

Polyacrylate-Core/TiO₂-Shell Nanocomposite Particles Prepared by *In Situ* Emulsion Polymerization

Zhaoquan Ai,^{1,2} Guilin Sun,² Qilong Zhou,² Changsheng Xie¹

¹College of Material Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

²Faculty of Chemistry and Material Science, Hubei University, Wuhan 430062, People's Republic of China

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ABSTRACT: We report the preparation of polyacrylate-core/TiO₂-shell nanocomposite particles through *in situ* emulsion polymerization in the presence of nano-TiO₂ colloid obtained by the hydrolysis of titanium tetrachloride. The resultant colloidal system can be stable for months without any precipitation. In a typical sample, the diameter of nanocomposite particles was about 150 nm, and the thickness of TiO₂-shell was 4–10 nm. Only cetyltrimethylammonium bromide was employed to provide the latex particles with positive charge, which was enough for the formation of fine TiO₂ coatings. Three initiators were tested. Ammonia persulfate was the most suitable one, because the cooperative effect was formed by the negatively charged TiO₂ particles and the terminal anionic group (SO₄²⁻, the fraction of

Ammonia persulfate) of the polymer chain on the surface of latex particles to maintain the stability of nanocomposite system. The pH value played a vital role in obtaining a tight TiO₂ coating. Transmission electron microscopy, X-ray diffraction and Atomic force microscopy were used to characterize this nanocomposite material. It was found that rutile and anatase coexisted in the nanocomposite film. This may suggest a potential application in the field of photocatalytic coating. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1466–1470, 2006

Key words: nanocomposite; polyacrylate; TiO₂ nanoparticle; core-shell structure; *in situ* emulsion polymerization

INTRODUCTION

Polymer nanocomposites that are of rapidly growing interest have attracted many research groups in recent years.^{1,2} These materials combine the properties of an inorganic component with those of the polymer system in an advantageous way, which can be used in the fields of catalysis,^{3,4} optics,^{5,6} magnetics,⁷ electronics,⁸ and coatings.⁹ Especially, a lot of efforts have been done to design and fabricate nanocomposites with core-shell structure, because they possess some special properties in these fields.^{1,10} Of course, such applications will not be realized if organic phase and inorganic phase cannot be blended homogeneously on nanometer scales. Some interaction between these two phases must be introduced to increase interfacial affinity. Therefore, a good dispersion of inorganic component can be achieved.

The procedures reported in the literature involve using chemically interfacial interaction (for instance, using a comonomer in polymerization to introduce functional groups on polymers¹¹ or treating inorganic particles with a coupling agent)^{12,13} to help the adhe-

sion of the two phases or controlled deposition of inorganic phase on the polymer surface through electrostatic attraction.¹⁴ In the former procedure, some basic comonomers, such as 4-vinylpyridine (4VP)^{15,16} and 1-vinylimidazole (1-VID),¹⁷ were used to generate strong acid–base interactions. A π -interaction between the aromatic ring and the silica surface¹⁸ was also found in the PS/silica nanocomposite system. Lu et al. demonstrated that PS beads terminated with amine groups could be directly coated with uniform shells of amorphous silica.¹⁰ In the latter procedure, Caruso et al. described the fabrication of polymer/silica spheres by using layer-by-layer (LBL) self-assembly technique,^{19,20} and via this LBL approach, polymer/zeolite A²¹ and polymer/titania²² core-shell microspheres were also prepared. Imhof reported the preparation of core-shell particles by the hydrolysis of a titanium alkoxide in the presence of cationic polystyrene latex.¹⁴ In addition, Zhang et al.²³ performed a work similar to ours. They reported the synthesis of hybrid microballs with polystyrene cores coated by titania nanoparticles in miniemulsion. Acrylic acid was used as a comonomer to promote locating TiO₂ nanoparticles on the polymer's surface.

Electrostatic interaction is one of the most simple and effective methods for synthesis of polymer nanocomposites. However, how to control this interaction between organic and inorganic phases in a compli-

Correspondence to: Z. Ai (aiz-q@sohu.com).

TABLE I
Experimental Information

| Sample no. | CTAB (g) | Initiator (g) | MMA/BA (g) | TC (g) ^a | T (°C) ^b | pH ^c | pH ^d | CR (%) ^e | SC (%) ^f | APS (nm) ^g |
|------------|----------|---------------|------------|---------------------|---------------------|-----------------|-----------------|---------------------|---------------------|-----------------------|
| 1 | 0.55 | APS (0.06) | 10/10 | 30 | 80 | 3–3.5 | 8–10.5 | 2.5 | 19.5 | 151 |
| 2 | 0.7 | APS (0.06) | 10/10 | 60 | 80 | 3–3.5 | 8–10.5 | 4.5 | 19.1 | 145 |
| 3 | 0.55 | APS (0.06) | 10/10 | 30 | 80 | 3–3.5 | 3–3.5 | 2 | 19.6 | 140 |
| 4 | 0.55 | APS (0.06) | 10/10 | 30 | 80 | 4 | 8–10.5 | 3.5 | 19.3 | 163 |
| 5 | 0.55 | AIBA (0.1) | 5/5 | 30 | 70 | 3–3.5 | 8–10.5 | 2 | 9.8 | 117 |
| 6 | 0.55 | AIBN (0.1) | 5/5 | 30 | 80 | 3–3.5 | 8–10.5 | — | — | — |
| 7 | 0.55 | AIBA (0.2) | 10/10 | 0 | 70 | 7 | 7 | 29 | 14.2 | 76 |

^a TiO₂ Colloid, the concentration is 1.2%.

^b Temperature during polymerization.

^c pH value during polymerization.

^d pH value after polymerization.

^e Coagulum ratio, which was calculated as follows: CR% = $G_2 / (G_1 - G_0) \times 100$ (where G_1 is the mass of the latex, G_2 is the mass of the dried coagulum, and G_0 is the mass of the volatile materials in the latex).

^f Solid content of colloidal system.

^g Average particle size of composite particles.

cated system (such as emulsion) is a big problem. Herein, we present a novel method to make film-forming polyacrylate-core/TiO₂-shell nanocomposites via *in situ* emulsion polymerization, which, to the best of our knowledge, was not reported. This method is remarkable for its simplicity (no surface modification of TiO₂ particles or addition of functional comonomer was necessary). It is enough for employing only cetyltrimethylammonium bromide (CTAB) to provide the latex particles with positive charge to ensure the formation of TiO₂ coatings without free TiO₂ nanoparticles. Cheap titanium tetrachloride (TiCl₄) was used as a precursor for TiO₂ nanoparticles. The selection of initiator played a vital role in the formation of TiO₂-coated nanocomposite particles. The effects of pH value before, during, and after polymerization were studied. The properties of nanocomposite films were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM).

EXPERIMENTAL

Material

Methyl methacrylate (MMA), *n*-butyl acrylate (BA) monomers (commercial grades; Beijing Dongfang Chemical, Beijing, China) were filtered through inhibitor removal columns before use. Cetyltrimethylammonium bromide (CTAB; Sinopharm Chemical Reagent, Shanghai, China), 2,2'-azobis(2-amidinopropane) dihydrochloride (AIBA; Huangshi Longjun Chemical Reagent, Huangshi, China), azobis(isobutyronitrile) (AIBN; Shanghai Haowei Chemical Reagent, Shanghai, China), titanium tetrachloride (TiCl₄; Tianjin Tianda Chemical Reagent, Tianjin, China), ammonium persulfate (APS; Beijing Qiuxian Chemical Manufacturer, Beijing, China), and NaOH (Tianjin Fuchen

Chemical Reagent, Tianjin, China) were all used as received. Water was deionized.

Synthesis of the nano-TiO₂ colloid

According to Kormann et al.,²⁴ nano-TiO₂ colloid was synthesized as follows: 8 mL of TiCl₄ that had previously been cooled to -20°C was slowly dropped into 500 mL of water that was cooled with ice under vigorous agitation. After keeping this solution at 70°C for 1 h, a little blue transparent colloid was obtained, which could be stable for nearly 1 month under ambient conditions.

Synthesis of the nanocomposite particles

The detailed recipes are listed in Table I. Typical synthesis of nanocomposite particles was performed by free radical emulsion polymerization in the presence of nano-TiO₂ colloid. MMA, BA, CTAB, and water were added to the nano-TiO₂ colloid in a four-necked round-bottom flask equipped with a mechanical stirrer. A certain amount of NaOH solution was slowly dropped to the flask to neutralize the reaction system. After half an hour of vigorous agitation, the reaction system was heated to 80°C, and afterwards the initiator was added. The temperature was kept at 80°C for 4 h while stirring (200 rpm), then the products were collected and neutralized by NaOH solution to pH = 8 if it is necessary.

Analytical methods

The morphology of the particles was examined with a JEM-100SX transmission electron microscope (TEM). Samples were prepared on carbon-coated grids.

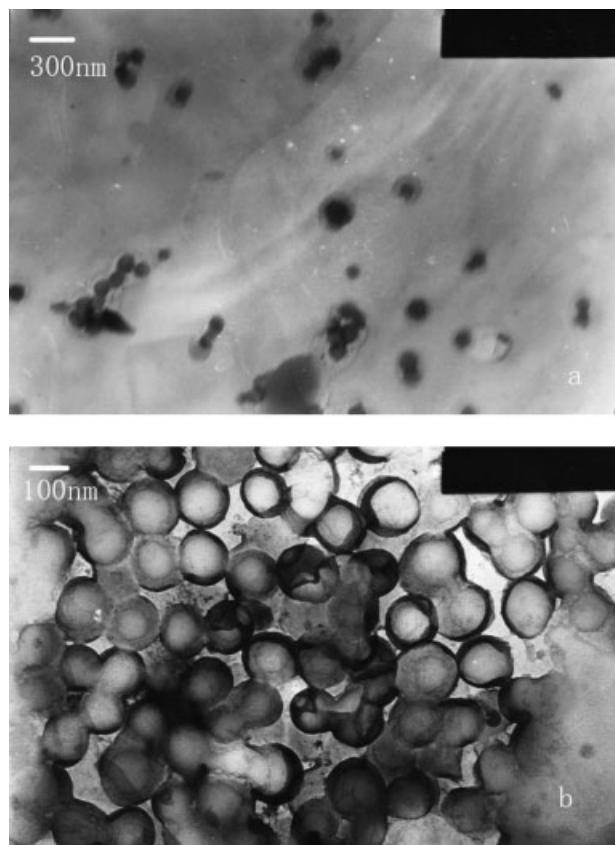


Figure 1 TEM images of nanocomposite particles obtained by (a) AIBA method (sample 5) and (b) APS method (sample 1), the thickness of TiO₂-shell was 4–10 nm.

The diameter of nanocomposite particles was measured with an Autosizer Loc-FC-963 Apparatus (Malvern Instruments, UK).

X-ray diffraction (XRD, D/MAX-3C, Rigaku) was used to characterize the crystalline phase of TiO₂, and calculate the primary particle size of TiO₂.

Atomic force microscopy (AFM, SPA-400, Digital Instruments) was carried out to analyze the surface morphology of the nanocomposite film.

RESULTS AND DISCUSSION

Selection of initiator

For the sake of enhancing the electrostatic interaction between organic and inorganic phases, we have introduced AIBA, a cationic initiator, in emulsion polymerization at first. However, this experiment was not encouraging. Nanocomposite particles with titania as core and polyacrylate as shell were formed. As Figure 1(a) shows, there is no TiO₂ on the surface of polymer latex particles, but some can be found inside these particles. This is because AIBA was absorbed on the surface of TiO₂ particles, and then the polymerization took place there.

In another experiment, AIBN, a nonionic initiator, was also tested. Although nano-TiO₂ was not trapped in the latex particles, aggregation of it occurred during polymerization. This phenomenon was contrary to our expectations again.

Finally, APS, an anionic initiator, was selected for testing. As showed in Figure 1(b), polyacrylate-core/TiO₂-shell structure was formed, and no aggregation of TiO₂ was found. We attributed this success to a cooperative effect, i.e., the negatively charged TiO₂ particles (which were absorbed by the CTAB and covered the place where the CTAB had occupied) and terminal anionic group (SO₄²⁻, the fraction of APS) of the polymer chain on the surface of latex particles made just negative charge exist on the surface and then maintained the stability of the colloidal system together. In addition, it is pretty tellable that the system could not be stable during or after polymerization in the absence of TiO₂ colloid, and in this case great amount of coagulum could occur. But this was not the case in the presence of TiO₂ colloid, just little coagulum was found. Apparently, this is due to the TiO₂ coatings, which cover the positive charge areas on the surface of latex particles and make the surface take on only negative charge. On the other hand, in the case without titania, positive and negative charge coexist on the particles surface, which can lead to attraction and aggregation of the particles. This may demonstrate that TiO₂ had a good effect on stabilizing the system. This effect, however, must be distinguished from the emulsifier-like effect.²⁵ In our case, increasing the amount of TiO₂ colloid did not decrease the mean diameter of the nanocomposite particles obviously (see Fig. 2). So, this effect can be called a stabilizer-like effect.

In all the above three tests, to prevent CTAB from being absorbed by TiO₂ before the formation of monomer droplets, we controlled the pH value below 3.6 (the isoelectric point of TiO₂ colloid is 3.6; in this situation, the surface of TiO₂ is positively charged) to ensure the formation of the micelle with CTAB as emulsifier. The effect of pH value will be discussed further in the next part.

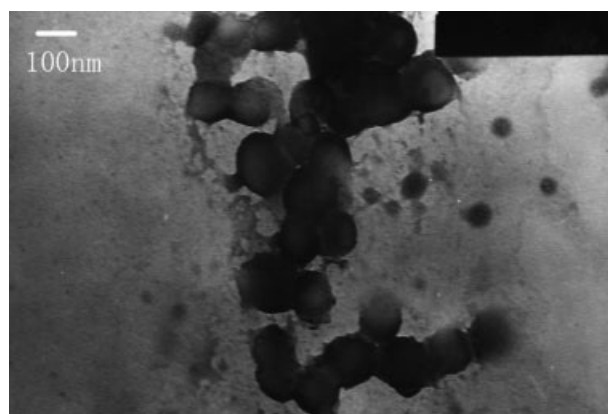


Figure 2 TEM image of nanocomposite particles (sample 2).

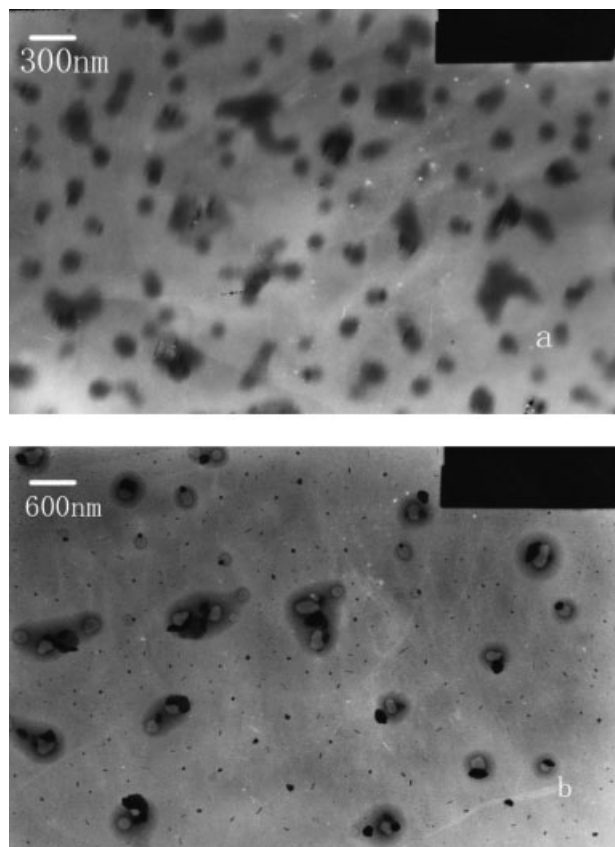


Figure 3 TEM images of nanocomposite particles obtained at (a) pH = 3–3.5 (sample 3) and (b) pH = 8 (sample 4).

Effect of pH value

In addition to the selection of initiator, the pH value of the system has a remarkable influence on the morphology of nanocomposite particles. It was found that the pH value had to be maintained in the range from 8.0 to 10.5 to ensure a tight TiO₂ coating on the surface of latex particles [see Fig. 1(b)]. At pH value below 8.0, the electrostatic interaction between TiO₂ and latex particles was not strong enough to generate a tight TiO₂ coating [but it was strong enough to collect a majority of TiO₂ particles around polymer-balls, almost no free TiO₂ particles can be seen, see Fig. 3(a)]. As Figure 3(a) shows, TiO₂ particles “float” around the latex particles, therefore the particles are not regular and smooth.

During polymerization, the pH value also plays an important role, which would not pass 3.6. At pH value above 3.6, negatively charged TiO₂ particles will be collected by the positively charged monomer droplets, and then with the proceeding of polymerization, the size of latex particles increase, consequently, the TiO₂ coating that have been on the surface of monomer droplets will be destroyed. As Figure 3(b) shows, TiO₂ gathers at one side of latex particles.

In summary, to obtain a tight TiO₂ coating on the surface of latex particles without aggregation of TiO₂,

the pH value during polymerization must be controlled at about 3, and after polymerization it must be adjusted to 8.0–10.5.

Study of properties of nanocomposite film

Nanocomposite emulsion was dried into film under ambient conditions at 80°C for X-ray diffraction (XRD) analysis. It is obvious that rutile-type and anatase-type TiO₂ coexist in the film [see Fig. 4(a)], which conforms to the result reported by Zhang and Gao.²⁶ The fraction of rutile in the samples can be estimated from the following equation²⁷:

$$\bar{\chi} = (1 + 0.8 I_A/I_R)^{-1}$$

where χ is the weight fraction of rutile, and I_A and I_R are the respective XRD peak intensities of the anatase and the rutile peaks, respectively. It can be calculated that χ of the sample in Figure 4(a) was 93.4%. Figure 4(b) displays the XRD pattern of pure TiO₂ powder that came from TiO₂ colloid dried at 80°C. Comparing Figure 4(b) with Figure 4(a), it is well worth noting that the crystal diffraction peak of TiO₂ in nanocomposite film is stronger than that of pure TiO₂. In addition, it can be calculated that the primary particle size of anatase and rutile are 4.5 and 3.3 nm, respec-

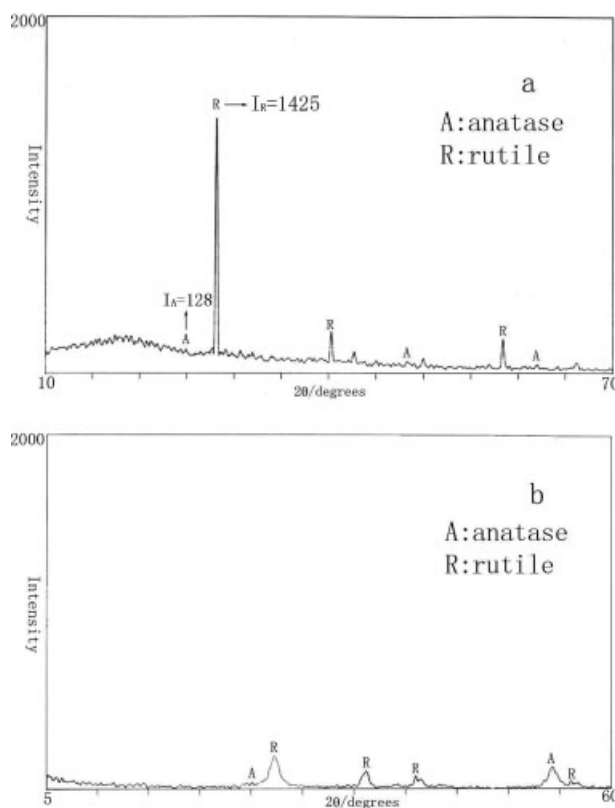


Figure 4 XRD patterns of TiO₂: (a) TiO₂ in nanocomposite film and (b) pure TiO₂.

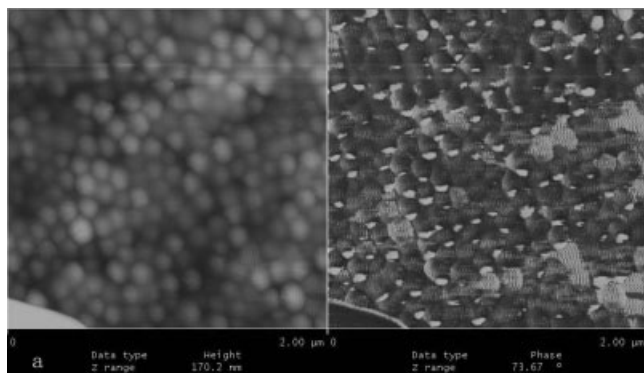


Figure 5 AFM images of nanocomposite film (obtained from sample 1) formed at room temperature and treated at 80°C for 1 h.

tively, according to the Scherrer equation.²⁸ The results are similar to those obtained by Kormann et al.²⁴ As a result, because nano-TiO₂ (rutile and anatase) possesses some attractive optical properties such as photocatalytic ability, and absorption of UV light, it is promising for this nanocomposite material to be applied in the field of photocatalytic coating.

However, to realize the above application, TiO₂ particles must distribute as much as possible on the surface of nanocomposite film without aggregation, although they are not trapped by the latex particles in the original colloidal system. In this context, TiO₂ can give play to its photocatalytic property to the largest extent. Figure 5 shows the atomic force microscopy (AFM) images of nanocomposite film, which was formed at room temperature and treated at 80°C for 1 h. The shape of the particles is still clearly visible. This is probably due to the TiO₂ coating that can prevent the particles from deforming. In future work, we intend to study the mechanism of the film formation of these nanocomposites and try to find a way in which more TiO₂ can distribute on the surface of the composite film, and a bigger challenge is to increase the concentration of titania in the composite film.

CONCLUSION

Polyacrylate-core/TiO₂-shell nanocomposite particles were prepared by *in situ* emulsion polymerization. In a typical sample, the diameter of nanocomposite particles was about 150 nm, and the thickness of TiO₂-shell was 4–10 nm. Electrostatic interaction was used as the key acting force to help the adhesion of organic and inorganic phases and promote the collection of negatively charged titania particles on positively charged polymer balls.

Only CTAB was employed to provide the latex particles with positive charge. Because a cooperative ef-

fect can be formed by the negatively charged TiO₂ particles and the terminal anionic group (SO₄²⁻, the fraction of APS) of the polymer chain on the surface of latex particles, APS can be selected as the most suitable initiator in the polymerization. The pH value plays a vital role in obtaining a tight TiO₂ coating on the surface of latex particles. During polymerization, it must be controlled at about 3, and after polymerization, it must be adjusted to 8.0–10.5.

AFM studies reveal that the shape of the particles will not be changed after heat treatment due to the presence of TiO₂ coating on the surface of latex particles. XRD analysis shows that rutile and anatase coexist in the nanocomposite film. Consequently, a promising application may be realized in the field of photocatalytic coating.

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