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Facile synthesis of monodisperse polymer/SiO_2/polymer/TiO_2 tetra-layer microspheres and the corresponding double-walled hollow SiO_2/TiO_2 microspheres

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ABSTRACT

Monodisperse tetra-layer poly(ethyleneglycol dimethacrylate-*co*-methacrylic acid) (P(EGDMA-*co*-MAA))/SiO_2/P(EGDMA-*co*-MAA)/TiO_2 tetra-layer microspheres were facilely synthesized by the combination of the distillation precipitation polymerization for the preparation of P(EGDMA-*co*-MAA) layers and the controlled sol–gel hydrolysis of inorganic precursors for the formation of silica (SiO_2) and titania (TiO_2) layers. The thickness of the outer titania shell-layer was well-controlled via altering the feed of titanium tetrabutoxide (TBOT) during the sol–gel hydrolysis, while the size of polymeric layers were facilely controlled via a multi-step addition of ethyleneglycol dimethacrylate (EGDMA) crosslinker and methacrylic acid (MAA) monomer during the polymerization. The corresponding double-walled hollow inorganic microspheres containing SiO_2 inner shell and TiO_2 outer shell with various thickness were obtained after the selective removal of P(EGDMA-*co*-MAA) components via the calcination of the tetra-layer polymer/SiO_2/polymer/TiO_2 microspheres under 550 °C for 4 h in air. The structure and morphology of the resultant microspheres were characterized by transmission electron microscopy (TEM), X-ray diffractometer (XRD), X-ray photoelectron microscopy (XPS), and thermogravimetric analysis (TGA). Further, the photocatalytic properties of the resultant double-walled hollow SiO_2/TiO_2 microspheres were studied by photocatalytic degradation of methyl orange (MO) with ultraviolet (UV) irradiation of a 500 W high-pressure mercury lamp.

1. Introduction

Hierarchical multi-layer core–shell microspheres have been of considerable interest due to their plasmonic, optical, catalytic properties, which can be facially obtained by tuning the size, monodispersity, building blocks, composition and morphology [1–5]. The interaction between or among the hierarchical layers with various composition and thicknesses provide unique characteristics compared with homogeneous microspheres. For instance, Radloff and Halas have demonstrated that tetra-layer concentric nanoshell plasmonic nanostructures exhibited new resonances in the analysis of the plasmon resonant modes and energy controllable hybrid modes via precise tuning of the thickness of the selected shell-layer and the total particle size [6]. Kumacheva and co-workers have synthesized polymer multi-layer microsphere with a quantum dots loaded core and alternating layers with low and high refractive indices, which could be used as optical resonators through increasing the refractive index contrast between the alternating layers and excluding polymers [7]. For these applications, controllable size tuning of each layer and the overcoming of incompatibility between the connecting layers play an essential role. Thus, it is highly desirable to investigate facial methods and building blocks for the construction of hierarchical multi-layer core–shell microspheres with adjustable dimension and structure.

Hollow structures, especially those with complex components and double-shelled or multi-shelled structures, have attracted expanding concern associated with their unique properties and potential applications [8–11]. Different from the single-layer hollow spheres, the concentric multi-layer hollow spheres containing various composition and complex structures exhibit enhancing performance. For example, Li and co-workers have prepared double-walled PMAA/PNIAPM concentric hollow polymeric microspheres with unique morphology and thermal and pH dual-stimuli-responsive properties as the controlled-release reservoirs [8]. Dähne et al. demonstrated that polymeric capsules possessing shell-in-shell structures showed the enhanced permeability and remarkable higher mechanical stability than single-layer capsules [9,10]. Eccentric sphere-in-sphere titanium hollow spheres can scatter UV-light more efficiently inside the cavity so as to greatly enhance photocatalytic activity [11].

Titania (TiO_2) is an essential functional material because of its peculiar and fascinating physicochemical properties and a wide variety of potential uses in diverse fields, including solar-cell, energy conversion, environmental purification, and water-treatment [12]. TiO_2 hollow structured materials, owing to their low density,

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high specific areas, good photocatalytic activity, as well as light-harvesting efficiencies, have received more and more attention [11,13,14]. Synthetic methods for the preparation of TiO_2 hollow materials can be classified to two main strategies: templating methodologies and template-free processes. Template-free method allows one-pot and large-scale synthesis of hollow titania particles with diverse morphologies and structures via Ostwald ripening process. For instance, discrete and chain-like aggregates of well-defined hollow TiO_2 microspheres were prepared by a "one-pot" approach under hydrothermal conditions [15], especially via a modified fluoride-mediated self-transformation strategy with urea as a basic catalyst [16,17]. Further, Zeng and Li have reported an aqueous synthetic method to fabricated hollow nanospheres of Sn^{4+}-doped anatase or rutile TiO_2 with high uniformity and tunable content of Sn in the mixed oxide nanospheres [18]. The templating method confines the formation of titania shell based on the preformed template followed by the selective removal of the sacrificial template, which is facile to be implemented and allows the preparation of hollow titania particles with well-controlled dimension, interior-cavity size, shell-thickness, morphology, permeability and surface properties. For instance, Yang et al. have prepared TiO_2 hollow spheres with tunable shell-thickness and cavity size and surface morphology by sol–gel technique in presence of sulfonated polystyrene (PSt) latex particles as templates [19]. Xia and co-workers have reported the synthesis of amorphous TiO_2 mesoscale hollow spheres by templating their sol–gel precursor solution on crystalline arrays of PSt with subsequent dissolution of the PSt beads in toluene [20]. Wang et al. prepared hollow titania spheres with dense, uniform shells of small anatase crystallites after calcination of core–shell particles consisting of PSt cores and titania shells, which were prepared by the hydrolysis of tetrabutoxy titanium (TBOT) with ammonium cations as catalyst in acetonitrile/ethanol mixed solvent (3/1, V/V) [21].

Herein, we report a synthetic procedure for monodisperse concentric poly(ethyleneglycol dimethacrylate-*co*-methacrylic acid) (P(EGDMA-*co*-MAA))/SiO_2/P(EGDMA-*co*-MAA)/TiO_2 tetra-layer microspheres via the combination of distillation precipitation polymerization for the formation of polymeric layers and the controlled sol–gel hydrolysis for the construction of the inorganic silica and titania layers. The thickness of P(EGDMA-*co*-MAA) and TiO_2 layers could be conveniently controlled via precise adjusting the successive polymerization steps and the feed of sol–gel precursor. In addition, the corresponding SiO_2/TiO_2 double-walled hollow spheres were subsequently developed after the selective removal of the polymeric components via calcination of the tetra-layer microspheres. Further, the photocatalytic properties of the hollow double-walled SiO_2/TiO_2 microspheres were studied with the decomposition of methyl orange (MO) under UV irradiation in presence of the hollow double-walled microsphere as a catalyst.

2. Materials and methods

2.1. Materials

Ethyleneglycol dimethacrylate (EGDMA, 98%), tetraethyl orthosilicate (TEOS, 98%) and 3-(trimethoxysilyl)propyl methacrylate (MPS, 98%) were all used as received from Aldrich Chem. Co., Inc. Methacrylic acid (MAA) was provided by Tianjin Chemical Reagent II Co. and purified by vacuum distillation. 2,2′-Azobisisobutyronitrile (AIBN) was available from the Chemical Factory of Nankai University and was recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagent II Co.) was dried with calcium hydride and purified by distillation before use. Titanium tetrabutoxide (TBOT) and methyl orange (MO) were purchased as analytical grade from Tianjin Chemical Reagent II Co. The other reagents were of analytical grade and used without any further purification.

2.2. Methods

2.2.1. Synthesis of P(EGDMA-co-MAA)/SiO_2/P(EGDMA-co-MAA) tri-layer microspheres

Monodisperse P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA) tri-layer microspheres were synthesized by the combination of distillation precipitation copolymerization and sol–gel hydrolysis of TEOS according to our previous paper [22]. Specially, the P(EGDMA-*co*-MAA) third layer were afforded by two-stage distillation precipitation copolymerization of EGDMA and MAA in acetonitrile with the MPS-modified P(EGDMA-*co*-MAA)/SiO_2 particles as seeds. Typically, 0.05 g of MPS-modified P(EGDMA-*co*-MAA)/SiO_2 seeds, 0.15 mL of EGDMA, 0.15 mL of MAA and 0.006 g of AIBN were dispersed in 40 mL of acetonitrile for the first-stage precipitation distillation polymerization. After the reaction, the resultant P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA) tri-layer microspheres were utilized as seeds in the further-stage polymerization. Typically, 0.25 mL of EGDMA, 0.25 mL of MAA, 0.010 g of AIBN and the resultant tri-layer seeds were dispersed in 40 mL of acetonitrile under ultrasonic irradiation. The further-stage distillation precipitation copolymerization procedure was the same as that above mentioned.

2.2.2. Preparation of P(EGDMA-co-MAA)/SiO_2/P(EGDMA-co-MAA)/TiO_2 tetra-layer microspheres

The coating reaction was performed by controlled hydrolysis of TBOT in acetonitrile/ethanol (1/3, V/V) mixed solvent with P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA) tri-layer particles as templates in presence of ammonium hydroxide aqueous solution. Typically, about 0.024 g P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA) tri-layer microspheres and 0.6 mL of ammonium hydroxide were introduced into an ethanol/acetonitrile (75/25 mL) mixture under vigorous stirring at room temperature. Then various amount of TBOT (0.30, 0.40, 0.50, 0.60 mL) dispersed in ethanol/acetonitrile (15/5 mL) mixture was quickly added into the above dispersion. The coating reaction system was continued for 3 h at room temperature with stirring. The resultant P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA)/TiO_2 tetra-layer microspheres were purified by five times of centrifugation, decantation, and redispersion in ethanol and then dried in a vacuum oven at 50 °C till constant weight.

2.2.3. Preparation of hollow SiO_2/TiO_2 double-walled hollow microspheres

Double-walled hollow silica-sphere-in-titania-sphere (SiO_2/TiO_2) were afforded by calcination of the resultant P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA)/TiO_2 tetra-layer microspheres at 550 °C for 4 h in air.

2.2.4. Investigation the photocatalytic properties of double-walled hollow SiO_2/TiO_2 microspheres

The SiO_2/TiO_2 double-walled hollow microspheres with TBOT feed of 0.60 mL were selected as a model photocatalyst for the degradation of MO under UV irradiation. Typically, 20 mL of MO aqueous solution (0.10 g/L), 50 mg of the hollow SiO_2/TiO_2 double-walled microspheres, and 80 mL of water were introduced into a Pyrex tube with magnetic stirring in dark prior to UV irradiation. After 2 h, the reaction mixture was irradiated by a 500 W high-pressure mercury lamp. The MO decomposition was monitored by UV–vis spectroscopy.

3. Characterization

The size, size distribution and morphology of P(EGDMA-*co*-MAA), P(EGDMA-*co*-MAA)/SiO_2 core–shell microspheres, P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA) tri-layer microspheres, P(EGDMA-*co*-MAA)/SiO_2/P(EGDMA-*co*-MAA)/TiO_2 and the corre-