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Synthesis and characterization of TiO_2/Ag/polymer ternary nanoparticles via surface-initiated atom transfer radical polymerization

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ABSTRACT

We report on the novel ternary hybrid materials consisting of semiconductor (TiO_2), metal (Ag) and polymer (poly(oxyethylene methacrylate) (POEM)). First, a hydrophilic polymer, i.e. POEM, was grafted from TiO_2 nanoparticles via the surface-initiated atom transfer radical polymerization (ATRP) technique. These TiO_2–POEM brush nanoparticles were used to template the formation of Ag nanoparticles by introduction of a $AgCF_3SO_3$ precursor and a $NaBH_4$ aqueous solution for reduction process. Successful grafting of polymeric chains from the surface of TiO_2 nanoparticles and the in situ formation of Ag nanoparticles within the polymeric chains were confirmed using transmission electron microscopy (TEM), UV–vis spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). FT-IR spectroscopy also revealed the specific interaction of Ag nanoparticles with the C=O groups of POEM brushes. This study presents a simple route for the in situ synthesis of both metal and polymer confined within the semiconductor, producing ternary hybrid inorganic–organic nanomaterials.

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1. Introduction

Synthesis of hybrid inorganic/organic nanoparticles has become one of the most important topics in nanotechnology because they are expected to have combined properties of both inorganic nanoparticles and organic molecules [1–3]. Titanium dioxide (TiO_2), one of the inorganic materials, is a wide band gap semiconductor and a photo catalyst with stable physical and chemical properties. It is relative cheap, non-toxic and has optical, electronic properties that are exploited for several technical applications [4–6].

Nanostructural inorganic materials such as TiO_2 can be doped or decorated with metal ions to increase their functional abilities [7,8]. Such nanomaterials are widely utilized to various applications such as optical devices [9] catalysis [10] and photocatalysis [11]. In particular, noble metals, e.g. Ag, Au, Pt, deposited onto TiO_2 structures can modify the surface properties of the material, resulting in alteration of the catalytic or chemical properties in photocatalytic activity or enhancement of surface electron interactions by plasmon resonance [12]. Among many noble metals, Ag seems to have the most significant substrate coupling effect, producing the TiO_2/Ag structure for photochromic switching [13,14].

Ag ions have attracted the interests of several researchers because of both their effects on antibacterial activity [15] and their novel influence on the improvement of photoactivity of semiconductor [16,17]. For the formation Ag nanoparticles, many methods have been developed mostly based on the solution synthesis using liquid medium, a reductant and a surfactant. However, the solid-sate in situ reduction method has been also developed recently using H_2 gas [18], heat treatment [19], $NaBH_4$ solution [20] and gamma/ultraviolet irradiation [21]. This technology can prevent the agglomeration of nanoparticles and allow the nanocrystals to be uniformly dispersed, which results in the highly ordered arrays of functional nanostructures.

Surface modification of nanoparticles has recently received great attention [22–25], but the study on the development of ternary nanoparticles consisting of a metal, a semiconductor and a polymer was not intensively investigated up to now [26]. In this study, we report on a simple route to deposit a metal on the surface of semiconductor/polymer hybrid materials. First, a hydrophilic polymer of poly(oxyethylene methacrylate) was grafted from TiO_2 nanoparticles via the surface-initiated atom transfer radical polymerization (ATRP) technique. These TiO_2–POEM nanoparticles were used as a template for the formation of Ag nanoparticles under the chemical reduction process. The resultant ternary materials were characterized using transmission electron microscopy (TEM),

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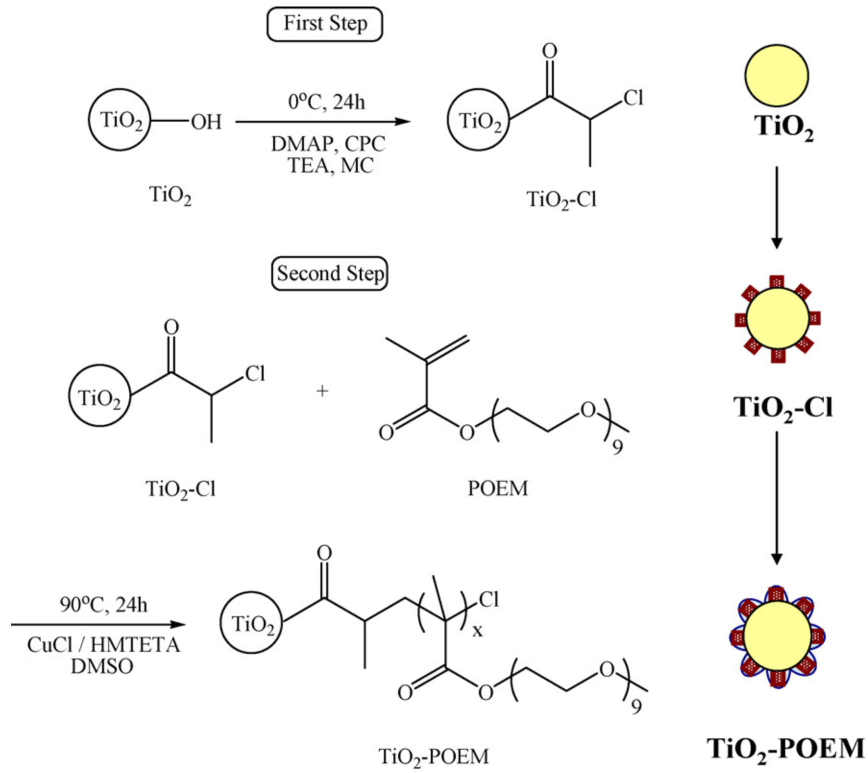

Fig. 1. Reaction scheme for the formation of TiO_2–POEM brush nanoparticles.

UV–vis spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopy.

2. Experimental

2.1. Materials

Commercial TiO_2 (P25) was purchased from Degussa. 2-Chloropropionyl chloride (CPC, >97%), triethylamine (TEA, >99.5%), 4-(dimethylamino) pyridine (DMAP, >99%), methylene dichloride (MC, >99.8%), poly(oxyethylene methacrylate) (poly(ethylene glycol) methyl ether methacrylate, POEM, M_n = 475 g/mol), dimethyl sulfoxide (DMSO), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), copper(I) chloride (CuCl), silvertrifluoromethanesulfonate ($AgCF_3SO_3$ >99%), sodium tetrahydridoborate ($NaBH_4$ >99%) were purchased from Aldrich. Ethanol (C_2H_6O >99.8%) was purchased from J.T. Baker. All solvent and chemicals were regent grade, and were used as received without further purification.

2.2. Synthesis of TiO_2–POEM nanoparticles

TiO_2–POEM brush nanoparticles were synthesized according to the two-step synthetic method [27]. In the first step, 3.68 g of DMAP was mixed with 20 ml of MC and 2.8 ml of TEA at 0 °C with ice. Next, 4.8 ml of CPC in 20 ml of MC was added to the solution. Then, 20.0 g of TiO_2 in 100 ml MC was added dropwise to the solution and then the solution was purged with nitrogen for 30 min. The mixture was stirred at room temperature for 24 h. After the reaction, the resulting solution was precipitated into methanol, and the product was separated by centrifuging. Finally, TiO_2–Cl nanoparticles were obtained and dried in a vacuum oven overnight at room temperature. In the second step, 8 ml of POEM was dissolved in 10 ml of DMSO. Then 0.0264 g of CuCl and 0.072 ml of HMTETA were added to the solution, and 2 g of TiO_2–Cl nanoparticles were added subsequently. The solutions were purged with nitrogen for 30 min. The mixture was placed in a 90 °C oil bath for 24 h. After polymerization, the resulting solution was precipitated into methanol, and the polymer was separated by centrifuging. The product was washed with methanol several times to remove impurities. Finally, TiO_2–POEM brush nanoparticles were obtained and dried in a vacuum oven overnight at room temperature.

2.3. Preparation of TiO_2–POEM/Ag nanocomposites

As-synthesized TiO_2–POEM nanoparticles (0.01 g) were dispersed in 1 ml of ethanol with 0.002 g of $AgCF_3SO_3$ for 2 h. The resulting mixture solutions were dropped and spread with glass-pipette on slide glass and dried at room temperature for 1 day in dark room. After the evaporation of solvent, the films were immersed in 1 wt% $NaBH_4$ aqueous solution for 30 min to induce the reduction of Ag ions to Ag nanoparticles.

2.4. Characterization

UV–vis spectroscopy was measured with spectrophotometer (Hewlett Packard) in the range of 200–800 nm. Fourier transform infrared (FT-IR) spectra of the samples were collected using Excalibur Series FT-IR (DIGLAB Co.) instrument between the frequency ranges of 4000–600 cm^{-1} using ATR facility, 64–64 scans were signal-averaged at a resolution of 4 cm^{-1}. Transmission electron microscope pictures were obtained from a Philips CM30 microscope operating at 300 kV to observe nanostructures of samples. X-ray diffraction experiment was carried out on a Rigaku 18 kw rotating anode X-ray generator with CuKα radiation (λ = 1.5406 Å) operated at 40 kV and 300 mA. The 2θ range was from 5° to 60° with a scanning speed of 3°/min, and the distance from the sample to detector was 185 mm. XPS measurement was carried out using a VG Scientific ESCALAB 220 spectrometer equipped with a hemispherical energy analyzer. A nonmonochromatized AlKα X-ray source ($h\nu$ = 1486.6 eV) was operated at 12.5 kV and 16 mA. Before data

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