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Synthesis of zinc oxide-encapsulated poly(methyl methacrylate)–chitosan core–shell hybrid particles and their electrochemical property

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ABSTRACT

The synthesis of hybrid materials possessing zinc oxide nanoparticles encapsulated in core–shell polymer particles having poly(methyl methacrylate) core and chitosan shell (PMMA–CS/ZnO) was carried out *via* an emulsifier-free emulsion polymerization. The ZnO nanoparticles modified by 3-(trimethoxysilyl)propyl methacrylate (TPMZnO) were first prepared before being charged to the polymerization system. The effects of polymerization time (from 2 h to 6 h) and the amount of TPMZnO added (0.018 g, 0.020 g, and 0.030 g) were studied. It was found that the polymerization time of 5 h yielded colloidally stable hybrid latex with% MMA conversion up to 90%. Moreover, the increase in the amount of TPMZnO resulted in a decrease in% MMA conversion from 90% to 80%. It was also found from TGA analysis that the amount of TPMZnO added affected the percentage of TPMZnO encapsulation. PMMA–CS/ZnO particles with the size ranging from 173 to 245 nm were observed by TEM. In addition, the PMMA–CS/ZnO hybrid latexes possessed high positive charges in the range of 40–51 mV. The electrochemical property of the electrodes fabricated from PMMA–CS/ZnO nanoparticles was illustrated by cyclic voltammetry.

1. Introduction

Hybrid materials of nanosized inorganic metal oxides dispersed in organic polymers have attracted a great deal of attention in recent years. The hybridization of the two materials could lead to an improvement and/or a combination of intrinsic properties of each single-component counterpart [1–3]. The nanosized inorganic components can exhibit interesting size-dependent properties, such as optical and electrical properties, while polymers can bring advantages such as tunable bulk properties and ease of fabrication. More importantly, polymers can also involve in stabilization, and the control of size, size distribution, and dispersibility of metal oxide nanoparticles. Zinc oxide (ZnO) nanoparticles (or quantum dots), among nanosized metal oxides, are of great interest and have been extensively investigated recently. ZnO nanoparticles, with a wide band gap (3.4 eV) and large exciton binding energy (60 meV), are found to be useful in a broad range of applications (optoelectronic devices, dye-sensitized solar cells, catalysts, and sensors). There are several works on syntheses, physicochemical properties, and applications of ZnO/polymer hybrids. For instance, Demir et al. presented fabrication of the hybrids based on poly(methyl methacrylate) (PMMA) and ZnO nanoparticles, which showed visible light transmittance, UV absorption, and moderately high refractive index [4]. Hung and Wang studied the effect of surface stabilization of nanoparticles on luminescent characteristics in ZnO/poly(hydroxyethyl methacrylate) nanohybrid films [5]. Sonawane and coworkers illustrated the sonochemical synthesis and anticorrosive performance of ZnO encapsulated in poly(butyl methacrylate) latex [6].

Chitosan (CS) is a biodegradable polysaccharide, which can be mostly found in crustacean shells [7]. It is composed of a copolymer of glucosamine and *N*-acetylglucosamine, derived from deacetylation of chitin, and is soluble in acidic media. It possesses good film-forming ability and high hydrophilicity and biocompatibility. Moreover, it is an attracting biopolymer for uses in immobilization of negatively charged biomolecules (i.e., enzyme or DNA) *via* an electrostatic interaction [8,9]. The fabrication of hybrid

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Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacylate; CS, chitosan; ZnO, zinc oxide; TPM, 3-(trimethoxysilyl)propyl methacrylate; TGA, thermogravimetric analysis; TEM, transmission electron microscopy; eV, electron volt; meV, millielectron volt; UV, ultraviolet; DNA, deoxyribonucleic acid; $(Zn(AcO)_2{\cdot}2H_2O$, zinc acetate dihydrate; TBHP, *tert*-butyl hydroperoxide; kDa, kilodalton; EtOH, ethanol; h, hour; UV–VIS, ultraviolet–visible; nm, nanometer; D, diameter; XRD, X-ray diffraction; kV, kilovolt; WE, working electrode; RE, reference electrode; CE, counter electrode; V, volt; mV, millivolt; CVs, cyclic voltammograms; mM, millimolar; E_p, electrode potential; I_p, current potential; FTO, fluorine doped tin oxide.

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materials based on chitosan with metal oxide nanoparticles was studied in several reports. For example, Kaushik et al. reported the preparation of iron oxide nanoparticles–chitosan (CH–Fe_3O_4) for use in glucose biosensor. The presence of Fe_3O_4 in this hybrid film can promote electron transfer due to a permeable structure of chitosan [10]. Due to their unique properties (e.g., high surface area, high catalytic efficiency, and chemical stability), the development of cholesterol biosensor using zinc oxide nanoparticles–chitosan film was presented by Khan et al. [11].

In this work, we report the novel preparation of hybrid materials of ZnO nanoparticles dispersed in poly(methyl methacrylate)–chitosan core–shell particles (PMMA–CS/ZnO), which was carried out *via* an emulsifier-free emulsion polymerization. Firstly, the ZnO nanoparticles, after a sol–gel process, were modified with 3-(trimethoxysilyl)propyl methacrylate (TPM), which could result in polymerizable and hydrophobic ZnO nanoparticles. Then, they were incorporated into the core–shell PMMA–chitosan core–shell particles through the emulsifier-free emulsion polymerization. Additionally, the physicochemical properties and electrochemical behavior of resulting PMMA–CS/ZnO hybrids were investigated.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($Zn(AcO)_2{\cdot}2H_2O$, p.a. $\geqslant$98.0% purum), lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, p.a. $\geqslant$99%, purum), sodium acetate (CH_3COONa), methyl methacrylate (MMA), and *tert*-butyl hydroperoxide (TBHP) were purchased from Fluka. TBHP was used without further purification. 3-(Trimethoxysilyl)propyl methacrylate (TPM, 98.0%, Aldrich) was used without treatment. Chitosan (CS) was purchased from Seafresh Chitosan Lab., Thailand. Its degree of deacetylation and average molecular weight were about 85% and 45 kDa, respectively. MMA was purified by reduced pressure distillation prior to use. All other chemicals were commercially available and of analytical grade.

2.2. Methods

2.2.1. Synthesis of ZnO nanoparticles

The synthesis of ZnO nanoparticles was carried out *via* a sol–gel method [12]. Firstly, 1.10 g $Zn(AcO)_2{\cdot}2H_2O$ was dissolved in 50 mL EtOH and sonicated at 50 °C for 30 min. Then, the zinc acetate solution was refluxed at 70 °C for 3 h under N_2 atmosphere, vigorous stirring, and probed with a condenser capped with a calcium chloride trap. The condensate became clear after 3 h. Then, 0.29 g $LiOH{\cdot}H_2O$ was dissolved in EtOH at room temperature in a separate beaker before being added into the refluxed zinc acetate solution. The dissolution of $LiOH{\cdot}H_2O$ in EtOH at room temperature was quite difficult to attain. Therefore, the sonication assistance was necessary. Finally, $LiOH{\cdot}H_2O$ was added dropwise to the zinc acetate solution at 0 °C with a continuous stirring for 2 h. The ZnO suspension with a bluish appearance was obtained. The synthetic scheme of ZnO nanoparticle formation reaction was shown as follows [13] (see Scheme 1):

$$Zn(CH_3COO)_2 + 2LiOH \xrightarrow[\text{for 2 h}]{0\ ^\circ C} ZnO + 2LiCH_3COO + H_2O$$

2.2.2. Synthesis of 3-(trimethoxysilyl)propyl methacrylate)-modified ZnO (TPMZnO) nanoparticles

The ZnO colloidal suspension obtained from the hydrolysis of $Zn(AcO)_2{\cdot}2H_2O$ with $LiOH{\cdot}H_2O$ mentioned above was then modified by TPM as followed. First, 0.10 g TPM in 3.3 mL of EtOH was added into the ZnO suspension under a stirring at 0 °C for 1 h. The mixture was then further stirred at room temperature overnight, followed by filtration to remove insoluble precipitates, and then TPMZnO nanoparticles were obtained. TPMZnO nanoparticles were stored in a refrigerator (at 4 °C) to inhibit their further growth [5]. For purification, TPMZnO (also ZnO) suspension was centrifuged at 15,000 rpm. The supernatant was removed by decantation, and the precipitate was redispersed with cold EtOH. The centrifugation–redispersion process was repeated for two times. Then, the TPMZnO followed by drying was resulted by precipitating with heptane at a volume ratio of heptane to TPMZnO sol $\geqslant$2, in a vacuum oven at 100 °C for 4 h. The dried powder of TPMZnO was stored in desiccators at room temperature before further use and characterization.

2.2.3. Synthesis of core–shell PMMA–CS/ZnO hybrid particles

PMMA–CS/ZnO composite particles were prepared *via* an emulsifier-free emulsion copolymerization as reported by Li et al. [14]. Briefly, 0.10 g of CS was dissolved in 1.0 M acetate buffer pH 4.0 under continuous stirring for 30 min. The CS solution was then poured in a three neck water-jacked flask equipped with a condenser, thermostat water bath, and N_2 inlet. The reaction was purged with N_2 gas for 30 min. After that, TPMZnO dispersed in MMA was transferred into the reaction flask, followed by the addition of TBHP aqueous solution (5×10^{-3} M) instantly, to induce polymerization. The polymerization reaction was achieved at 80 °C to attain the core–shell PMMA–CS/ZnO hybrid particles. The amounts of MMA and TBHP added were kept constant at 2 and 1 g, respectively. TMPZnO was varied as 0.018, 0.020, and 0.030 g, and the resulting hybrid particles were labeled as PMMA–CS/ZnO1, PMMA–CS/ZnO2, and PPMA–CS/ZnO3, respectively.

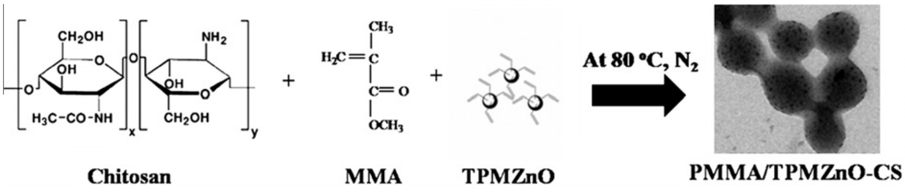
2.2.4. Characterization

Physicochemical properties of unmodified ZnO and TPMZnO nanoparticles were then characterized. Their particle sizes were estimated by UV–VIS spectroscopy (JASCO V-530). The absorption spectra of the ZnO and TPMZnO ethanol dispersions (ethanol was used as a blank) were recorded using a deuterium lamp (at $\lambda = 325$ nm) as a light source. The particle size obtained from UV–VIS spectroscopy was calculated from the onset of the absorption band based on the following calibrated equation [15]:

$$\frac{1240}{\lambda_{\frac{1}{2}}} = 3.301 + \frac{294.0}{D^2} + \frac{1.09}{D} \qquad (1)$$

where $\lambda_{1/2}$ is a wavelength at half absorption (nm) and D is a diameter of particle (Å).

The crystal size and crystal phase were observed by Bruker D8 ADVANCE (locked couple mode, 40 kV, 40 mA) with Diffract plus



Scheme 1. Preparation of PMMA–CS/ZnO hybrid particles.