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Preparation and characterization of polymer/inorganic nanoparticle composites through electron irradiation

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In this paper, we report a new method to prepare the polymer/inorganic nanoparticle composites using electron irradiation-induced polymerization. The mixture of nanoparticles and MMA solution were co-irradiated by 1.6 MeV electron beam to a dose of 10, 20 and 30 kGy at a dose-rate of 60 kGy/h in air at room temperature. The products after irradiation were extracted using a soxhlet extractor with boiling xylene and investigated by X-ray diffraction (XRD), Fourier transmission infrared (FTIR), X-ray photoelectron spectroscopy (XPS), optical absorption spectra (OAP) and photoluminescence (PL). The FTIR and XPS results show that there exist some unextractable PMMA in the nanocomposites after extraction, indicating a strong interaction between the PMMA and nanoparticles. PL results show that new luminescence peaks appear at 415 and 420 nm for the nanocomposites of anatase and γ-Al_2O_3.

1. Introduction

Namomaterials have many attractive features and therefore are regarded as the most prospective materials in the 21st century. Nanoparticles possess many special characteristics that can be used in many fields such as optics, electricity, magnetism and catalysis [1]. However, nanoparticles easily aggregate because of their extremely-high specific surface energy; thus, preparing nanocomposites becomes an economical and effective method for using nanoparticles. Polymer/inorganic nanoparticle composites have attracted more and more attentions. They combine the advantages of polymers (e.g., elasticity, transparency, or dielectric properties) and inorganic nanoparticles (e.g., specific absorption of light, magnetoresistance effects, chemical activity, and catalysis etc.). Nanocomposites even exhibit many new characters that single-phase materials do not have. Many approaches have been tried to change the surface characters of the nanoparticles using different techniques such as the vapor deposition [2], precursor technique [3], nanoreactor technique [4], supermolecular self-assembly process [5], ultrasonic irradiation [6–9] and plasma polymerization [10–12].

Electron beam irradiation, which produces radicals along the polymer chain, can be used for graft polymerization onto the polymer surface. Previous work has demonstrated that electron irradiation of polymer films provides a reactive surface which can be used for grafting of a vinyl monomer [13]. Graft polymerization is also possible even if the polymer is quite stable when the high energy of an electron beam is used [14]. To our knowledge, there are few reports about the surface modification of inorganic nanoparticles with polymer by electron irradiation. Electron irradiation can be performed simply and effectively under normal pressure at room temperature. If electron irradiation can induce graft polymerization on the surface of nanoparticles, it will be an effective and attractive method to modify the surfaces of inorganic materials and prepare polymer/inorganic nanoparticle composites.

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In the present study, the electron irradiation technique is employed to prepare polymer/inorganic nanoparticle composites. Several inorganic nanoparticles/poly methyl methacrylate nanocomposites prepared by electron irradiation were investigated by X-ray diffraction (XRD), Fourier transmission infrared (FTIR), X-ray photoelectron spectroscopy (XPS), optical absorption spectra (OAP) and photoluminescence (PL).

2. Experimental details

2.1. Materials

The investigation was carried out on commercial anatase (20 nm), rutile (needle-like, 40 × 10 nm) and γ-Al_2O_3 (60 nm) nanoparticles purchased from Zhejiang Zhoushan Mingri Nano Materials Co Ltd. Before electron irradiation all the nano powders were heated at 120°C for 8 h in order to eliminate the possible adsorbed water on the surface of the nanoparticles.

Methyl methacrylate (MMA), which was purchased from Chinese Shanghai First Chemical Work of Reagent, was distilled at reduce pressures and preserved at 4°C before electron irradiation. All other reagents were analytical pure and were used without further purification.

2.2. Preparation of polymer/inorganic nanoparticles

The dried nanoparticle (w_0) were accurately weighed out and fully mixed with prepared MMA solution (20% in volume) in cultural dishes. The solvent of MMA solution was the mixture of *n*-heptane/chloroform (2:3 in volume). Then the solution was irradiated with 1.6 MeV electron beam to a dose of 10, 20 and 30 kGy at a dose-rate of 60 kGy/h in air at room temperature. After the irradiation, the synthetic polymer/nanopowder composites were wrapped with filter paper, and extracted 24 h using a Soxhlet extractor with boiling xylene (the homopolymer is thought to be completely removed by this way). The extracted composites were dried in air at 70°C until a constant weight (w) was reached. We termed the extracted composite after elelctron irradiation as nanocomposite.

2.3. Characterizations

The percent graft (G) was determined gravimetrically. G was calculated by the Equation 1, where w_0 is the weight of nanopowders before irradiation and w is the weight of nanopowders after irradiation and extraction.

$$G = \frac{w - w_0}{w_0} \times 100\% \tag{1}$$

X-ray diffraction (XRD) analyses were performed in a X-ray diffractometer Type PHILIPS X'Pert Pro MPD with Cu-K_α ($\lambda = 0.15406$ nm). Fourier transform infrared (FTIR) spectra of the sample in KBr pellets were recorded using a Nicolet 560 FTIR spectrometer. The Spectra were collected from 4000 to 400 cm^{-1}, with a 4 cm^{-1} resolution over 20 scans. The samples were also analyzed by XPS using a XSAM 800 Flexo electron spectrometer with monochromatic Al-K_α X-ray source ($h\nu = 1486$ eV). The instrument was standardized against the C1s spectral line at 285 eV, and the spectra were interpreted and deconvoluted using the KRATOS computer software package.

Steady state photoluminescence measurements were carried out on the dispersion of nanopowders in purified water. For the optical measurements, nanopowders were first suspended in purified water. The solutions were then dispersed with 50 W KQ-50B ultrasonic irradiation. Photoluminescence was recorded using a Shimadzu RF-5301PC fluorometer employing a 150 W Xe lamp as the light source. Excitation and emission monochromators were on mutually perpendicular directions. Optical absorption was examined by optical spectrophotometric measurements on a Shimadzu UV-2550 double beam spectrophotometer, with a deuterium lamp for UV and a tungsten halogen lamp for visible region.

3. Results and discussion

Percent graft. The percent grafts of the nanoparticles after electron irradiation at different doses are shown in Fig. 1. The percent graft increases with increasing electron dose. The maximum percent grafts for anatase, rutile TiO_2 and γ-Al_2O_3 nanoparticles exposed to 30 kGy electron irradiations are 7, 7.5 and 10.5%, respectively.

XRD. Fig. 2a and b show the X-ray diffraction patterns of pure anatase and rutile and the corresponding nanocomposites. The characteristic Bragg diffraction peaks of anatase and rutile can be observed in the nanocomposites. No obvious changes can be found in the XRD patterns after electron irradiation-induced polymerization, indicating that the irradiation-induced polymerization has no influence on the crystal structure.

FTIR. The comparison between the nanocomposite obtained after 24 h extraction and pure nanoparticles is shown in Fig. 3. As compared with pure samples, a new peak attributed to carbonyl stretching vibration appears at about 1725 cm^{-1} after electron irradiation, which is close to the characteristic peak of PMMA at 1730 cm^{-1}.

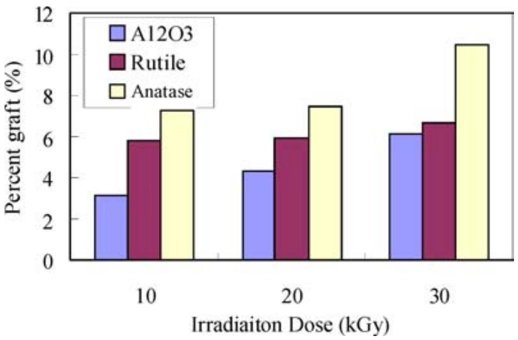

Figure 1 The percent grafts of the nanoparticles after different doses of electron irradiation.

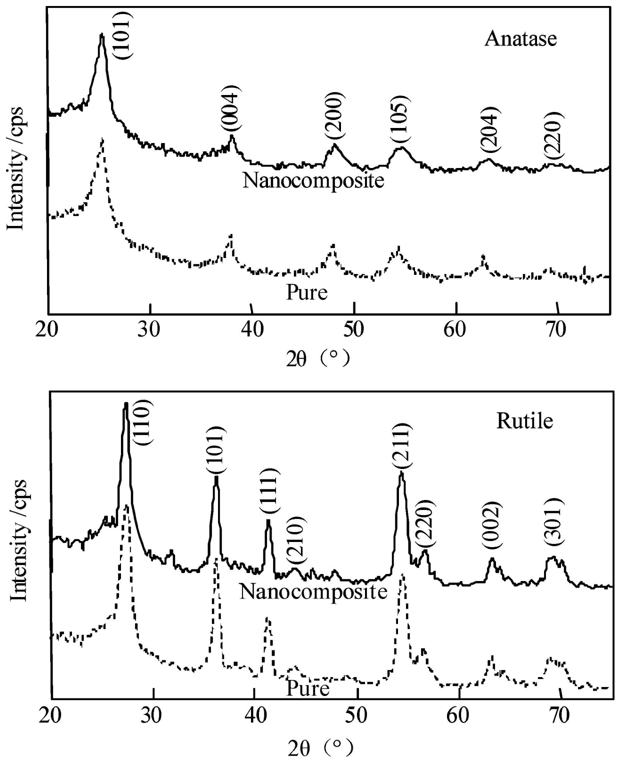

Figure 2 X-ray diffraction patterns for the pure anatase and rutile nanopowders and the corresponding nanocomposites.

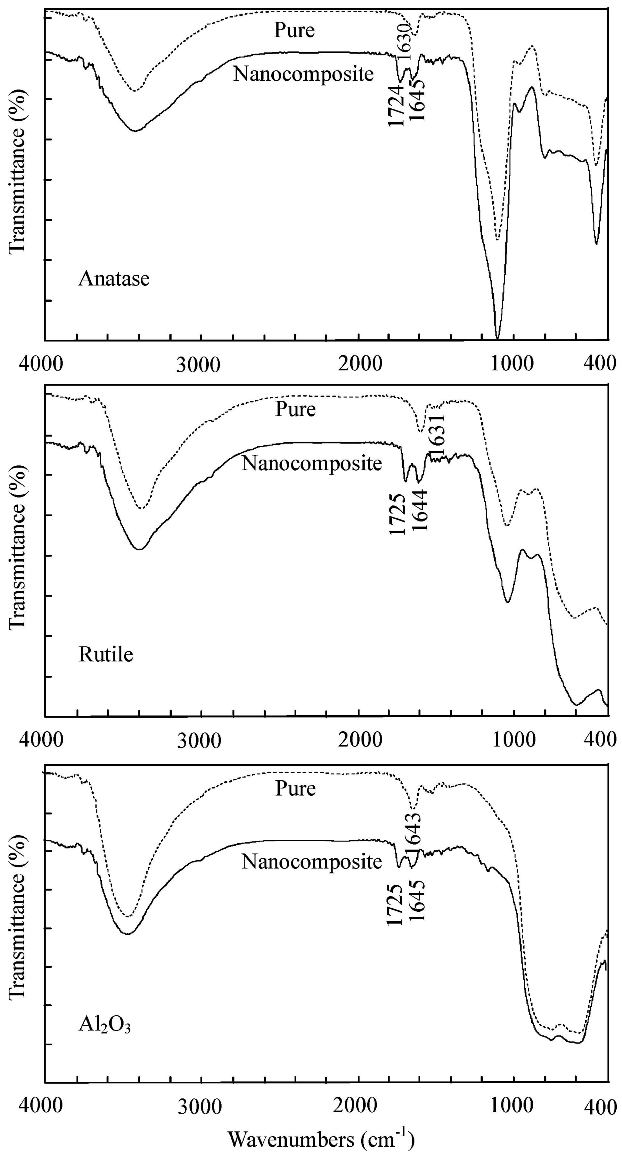

Figure 3 FTIR spectra of the pure anatase, rutile and γ-Al_2O_3 nanopowders and the corresponding nanocomposites.

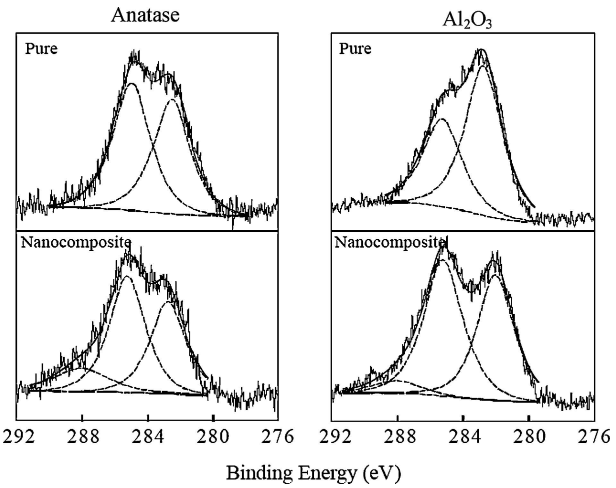

Figure 4 C1s narrow scan X-ray photoelectron spectra of pure anatase and γ-Al_2O_3 and the corresponding nanocomposites.

The new peak is an indication of the existence of unextractable PMMA. The carbonyl vibration peaks of two nanoparticle/PMMA nanocomposites both shift to the lower wavenumbers. In contrast, the characteristic absorption peaks of anatase (1630 cm^{-1}), rutile (1631 cm^{-1}) and γ-Al_2O_3 (1642 cm^{-1}) shift to higher wavenumbers (1645 cm^{-1}) after irradiation-induced polymerization. These results show that there are strong interactions between the PMMA and nanoparticles.

XPS. High-resolution XPS collections of the C 1s binding energy regions are shown in Fig. 4. Carbon is present in the pure nanoparticles because they can easily absorb pollutant in air due to their extremely high specific surface energy and numerous surface defects. The carbon is so tightly absorbed that it cannot be eliminated by vacuum during XPS measurement. For the pure nanoparticles, the photoelectron spectra of C 1s curve can be fitted by two peaks at 282.5 and 285.0 eV for anatase, and 282.7 and 285.2 eV for γ-Al_2O_3, respectively. The peak 285 eV is attributed to the C–C bond resulting from diffusion pump oil. The 282 eV may be due to carbide contaminant [15, 16]. The C 1s curves for the nanocomposites can be fitted by three peaks at 282.7, 285.2, 288.0 eV for anatase and 282.0, 285.2, 288.0 eV for γ-Al_2O_3, respectively. The new peak at 288 eV is corresponding to carbonyl groups C–O [17]. The C–O at 286.67 eV for the methoxy group of the ester chemical function overlaps with the peak at 285 eV; thus, it was not deconvoluted.

High-resolution XPS collections of the O 1s binding energy regions are shown in Fig. 5. For the pure nanopar-

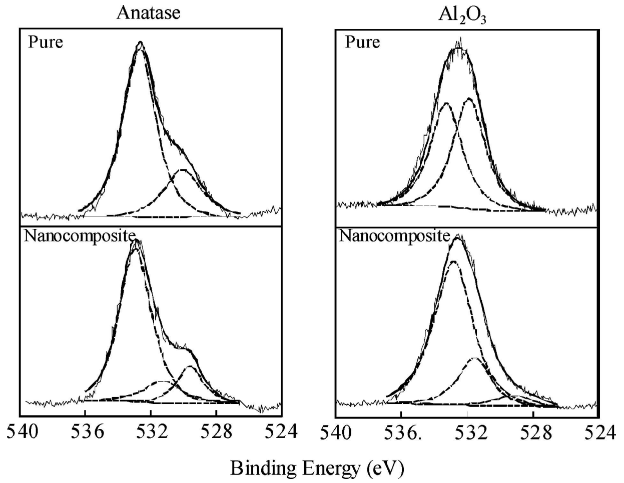

Figure 5 O1s narrow scan X-ray photoelectron spectra of pure anatase and γ-Al_2O_3 and the corresponding nanocomposites.

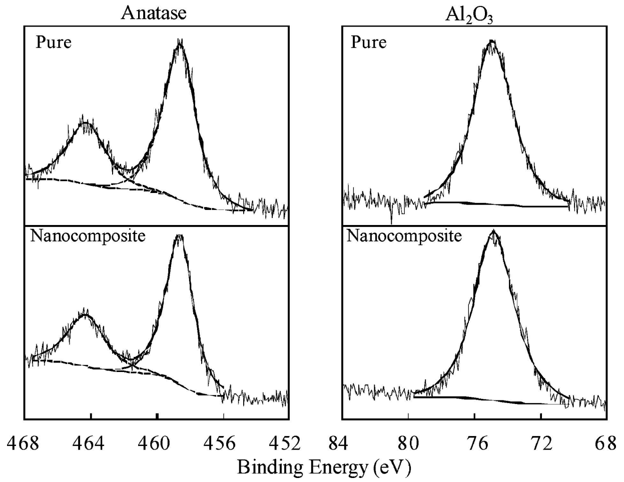

Figure 6 Ti2p and Al2p narrow scan X-ray photoelectron spectra of pure anatase and γ-Al_2O_3 and the corresponding nanocomposites.

ticles, the photoelectron spectra of O 1s curve can be fitted by two peaks at 530.0, 532.7 eV for anatase, and 531.3, 533.3 eV for γ-Al_2O_3, respectively. The high binging energy component is usually attributed to the presence of loosely-bound oxygen on the surface of nanoparticles. The other component is the binding energy of interior of nanoparticles. The O 1s curves for the nanocomposites can be fitted by three peaks at 529.6, 531.2, 532.8 eV for anatase and 529.1, 531.6, 532.1 eV for γ-Al_2O_3, respectively. The new peak at about 529 eV is an indication of the surface modification of the nanoparticles by PMMA.

There are no changes in the Ti 2p and Al 2p peaks (shown in Fig. 6) after the electron irradiation.

OAP & PL. The optical absorption spectra of the pure anatase, rutile TiO_2 and γ-Al_2O_3 nanoparticles and the corresponding nanocomposite are shown in Fig. 7. There's no obvious change in the absorption spectra after irradiation-induced polymerization.

Fig. 8 shows the steady state luminescence curves for pure anatase, rutile TiO_2 and γ-Al_2O_3 nanoparticles and the corresponding nanocomposite at room temperature. Excitation wavelength was kept constant at 305 nm. No luminescence peaks appear in the pure nanoparticles. However, luminescence peaks at 415 and 420 nm can be observed for the nanocomposites of anatase TiO_2 and γ-Al_2O_3, respectively.

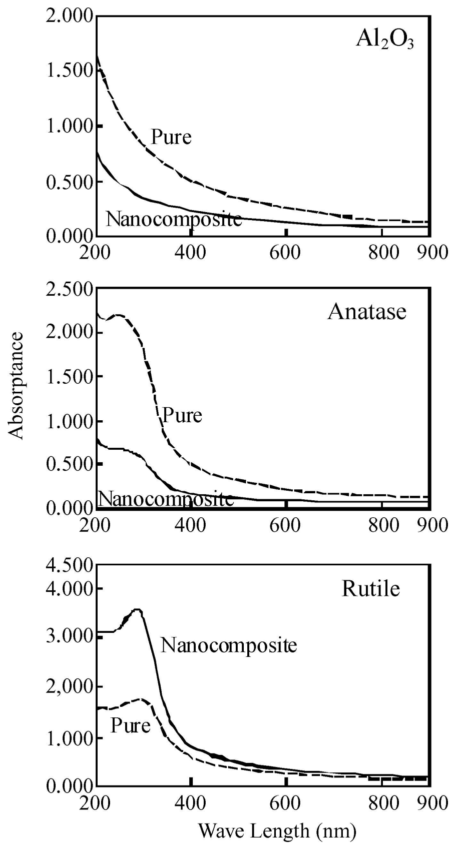

Figure 7 UV-vis absorption spectra of the pure anatase, rutile and γ-Al_2O_3 nanopowders and the corresponding nanocomposites.

The solvent extraction, FTIR and XPS results clearly show that there exist some unextractable PMMA in the nanocomposites. The unextractable polymer indicates the presence of chemical bonds between the polymer and the nanoparticles. The polymerization reaction mechanism is based on the free radical mechanism on the nanocrystal surface. Oxygen atom defects are generated by the electron irradiation. It was believed that radiation caused the lose of the oxygen atom bonding with aluminum or titanium and produced radiation default in aluminum oxide (Al_2O_3) or titanium oxide (TiO_2). One electron of the double bond was opened in vinyl monomers, and coordinated to aluminum or titanium of the nanocrystals; the other initiated free radical graft polymerization of MMA on the surface. The same results have been reported on micro-meter Al_2O_3 [18, 19]. Grafting polystyrene onto sorbate-modified titanium dioxide surface possesses similar graft style between titanium atom and sorbet [20]. The connection of the PMMA to the particles is schematically shown in Fig. 9.

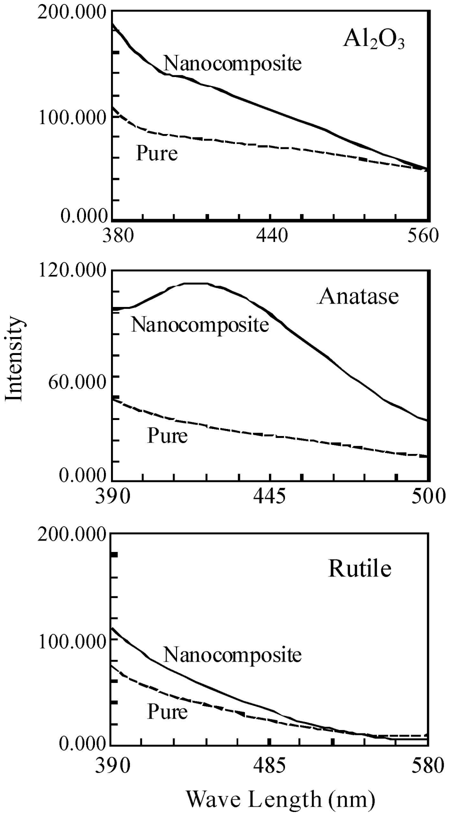

Figure 8 Photoluminescence of the pure anatase, rutile and γ-Al_2O_3 nanopowders and the corresponding nanocomposites with the excitation wavelength = 305 nm at room temperature.

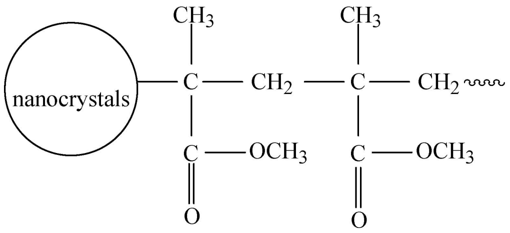

Figure 9 Structure of the connection of PMMA to the surface of nanocrystals through graft polymerization.

After the irradiation-induced polymerization on the anatase TiO_2 and γ-Al_2O_3 nanoparticles, a new photoluminescence peak at about 415 and 420 nm can be found at room temperature. Zou *et al.* [21] found that TiO_2 ultrafine particles coated with a layer of stearic acid can have 540 nm fluorescence. The mechanism of the photoluminescence is unclear, but it should be induced by the surface modification of the nanoparticle by the irradiation-induced polymerization. The photoluminescence maybe caused by the carbonyl adjacent to the surface of the nanoparticle. For biacetyl, CH_3-(C=O)-(C=O)-CH_3, it is well known that the carbonyl group is responsible for luminescence in aliphatic compounds [22]. Vollath *et al.* [23, 24] also found PMMA coated oxide core can emit blue emission at about 420 nm, originated from the carbonyl group of the coating polymer. The PMMA coated oxide core has a similar structure to our work. The polymerized nanoparticles might be readily dispersed into some polymer matrix due to the surface modification. Composites of anatase TiO_2 or γ-Al_2O_3 nanoparticles with a polymer matrix have potential applications for the development of a class of luminescent polymer/nanoparticles composite.

4. Conclusions

The MMA monomers can be polymerized on the surface of nanoparticles by electron irradiation in air at room temprature. FTIR, extraction experiments and XPS results show that there exist unextractable PMMA in the nanocomposites. The active species initiating grafting polymerization by electron irradiation may happen on the nanoparticle surface. A new luminescence peak at 415 and 420 nm can be observed in the nanocomposite of anatase TiO_2 and γ-Al_2O_3 after the electron irradiation, respectively.

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