TiO_2 Nanoparticles Functionalized by a Temperature-sensitive Poly(*N*-isopropylacrylamide) (PNIPAM): Synthesis and Characterization

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TiO_2 nanoparticles functionalized by poly(*N*-isopropylacrylamide), PNIPAM in short, were prepared *via* seeded emulsion polymerization of *N*-isopropylacrylamide (NIPAM) in the presence of *N*,*N*′-methylene-bis(acrylamide) (MBAA) as the crosslinking monomer. The morphology and structure of the TiO_2/PNIPAM hybrid hydrogel were characterized by means of transmission electron microscopy, X-ray powder diffraction, and FT infrared spectroscopy. The response of the composite to temperature variations was also investigated. The results indicate that the title inorganic/organic hybrid has a sphere-like shape and is composed of inorganic TiO_2 nanoparticles and a biocompatible polymer matrix, showing excellent thermosensitivity, as evident from relevant optical photographs at different temperatures. The thermosensitive TiO_2 nanoparticles doped in PNIPAM matrix may have potential application in the remediation of wastewater streams.

Key words: Seeded Emulsion Polymerization, Titanium Dioxide, Functionalized Nanocomposite

Introduction

During the past decade, much work has been done on stimuli-responsive polymers for technological applications and fundamental studies. These stimuli-responsive polymers can change physico-chemical and colloidal properties in response to external stimuli like temperature, pH, ionic strength, magnetic field, *etc.* [1 – 3]. Among stimuli-responsive polymers, thermoresponsive polymers, particularly those based on poly(*N*-isopropylacrylamide) (PNIPAM) have attracted much attention and were extensively investigated since the microgel of PNIPAM was first reported by Pelton and Chibante in 1986 [1]. Chains of this polymer undergo a thermally induced conformational change from the swelled, hydrophilic state to the shrunken, hydrophobic state below and above the lower critical solution temperature (LCST) of around 32 °C in aqueous phase [4, 5].

More recently, with the development of the preparation and application of PNIPAM microgels and copolymers, increasing interest has been devoted to the exploration of thermoresponsive nanocomposites, which combine the advantages of PNIPAM polymers with those of inorganic nanoparticles and can be used in extended fields. The synthesis of thermoresponsive PNIPAM-functionalized nanocomposites is usually performed by "grafting" [6 – 8] or introducing vinyl groups to the surface of the particles, facilitating successive precipitation polymerization of PNIPAM [9, 10]. In order to prepare semiconductor/PNIPAM composites, Li *et al.* [11] employed a PNIPAM hydrogel as a solid matrix for the physical immobilization of CdTe quantum dots; Gao *et al.* [12] synthesized fluorescent microspheres utilizing hydrogen bonding between thioglycerol on CdTe nanocrystals and amide groups in PNIPAM chains. One motivation for our research is the usefulness of TiO_2 as a photocatalyst for the remediation of wastewater streams [13]. The localization of inorganic nanoparticles in a microgel template allows an easy separation from the reaction mixture and the re-use in numerous reaction cycles [14]. Gupta *et al.* [15] described the fabrication of an interpenetrating-microgel-TiO_2 composite and referred to the photocatalysis of TiO_2 nanoparticles. In this paper, we report the preparation of thermoresponsive TiO_2/PNIPAM hybrid hydrogels by seeded emulsion polymerization of *N*-isopropylacrylamide in the presence of *N*,*N*′-methylene bis(acrylamide) as the crosslinking monomer. The characterization of the target product is also reported.

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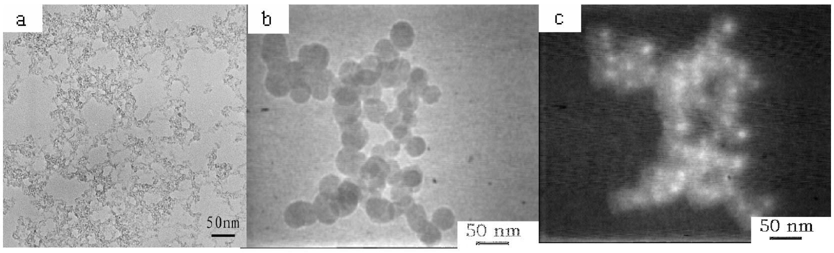

Fig. 1. TEM images of TiO_2 nanoparticles (a) and PNIPAM functionalized TiO_2 nanoparticles (b) and (c); (b) represents a bright-field image, and (c) a dark-field image.

Results and Discussion

Fig. 1 shows the TEM images of TiO_2 nanoparticles (Fig. 1a) and PNIPAM-functionalized TiO_2 nanoparticles (Fig. 1b). The micrographs show that the TiO_2 nanoparticles were well dispersed, and the PNIPAM-functionalized TiO_2 nanoparticles had fairly homogeneous and spherical shape. Fig. 1c is the corresponding dark-field image of Fig. 1b, in which the bright dots refer to inorganic nanoparticles, according to the principle of TEM.

XRD studies were carried out for the specimens to determine the crystalline phase of the obtained TiO_2/PNIPAM composite. Typical XRD patterns obtained for the pure nano-sized TiO_2 and TiO_2/PNIPAM composite are shown in Fig. 2. The diffraction pattern of pure nano-sized TiO_2 coincides well with that of anatase TiO_2 (JCPDS File No.21-1272), and no diffraction lines corresponding to other polymorphs of TiO_2 are observed. The broadening of the peaks in Fig. 2a is due to the existence of very small TiO_2 particles. The as-prepared TiO_2 nanoparticles are approximately $3 \sim 5$ nm in size, as calculated using the Scherrer formula and also confirmed by TEM. Moreover, as shown in Fig. 2b, the diffraction peaks of TiO_2 nanoparticles functionalized by PNIPAM show obvious signs of superimposition, which should be related to the interaction between the inorganic nanoparticles and the polymeric matrix. Unfortunately, it is infeasible to estimate the size of the inorganic-organic composite from the XRD data, owing to very weak signal intensities and interference between neighboring XRD peaks.

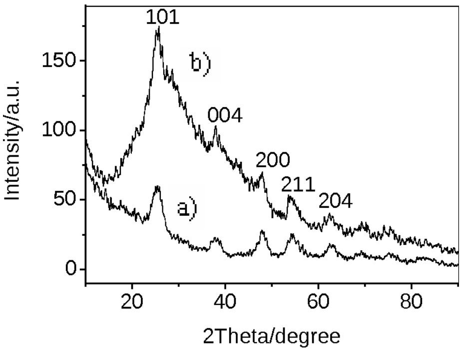

Fig. 2. XRD pattern of TiO_2 nanoparticles (a) and TiO_2 nanoparticles functionalized by PNIPAM (b).

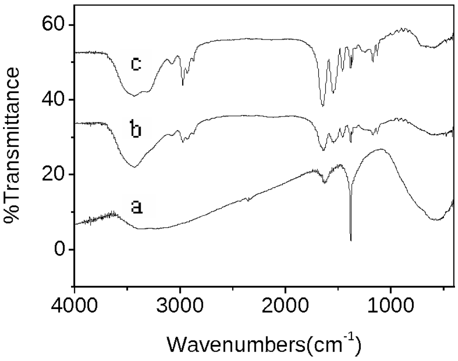

Fig. 3. FTIR spectra of TiO_2 nanoparticles (a), PNIPAM-functionalized TiO_2 nanoparticles (b) and a PNIPAM homopolymer (c).

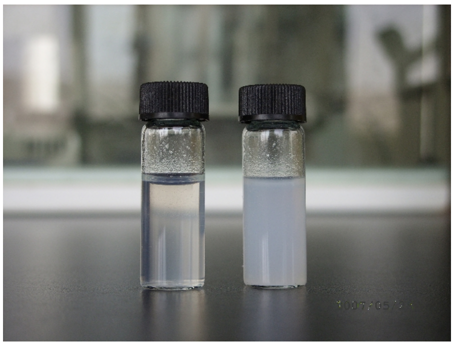

Fig. 4. Photographs of PNIPAM-functionalized TiO_2 nanoparticles at 25 °C (left) and 38 °C (right).

Fig. 3 shows the FTIR spectra of TiO_2 nanoparticles (a), PNIPAM-functionalized TiO_2 nanoparticles (b) and a PNIPAM homopolymer (c). Comparing the spectrum of PNIPAM-functionalized TiO_2 nanoparticles (Fig. 3b) with that of the PNIPAM

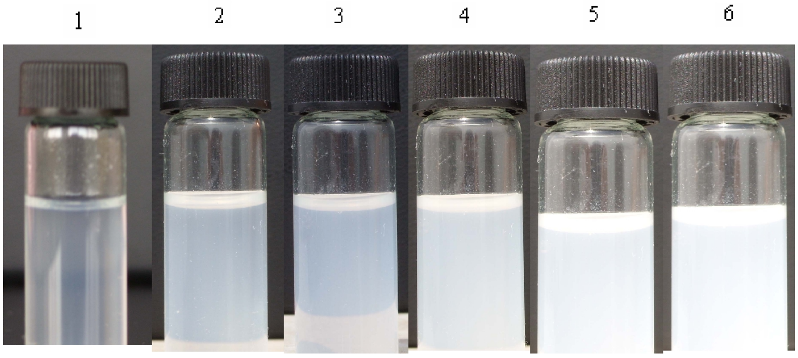

Fig. 5. Photographs of PNIPAM-functionalized TiO_2 nanoparticles under sunshine.

homopolymer (Fig. 3c), it is seen that the former shows an obvious increase in absorption, which results from the characteristic absorption bands of the TiO_2 nanoparticles [16]. Peak assignments for 2972 cm^{-1} (CH_3 asymmetric stretching) and 1645 and 1539 cm^{-1} (secondary amide C=O stretching) indicate the main contribution of PNIPAM to the TiO_2/PNIPAM composite. This implies that TiO_2 nanoparticles have been successfully functionalized by PNIPAM.

Fig. 4 shows the optical photographs of PNIPAM-functionalized TiO_2 nanoparticles dispersed in distilled water. As a visible thermoresponse, the optical color of the polymer-encapsulated TiO_2 nanoparticles in aqueous suspension experiences a dramatic change from transparent to opaque as the temperature increases from r. t. to 38 ℃, which is attributed to the thermosensitivity of the PNIPAM with a LCST. Below LCST, water is a relatively good solvent for the NIPAM polymer on TiO_2 nanoparticles, and the polymer chains are mostly extended; therefore, the suspension of the composite appears as a transparent solution. In the transition regime, water becomes a poor solvent as polymer-water hydrogen bonds are broken, and PNIPAM undergoes conformation changes and exposes much of its hydrophobic surface. Fig. 5 shows aqueous suspensions of PNIPAM-functionalized TiO_2 nanoparticles exposed to sunshine. The optical color gradually turns cloudy under sunshine, and the transformation from transparent to opaque is sensitive, quick (less than one minute) and reversible.

The thermogram of the PNIPAM-functionalized TiO_2 nanoparticles is shown in Fig. 6. The weight loss from r. t. to around 600 ℃ is about 77 %, which is caused by the release of absorbed water and surfactant and by decomposition of PNIPAM as well, implying that the content of TiO_2 nanoparticles in the composite is about 13 %.

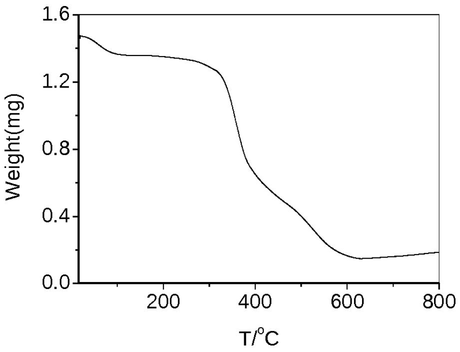

Fig. 6. TGA of PNIPAM-functionalized TiO_2 nanoparticles.

Conclusions

In summary, a PNIPAM-functionalized TiO_2 nanocomposite was successfully synthesized *via* seeded emulsion polymerization of NIPAM in the presence of MBAA as the crosslinking monomer. In the synthesized composite, not only the photocatalysis of TiO_2 nanoparticles can be utilized, but also the separation of nanoparticles from the reactant is easy. Therefore, the inorganic-organic composite is a promising candidate for the remediation of wastewater streams. Moreover, the method we used is simple and can be extended to the synthesis of other composites.

Experimental Section

Materials

The monomer NIPAM (prepared in our laboratory) was recrystallized from hexane and dried under vacuum before use. The cross-linker *N*,*N*-methylene-bisacrylamide (MBAA) was provided by Fluka, the other chemicals were supplied by the Tianjin Chemical Reagent Company of China. Thrice-distilled water and titanium dioxide (TiO_2) nanoparticles were prepared in our laboratory.

Characterization

The morphology and size of the products were analyzed by means of transmission electron microscopy (TEM, TEM-100CX-II; accelerating voltage 100 kV). The FTIR spectra of the products were recorded using a Nicolet Avatar 360 spectrometer. The XRD patterns of pure TiO_2 nanoparticles and hybrid microgel were measured using an X'Pert Pro X-ray diffractometer (Phillips, Holland, Cu$K_{\alpha 1}$ radiation). Thermogravimetric analysis (TGA) was carried out on an Exstar 6000 thermal analysis instrument at a heating rate of 10 °C min^{-1}.

Synthesis of PNIPAM-functionalized TiO_2 nanoparticles

The pre-synthesized TiO_2 nanoparticles and 7.0 mg of cetyltrimethylammonium bromide (CTAB) were dissolved in thrice-distilled water with stirring, then a certain amount of NIPAM and MBAA was added, and the resultant solution was purged with nitrogen gas for 15 min. After the solution was kept at 75 °C for 15 min, the initiator ammonium persulfate (APS) was added to initiate polymerization. After polymerization for 8 h, the product was cleaned by centrifugation, and the supernatant was separated to remove unreacted material, soluble side products, and seeds of the pure polymer [12, 17, 18].

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