotometer in the range of 200 nm to 1000 nm on the dried coating peeled off the substrate.

2.4 Synthesis and Characterization of Polyfluoroester grafted Silica Particles

2.4.1 Synthesis and Characterization of Seed MPS-Silica Particles from TEOS

400 ml of dry ethanol and 29.6 ml ammonium hydroxide was stirred magnetically for 30 min at 65 °C in the three-neck flask equipped with a condenser. TEOS (12 ml, 11.28 g, 0.0536 mol, 0.14 mol/l) was added into the solution above and stirred for 24 h. Then 1.28 ml MPS were added into flask and reaction continued for more than 10 h. Then the temperature was raised to 80 °C and held for 1 h. The MPS-silica was and characterized by solid state $^{13}$C NMR, solid state $^{29}$Si NMR.

$^{13}$C NMR of MPS-S64 : (400 MHZ) $\delta$=67.16(-Si-CH$_2$CH$_2$CH$_2$O), 23.47 (-Si-CH$_2$CH$_2$CH$_2$CH$_2$O), 9.62 (-Si-CH$_2$ CH$_2$CH$_2$O), 167.99 (-C=O), 138.16 (-C(CH$_3$)=CH$_2$), 123.73 (-C(CH$_3$)=CH$_2$), 18.28 (-C(CH$_3$)=CH$_2$) ppm;

$^{13}$C NMR of MPS-S58: (400 MHZ) $\delta$=67.35 (-Si-CH$_2$CH$_2$CH$_2$O), 23.09 (-Si-CH$_2$CH$_2$CH$_2$O), 9.23 (-Si-CH$_2$ CH$_2$CH$_2$O), 169.34 (-C=O), 137.97 (-C(CH$_3$)=CH$_2$), 124.31 (-C(CH$_3$)=CH$_2$), 17.32 (-C(CH$_3$)=CH$_2$) ppm;

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\(^{13}\)C NMR of MPS-S52: (400 MHZ) \(\delta=67.16\) (-Si-CH\(_2\)CH\(_2\)CH\(_2\)O), 23.47 (-Si-CH\(_2\)CH\(_2\)CH\(_2\)O), 8.66 (-Si-CH\(_2\)CH\(_2\)CH\(_2\)O), 169.99 (-C=O), 138.16 (-C(CH\(_3\))=CH\(_2\)), 124.50 (-C(CH\(_3\))=CH\(_2\)), 18.28 (-C(CH\(_3\))=CH\(_2\)) ppm;

\(^{13}\)C NMR of MPS-S42: (400 MHZ) \(\delta=67.16\) (-Si-CH\(_2\)CH\(_2\)CH\(_2\)O), 23.28 (-Si-CH\(_2\)CH\(_2\)CH\(_2\)O), 9.23 (-Si-CH\(_2\)CH\(_2\)CH\(_2\)O), 169.53 (-C=O), 138.16 (-C(CH\(_3\))=CH\(_2\)), 124.50 (-C(CH\(_3\))=CH\(_2\)), 18.47 (-C(CH\(_3\))=CH\(_2\)) ppm;

\(^{29}\)Si NMR of MPS-S64: (400 MHZ) \(\delta=-109.53\) (Si(OSi\(_4\), Q\(_4\)), -99.68 (Si(OSi\(_3\)OH, Q\(_3\)), -56.56 (T\(_2\)), -66.42 (T\(_3\)) ppm

\(^{29}\)Si NMR of MPS-S58: (400 MHZ) \(\delta=-110.30\) (Si(OSi\(_4\), Q\(_4\)), -100.45 (Si(OSi\(_3\)OH, Q\(_3\)), -57.33 (T\(_2\)), -65.95 (T\(_3\)) ppm

\(^{29}\)Si NMR of MPS-S52: (400 MHZ) \(\delta=-111.53\) (Si(OSi\(_4\), Q\(_4\)), -100.45 (Si(OSi\(_3\)OH, Q\(_3\)), -57.33 (T\(_2\)), -65.95 (T\(_3\)) ppm

\(^{29}\)Si NMR of MPS-S42: (400 MHZ) \(\delta=-109.07\) (Si(OSi\(_4\), Q\(_4\)), -100.45 (Si(OSi\(_3\)OH, Q\(_3\)), -57.33 (T\(_2\)), -67.19 (T\(_3\)) ppm

2.4.2 Synthesis and Characterization of Polyfluoroester grafted Silica via Emulsion Polymerization of MPS with Fluorester

The grafted silica (MPS-silica) solid was dried in an oven at room for 24 h after some impurities such as ammonia, oligomer of MPS were removed by four cycles of centrifugation (7 500 rpm, 60 min) and redispersion with ethanol. Monodisperse core-shell nanoparticles were synthesized by emulsion polymerization. In a typical experiment,
there needs 1.2 g of grafted silica spheres, the MPS-silica, dispersed in 10 ml of ethanol by ultrasonication, 0.03 g of sodium dodecyl benzene sulfonate (SDBS) as emulsifier, 0.24 g of NaHCO₃ as buffer agent, 100 ml of water as the dispersion medium, 0.1 g of Potassium persulfate (KPS) as initiator and 2,2,2-Trifluoroethyl methacrylate (TFEMA) (It was in different amount when used for a further study which will be discussed later) were placed into a three-neck flask with a stirring. The polymerization was then carried out in an atmosphere of nitrogen for 10 h at 80℃. The emulsion of monodisperse core-shell nanoparticles (330 nm in diameter) was obtained without any post preparative treatments and was characterized by solid state ¹³C NMR, solid state ²⁹Si NMR (almost same with the ones of MPS-silica).

¹³C NMR of PTFEMA-S58-3.5: (400 MHZ) δ=255.54 (CF3), 176.65 (-C=O), 124.69 (-CH=CH-), 97.94 (OCH2CF3), 62.35 (-Si-CH₂CH₂CH₂O), 46.16 (-CH (CH₃)-CH=CH-CH(CH₃)-) ppm;

¹³C NMR of PTFEMA-S58-9.0: (400 MHZ) δ=254.78 (CF3), 176.65 (-C=O), 125.27 (-CH=CH-), 97.94 (OCH2CF3), 62.35 (-Si-CH₂CH₂CH₂O), 46.18 (-CH (CH₃)-CH=CH-CH(CH₃)-) ppm;

2.5 Coating Casting

The coating casting was finished in solution casting method. It was performed by hand movement on glass pane cleaned and dried with acetone by using a drawdown bar. There were two layers of the coating. The first layer on the glass pane is as the matrix, which was formed by the miscible solution of the 3HDI solution in methyl ethyl ketone (MEK)
(60%wt) and the 2-butyl-2-ethyl-1, 3-propanediol (BEPD) solution in MEK (60%wt) as that the weight rate of -NCO/-OH is 1.1/1 because the diol with the most hydrophobic character, BEPD, resulted in polyester with the best hydrolytic stability. The reaction mechanism is presented below. Since the –NCO equivalent in the 3HDI solution and the hydroxyl equivalent in the BEPD solution are 5.15mmol/g and 2.61mmol/g, after the calculation, the recipe of the first layer as the matrix is shown in Table 2-1. And the thickness of this layer was 150 µm (6 mil).

Then, the second layer is the AR coating. The recipe of the core-shell nanoparticles/matrix solution as AR coating formulation was listed in the Table 2-2 when the total weight of each formulation is 6 grams and all the concentration is based on weight percent. The thickness was controlled on 25 µm (1 mil) by the drawdown bar.

The first layer was dried in air for more than 1h, then, treated at 150°C for 30min. After that, casting a second layer onto the pre-dried matrix film was in the same way with the first layer made with. The wet film was then dried at room temperature for 3 h. Then, the characterizations of the AR coatings were done with them removed from the glass pane.
And for a deep study, the AR coating was prepared in three particle concentrations, 0.5%, 1% and 3%, for the UV-Vis and SEM characterization.

2.6 Results and Discussion

The objective of this project was to apply monodisperse silica-polymer core-shell nanoparticles into coatings for an antireflective property to prepare AR coatings. For the silica-polymer core-shell structure, the core seeds were MPS-silica, silica nanoparticles grafted with 3-(trimethoxysilyl) propyl methacrylate (MPS, 98%) as shown in Figure 2-2. Since the core-shell nanoparticles should have a good migration towards coating-air interface, polyfluoroester grafted silica comes out as the final core-shell nanoparticles after an emulsion polymerization. The fluorinated alkyl group comes from 2, 2-Trifluoroethyl methacrylate (TFEMA, 99%) as shown in Figure 2-3 and can reduce the surface energy to help the silica colloids drive to the interface between coating and air.

![Figure 2-2 Structure of 3-(trimethoxysilyl) propyl methacrylate (MPS)](image-url)
The monodispersity and diameters of the core-shell nanoparticles were found depending on the size of the grafted silica nanoparticles. The size of the seed nanoparticles was controlled by changing the reaction temperature. The amount of fluorinated alkyl groups was also varied for finding a perfect core-shell system of the silica colloids. The MPS-silicas and the fluoriosilica colloids, PTFEMA-silicas, were characterized by TEM, DLS, TGA, solid state $^{13}$C NMR and solid state $^{29}$Si NMR. The coatings were characterized by SEM and UV-Vis transmittance spectra.

2.6.1 Synthesis and Characterization of seed MPS-Silica Particles from TEOS
The seed as the core, MPS-silica particle, was synthesized from an oligomer TEOS grafted with MPS as shown in Figure 2-5. For the aim to get different size core MPS-silica particles, different temperatures were set during the first step reaction. And the result about how the size of MPS-silica particles changes with the temperature was listed in Table 2-4 which was attained by Dynamic Light Scattering (DLS) technique. The DLS results of five kinds of MPS-silica provided a curve describing the size of the MPS-silica changing with the reaction temperature which is shown following in Figure 2-6.

The average diameter of each kind of MPS-silica is close to the result obtained from the TEM as shown in Figure 2-7 and 2-8. From the DLS results, another valuable conclusion for the MPS-silica was that they were all monodisperse which meant the MPS-silica particles met the requirement of the seed particles used for the core-shell structure. From the TEM results, that the particles were all monodisperse can also be seen.

The solid state $^{13}$C and solid state $^{29}$Si NMR of MPS-silica synthesized under 64°C, 58°C, 52°C and 42°C were revealed in Figure 2-9 to 2-12 and Figure 2-13 to 2-16 with the assignment of each resonance noted. In different temperature, the results were close to
each other. So, the ones attained in 58 °C for example, the chemical shift at δ 67.35 ppm corresponds to (-Si-CH₂CH₂CH₂O), at 23.09 ppm due to (-Si-CH₂CH₂CH₂O), and at 9.23 ppm to (-Si-CH₂CH₂CH₂O). And the one at 169.34 ppm can be assigned to (-C=O), 137.97 ppm to (-C(CH₃)=CH₂), 124.31 ppm to (-C(CH₃)=CH₂), and 17.32 ppm to (-C(CH₃)=CH₂). In the solid state ²⁹Si NMR, δ -110.30 came from Si(OSi)₄ while -100.45 made by Si(OSi)₃OH. The MPS-S58 was chosen as the seed to synthesize the PTFEMA-silica in next step. In addition, all the MPS-silica was named like that. “MPS-S” means MPS-silica and the number after shows the temperature it used for the synthesis. “MPS-S58” means the MPS-silica synthesized under 58 °C. In the same way, “PTFEMA-S58” means the PTFEMA-silica (core-shell) synthesized with the MPS-S58 as the seed. In the later discussion, “PTFEMA-S58-3.5” or “PTFEMA-S58-9.0” and so on also have another number following which shows the amount of TFEMA used each time is different which has a great influence. The NMR results will be discussed again later to have a compare with the solid state ¹³C and solid state ²⁹Si NMR of PFEMA-silica for investigating the synthetic route.
### Table 2-1 Recipe of the first layer matrix coating formulation

<table>
<thead>
<tr>
<th>Materials</th>
<th>Mass(g)</th>
<th>MEK Mass(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3HDI</td>
<td>0.2685</td>
<td>5.16</td>
</tr>
<tr>
<td>BEPD</td>
<td>0.4815</td>
<td>4.09</td>
</tr>
</tbody>
</table>

### Table 2-2 Recipe of the second layer AR coating formulation

<table>
<thead>
<tr>
<th>Sample</th>
<th>1% core-shell nanoparticle solution with MEK</th>
<th>Matrix solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>0.03g</td>
<td>5.97g</td>
</tr>
<tr>
<td>1%</td>
<td>0.06g</td>
<td>5.94g</td>
</tr>
<tr>
<td>3%</td>
<td>0.18g</td>
<td>5.82g</td>
</tr>
</tbody>
</table>

### Table 2-3 the size of MPS-silica particles in different reaction temperature

<table>
<thead>
<tr>
<th>MPS-silica particle</th>
<th>Temperature (°C)</th>
<th>Average diameter from DLS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPS-S68</td>
<td>68</td>
<td>33.5</td>
</tr>
<tr>
<td>MPS-S64</td>
<td>64</td>
<td>83.0</td>
</tr>
<tr>
<td>MPS-S58</td>
<td>58</td>
<td>99.3</td>
</tr>
<tr>
<td>MPS-S52</td>
<td>52</td>
<td>101.5</td>
</tr>
<tr>
<td>MPS-S42</td>
<td>42</td>
<td>114.7</td>
</tr>
</tbody>
</table>
Figure 2-6 the size of MPS-silica particles changing with reaction temperature.
Figure 2-7 TEM of MPS-silica in 42°C and 52°C: (a) MPS-S42; (b) MPS-S52.
Figure 2-8 TEM of MPS-silica in 58°C and 64°C: (a) MPS-S58; (b) MPS-S64.
Figure 2-9 The solid state $^{13}$C NMR of MPS-S64

The solid state $^{13}$C NMR of MPS-S64: (400 MHZ) $\delta$=67.16 (-Si-CH$_2$CH$_2$O), 23.47 (-Si-CH$_2$CH$_2$CH$_2$O), 9.62 (-Si-CH$_2$CH$_2$CH$_2$O), 167.99 (-C=O), 138.16 (-C(=CH$_3$)=CH$_2$), 123.73 (-C(=CH$_3$)=CH$_2$), 18.28 (-C(=CH$_3$)=CH$_2$) ppm;
Figure 2-10 The solid state $^{13}$C NMR of MPS-S58

The solid state $^{13}$C NMR of MPS-S58: (400 MHZ) $\delta=67.35$ (-Si-CH$_2$CH$_2$CH$_2$O), 23.09 (-Si-CH$_2$CH$_2$CH$_2$O), 9.23 (-Si-CH$_2$CH$_2$CH$_2$O), 169.34 (-C=O), 137.97 (-C(CH$_3$)=CH$_2$), 124.31 (-C(CH$_3$)=CH$_2$), 17.32 (-C(CH$_3$)=CH$_2$) ppm;
Figure 2-11 The solid state $^{13}$C NMR of MPS-S52

The solid state $^{13}$C NMR of MPS-S52: (400 MHZ) $\delta=67.16$ (-Si-CH$_2$CH$_2$O), 23.47 (-Si-CH$_2$CH$_2$CH$_2$O), 8.66 (-Si-CH$_3$CH$_2$CH$_2$O), 169.99 (-C=O), 138.16 (-C(CH$_3$)=CH$_2$), 124.50 (-C(CH$_3$)=CH$_2$), 18.28 (-C(CH$_3$)=CH$_2$) ppm;
Figure 2-12 The solid state $^{13}$C NMR of MPS-S42

The solid state $^{13}$C NMR of MPS-S42: (400 MHZ) $\delta=67.16$ (-Si-CH$_3$CH$_2$CH$_2$O), 23.28 (-Si-CH$_2$CH$_2$CH$_2$O), 9.23 (-Si-CH$_2$CH$_2$CH$_2$O), 169.53 (-C=O), 138.16 (-C(CH$_3$)=CH$_2$), 124.50 (-C(CH$_3$)=CH$_2$), 18.47 (-C(CH$_3$)=CH$_2$) ppm;
The solid state $^{29}$Si NMR of MPS-S64: (400 MHZ) $\delta$=-109.53 (Si(OSi)$_4$, Q$^4$), -99.68 (Si(OSi)$_3$OH, Q$^3$), -56.56 (T$^2$), -66.42 (T$^3$) ppm

Figure 2-13 The solid state $^{29}$Si NMR of MPS-S64
Figure 2-14 The solid state $^{29}$Si NMR of MPS-S58

The solid state $^{29}$Si NMR of MPS-S58: (400 MHZ) $\delta$=-110.30 (Si(OSi)$_4$, Q$^4$), -100.45 (Si(OSi)$_3$OH, Q$^3$), -57.33 (T$^2$), -65.95 (T$^3$) ppm
The solid state $^{29}$Si NMR of MPS-S52: (400 MHZ) $\delta$= -111.53 (Si(OSi)$_4$, Q$^4$), -100.45 (Si(OSi)$_3$OH, Q$^3$), -57.33 (T$^2$), -65.95 (T$^3$) ppm
The solid state $^{29}$Si NMR of MPS-S42: (400 MHZ) $\delta=$ -109.07 (Si(OSi)$_4$, Q$^3$), -100.45 (Si(OSi)$_3$OH, Q$^3$), -57.33 (T$^2$), -67.19 (T$^3$) ppm
2.6.2 Synthesis and Characterization of Polyfluoroester grafted Silica via Emulsion Polymerization of MPS with Fluoroester

Monodisperse core-shell nanoparticles were synthesized by emulsion polymerization with the particles attained from the first step by grafting the MPS onto TEOS oligomer. In fact, when designing the experimental scheme, the MPS was used to occupy olefin double bond as the point for TFEMA to be grafted onto for achieving the PTFEMA (TFEMA polymer) shell coated onto the core which can be verified from the compare of the chemical shift in the NMR results of the two kinds particles attained from the first and second steps. And for a further study about getting a good shell, four kinds of PTFEMA-silica were synthesized with TFEMA in different amounts. Here, shown as the example, the MPS-silica used was 99nm (the average diameter from DLS).

![Figure 2-17 Synthetic route for PFEMA-silica from MPS-silica](image)

For the final core-shell structure particle, the PTFEMA-silica, DLS technique was used to investigate the size of the particles and the result is shown below in Table 2-4.
TEM (Transmission Electron Microscope) technique was applied to observe the morphology and size of PTFEMA-silica particles which is presented below in Figure 2-18, Figure 2-19 and Figure 2-20. From the TEM results about the PTFEMA-silica, it can be seen that the amount of TFEMA presents a great influence on the core-shell structure formation of the PTFEMA-silica. Comparing the average diameters of the four kinds of PTFEMA-silica synthesized with TFEMA in 2.0ml/1.2g \((\text{MPS-S58})\), 3.5ml/1.2g \((\text{MPS-S58})\), 9.0ml/1.2g \((\text{MPS-S58})\) and 14.0ml/1.2g \((\text{MPS-S58})\) provided that when the dosage of TFEMA was so large or so small, like 14.0ml/1.2g \((\text{MPS-S58})\) and 2.0ml/1.2g \((\text{MPS-S58})\), it was difficult to build the core-shell structure due to the aggregation of the shell material or the cores. But, when the dosage rate of TFEMA (ml): MPS-silica (g) was 9ml: 1.2g (same as 9ml/1.2g \((\text{MPS-S58})\)) or 3.5ml: 1.2g there was a mass of core-shell structure particles taking shape. And 9ml/1.2g \((\text{MPS-S58})\) must be closer to the most suitable rate of TFEMA (ml): MPS-silica (g) while as it was 3.5ml/1.2g \((\text{MPS-S58})\) the average diameter even larger than the 9ml/1.2g \((\text{MPS-S58})\) ones which meant that there must be more aggregation happening in 3.5ml/1.2g \((\text{MPS-S58})\) reaction. So, in further study, it would be a good idea to try more different rate of TFEMA (ml): MPS-silica (g) around 9ml/1.2g \((\text{MPS-S58})\) for a perfect formula. Maybe, an accurate control of the thickness of the shell could be realized not only recognizing the core-shell structure. On the other hand, the TEM results were almost in conformity with the DLS ones which verified the analysis above.
Table 2-4 the size of PTFEMA-silica particles attained from MPS-S58 by DLS

<table>
<thead>
<tr>
<th>PTFEMA-silica</th>
<th>The amount of TFEMA (ml/1.2g&lt;sub&gt;MPS-S58&lt;/sub&gt;)</th>
<th>Average diameter from DLS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFEMA-S58-2.0</td>
<td>2.0</td>
<td>653.7</td>
</tr>
<tr>
<td>PTFEMA-S58-3.5</td>
<td>3.5</td>
<td>352.1</td>
</tr>
<tr>
<td>PTFEMA-S58-9.0</td>
<td>9.0</td>
<td>296.6</td>
</tr>
<tr>
<td>PTFEMA-S58-14.0</td>
<td>14.0</td>
<td>609.3</td>
</tr>
</tbody>
</table>
Figure 2-18 TEM of PTFEMA-silica with the amounts of TFEMA were 2.0 ml/1.2g(MPS-S58) and 14.0 ml/1.2g(MPS-S58): (a) PTFEMA-S58-2.0; (b) PTFEMA-S58-14.0.
Figure 2-19 TEM of PTFEMA-silica with the amounts of TFEMA were 9.0 ml/1.2g\textsubscript{(MPS-S58)} PTFEMA-S58-9.0.
Figure 2-20 TEM of PTFEMA-silica with the amounts of TFEMA were 3.5 ml/1.2g_{MPS-S58} PTFEMA-S58-3.5.

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The solid state $^{13}\text{C}$ and solid state $^{29}\text{Si}$ NMR was also applied to investigate the PTFEMA-silica as shown following in Figure 2-21 to Figure 2-24. From two kinds of PTFEMA-silica different in the dosage of TFEMA, the $^{13}\text{C}$ or the $^{29}\text{Si}$ results were close.

But when compared with the ones from MPS-silica, there reveals a remarkable change that the peak of the “i” (-C(CH$_3$)=CH$_2$) with $\delta=137.97$ in MPS-silica disappeared in PTFEMA-silica solid state $^{13}\text{C}$ NMR. At the same time, there arised a new peak at with $\delta=46.16$ which corresponds to the new “i” and “m” (-CH (CH$_3$)-CH=CH-) in the PTFEMA-silica. That means the synthetic route mentioned before was confirmed.

$\delta=124.69$ (-CH=CH-) and $\delta=97.94$ (OC$_2$H$_2$CF$_3$) as new peaks also proved that the TFEMA took place the reaction for silica-polymer core-shell PTFEMA-silica particles.
Figure 2-21 The solid state $^{13}$C NMR of PTFEMA-S58-3.5

$^{13}$C NMR of PTFEMA-S58-3.5: (400 MHz) $\delta=255.54$ (CF$_3$), 176.65 (-C=O), 124.69 (-CH=CH-), 97.94 (OCH$_2$CF$_3$), 62.35 (-Si-CH$_2$CH$_2$CH$_2$O), 46.16 (-CH (CH$_3$)-CH=CH-CH(CH$_3$)-) ppm;
Figure 2-22 The solid state $^{13}$C NMR of PTFEMA-S58-9.0

$^{13}$C NMR of PTFEMA-S58-9.0: (400 MHZ) $\delta = 254.78$ (CF3), 176.65 (-C=O), 125.27(-CH=CH-), 97.94 (OCH$_2$CF$_3$), 62.35 (-Si-CH$_2$CH$_2$CH$_2$O), 46.18 (-CH (CH$_3$)-CH=CH-CH(CH$_3$)-) ppm;
Figure 2-23 The solid state $^{29}$Si NMR of PTFEMA-S58-3.5
Figure 2-24 The solid state $^{29}$Si NMR of PTFEMA-S58-9.0
Thermal gravimetric analysis (TGA) is a technique used for characterization of the thermal stability. It is the measurement of weight loss. As what is shown in Fig.2-25, the weight loss of the core-shell nanoparticles, PTFEMA-silica, started obviously at about 233.23°C. That means it can satisfy most applications as a material for AR coatings. In addition, there were two parts in the whole loss process. They must be the weight loss of the shell material and the core material. The fastest loss speed of either of them was 0.7687%/°C at 269.17°C and 1.015%/°C at 359.03°C.

Figure 2-25 TGA of PTFEMA-S58-9.0
2.6.3 Coating Formation

2.6.3.1 UV-Vis Evaluation of AR properties

In this thesis, the whole objective is to prepare a new anti-reflective coating. Therefore, the transmittance of the coating is necessary. Three AR coatings with different concentration were formed for the transmittance characterization. They were 0.5\%, 1\%, and 3\%. The matrix without any sample particles was also prepared for a compare. And the blank was set by using the glass slide without anything on it even without the matrix. The result is obvious that every AR coating has a higher transmittance than the matrix coating. And the 1\% coating is better than either 0.5\% coating or 3\% coating. This result provides a powerful prove for that the silica-polymer core-shell nanoparticles can be used as an antireflective material for AR coatings.
Figure 2-26 UV-Vis transmittance for AR coatings in different concentration
2.6.3.2 SEM Characterization of AR film

For the coating formation, SEM shows the morphology of those three AR coatings with different concentrations from each other.

Figure 2-27 SEM of AR coating in different concentration: (a) 0.5%; (b) 1%; (c) 3%.
CHAPTER III

CONCLUSION

The object of the whole thesis is attempting to know if particles with core-shell structure can be used in coating casting to improve the antireflective property of AR coatings. From the results mentioned above and the analysis in three aspects about the MPS-silica, the PTFEMA-silica and the AR coating. And finally, it was proved that the silica-polymer core-shell nanoparticles absolutely can have an application in AR coatings. After the study about the MPS-silica, the positive result is that the size of them can be controlled by changing the reaction temperature and the average diameter decreases with the temperature increasing. And they can always be monodisperse which is valuable for a coating material application. For the synthetic route, it is confirmed that the first step is MPS grafting onto the TEOS oligomer to synthesize the MPS-silica as the seed for the second step. Since MPS grafted on the seed providing the olefin double bond which realizes the reaction going on with grafting TFEMA or PTFEMA onto the seed to finish the shell covering the core. In addition, another problem comes from the control about the dosage of TFEMA during the synthesis. The result is when the dosage is around 9.0ml/1.2g (MPS-S58) and 3.50ml/1.2g (MPS-S58) the core-shell structure can be achieved. In other case, when the dosage of TFEMA was so large or so small, like 14.0ml/1.2g (MPS-S58) and 2.0ml/1.2g (MPS-S58), it was difficult to build the core-shell structure due to the
aggregation of the shell material or the cores. So, in further study, it would be a good idea to try more different ratio of TFEMA (ml): MPS-silica (g) around 9ml/1.2g (MPS-S58) for a perfect formula. Maybe, an accurate control of the thickness of the shell could be realized not only recognizing the core-shell structure.
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