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Full Length Article

Photocatalytic growth of Ag nanocrystals on hydrothermally synthesized multiphasic TiO_2/reduced graphene oxide (rGO) nanocomposites and their SERS performance

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ABSTRACT

TiO_2/reduced graphene oxide (rGO) nanocomposites were prepared via a facile one-step hydrothermal method using $TiCl_3$ as the TiO_2 precursor. Cetyltrimethyl ammonium bromide (CTAB) was introduced as a stabilizer for GO in solution. The effects of GO content, Ti^{3+} concentration and urea additive on phase constituent and morphology of the TiO_2 crystallites in the nanocomposites were systematically investigated. UV–vis absorption ability of the as-made composites was further tested and discussed. Ag nanocrystals (NCs) were photocatalytically grown on the surfaces of biphasic (anatase + brookite) and triphasic (anatase + brookite + rutile) TiO_2/rGO nanocomposites to evaluate their surface-enhanced Raman scattering (SERS) performances. Morphology evolution of the Ag NCs in response to different photocatalytic ability of the TiO_2/rGO nanocomposite was also investigated in detail. The nanocomposite with triphasic TiO_2 of proper phase constituents was confirmed to favor the growth of Ag particles of two distinctly different sizes and to produce SERS substrates of substantially better performance.

1. Introduction

Surface-enhanced Raman scattering (SERS) is a powerful analytical tool which is first reported by Fleischmann et al. in 1974 [1]. After decades of study it is commonly accepted that SERS is a combination of the enhancement of localized electromagnetic (EM) effect and chemical effect (CE) with the former prevails in the total contribution [2–6]. Many attempts have been made to extensively investigate noble metal nanoparticles such as Au, Ag, Pt and Cu for SERS applications [7,8]. In general, the SERS signals will be greatly enhanced by a rough surface when the analyte molecules are absorbed around the nanometer-scale gaps or protrusions of metallic particles (hot spots) [9,10]. Based on previous research outcomes one may conclude that the SERS effect strongly depends on the shape, size, interspacing, ordering and periodicity of the active particles on SERS substrates [11,12]. When the particle size and interspacing are confined on the nanometre scale, the EM effect of neighbouring particles will result in an enormous enhancement of Raman signals especially when the interparticle spacing is less than 20 nm [13]. According to the aforementioned phenomena, many well designed SERS substrates such as metal film over nanospheres (MFONs) [14,15], aggregated colloids [16,17], periodic particle array [18] and nanofingers [19,20] that have a great response to Raman signal were developed.

Since the first demonstration of photocatalytic water splitting on TiO_2 electrodes by Fujishima and Honda, the photocatalytic properties of TiO_2 have been extensively studied [21]. Due to its relatively wide bandgap (~3.0–3.2 eV), the light absorption of TiO_2 is limited in the UV region. Moreover, compared with the time scale of chemical interactions of TiO_2 with the adsorbed chemicals (10^{-8}–10^{-3} s), the photoexcited electrons and holes have a faster flash recombination time on the order of 10^{-9} s [22]. This time scale difference between the two processes results in an intrinsic recombination of electron-hole pairs, which will cause efficiency loss during photocatalytic reaction. To enhance the photocatalytic performance of TiO_2, a variety of strategies have been reported such as metallic and non-metallic doping [23–26], noble-metal loading [27], as well as metal oxide and metal hydroxide loading [28–30].

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However, non-metallic doping of TiO_2 (e.g. N-doping) is usually hard to reach high concentration of the doped ions and/or exhibits low stability against photocorrosion [31,32]. The strategy of loading metal oxide on TiO_2 is somehow limited by its multiple reaction steps and may decrease the photocatalytic activity via losing active surface sites of the photocatalyst.

Graphene, which is a single-layered sheet of sp^2-hybridized carbon atoms in a tightly packed two-dimensional honeycomb lattice, possesses many unique properties such as high thermal conductivity ($\sim$5000 W m^{-1} K^{-1}) [33], large theoretical specific surface area ($\sim$2630 m^2 g^{-1}) [34], good optical transparency ($\sim$97.7%) [35], high charge-carrier mobility at room temperature (200000 cm^2 V^{-1} s^{-1}) [36], and high Young's modulus ($\sim$1 TPa) [37]. Taking advantages of these unique properties, numerous attempts have been made to combine graphene with TiO_2 to enhance the photocatalytic performance of the latter because graphene can provide charge separation and play as an electron carrier in the composite material [38–40]. Many synthetic methods have been reported to integrate TiO_2 with graphene, such as chemical reduction, microwave-assisted synthesis, sol-gel processing, atomic layer deposition and solvothermal reaction [41–45]. Notably, the previous research on TiO_2/rGO composites generally concerns single or biphasic TiO_2 of anatase and rutile, while the study on nanocomposites involving brookite-type TiO_2 of tunable content has been rare.

In this article, TiO_2/rGO composites in the presence of biphasic (anatase + brookite) and triphasic (anatase + brookite + rutile) TiO_2 have been synthesized via a facile one-pot hydrothermal method, and the effects of GO content, $TiCl_3$ concentration and urea additive (pH modifier) on phase composition, particle morphology and physicochemical properties were thoroughly discussed. The photo-absorption ability of the composite was revealed by UV–vis spectroscopy, followed by a detailed discussion on the effects of phase composition and graphene attendance. Ag particles were then photocatalytically deposited on the nanocomposite surfaces, and the influences of the photocatalytic capability of the TiO_2/rGO composites on morphology of the resultant Ag particles were revealed. Finally, the SERS performance of the resultant Ag NCs was evaluated via the detection of Rhodamine 6G (R6G) molecules and was correlated to the crystal morphologies of Ag.

2. Experimental methods

2.1. Chemicals and materials

The reagents of hydrochloric acid (HCl, 36%), sulfuric acid (H_2SO_4, 95%), phosphoric acid (H_3PO_4, 85%), potassium permanganate ($KMnO_4$, reagent grade), hydrogen peroxide (H_2O_2, 30%), graphite powder ($\sim$200 mesh), titanium trichloride solution ($TiCl_3$, 22 wt.% with 1–5 wt.% of Hydrochloric acid), silver nitrate ($AgNO_3$, 99.9%), cetyltrimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$, reagent grade), urea ($CO(NH_2)_2$, reagent grade), ethanol (C_2H_5OH, 99.5%) and Rhodamine 6G (R6G, $C_{28}H_{31}ClN_2O_3$, practical grade) were all purchased from Wako Pure Chemical Industries (Osaka, Japan). Milli-Q (MA, USA) purified water was used throughout the experiment.

2.2. Synthesis of TiO_2/reduced graphene oxide (rGO) nanocomposite and silver deposition

2.2.1. Synthesis of graphite oxide (GO)

Graphite oxide (GO) was produced from the graphite powder by an improved Hummers' method [46]. In brief, a concentrated mixture of H_2SO_4 (120 mL) and H_3PO_4 (13 mL) was added into a beaker containing a mixture of graphite powder (1 g) and $KMnO_4$ (6 g), followed by reaction at 50 °C for 12 h under magnetic stirring. The resultant product was then cooled to $\sim$4 °C in an ice bath and subsequently 5 mL of 30% H_2O_2 was poured into the beaker. After stirring for another 30 min, the resultant yellowish-brown suspension was washed in succession with water, 30% HCl, and ethanol. Each solvent was used twice to ensure removal of additional ions. For each wash, the suspension was centrifuged (10,000 rpm for 30 min) and the supernatant was decanted away. After the washing, the GO precipitate was dispersed in 500 mL of water and was exfoliated via ultrasonication for 1 h. The exfoliated GO was further centrifuged (10,000 rpm for 60 min) and the supernatant was decanted away. Finally, the product was dried in an air oven at 60 °C before characterization.

2.2.2. Synthesis of TiO_2/reduced graphene oxide (rGO) nanocomposite

To prepare dispersed GO nanosheets, the above dried exfoliation product was dispersed in 100 mL deionized water (0.1 g/L), followed by ultrasonication for 1 h under ambient conditions and then natural cooling to room temperature. In a typical synthetic procedure for TiO_2/rGO nanocomposites, $TiCl_3$ solution (*a* mL) was dripped into *b* mL of GO suspension (with or without *c* g of CTAB dispersant before adding $TiCl_3$) and deionized water was then added in to make a total volume of 50 mL. Under vigorous magnetic stirring, a certain amount of urea (*d* M urea in the mixture) was added in, followed by magnetic stirring for 10 min. The thus-made solution was then transferred to a Teflon-lined autoclave of 120 mL capacity and was autoclaved at 180 °C in an air oven for 24 h. After natural cooling to room temperature, the resultant solids were collected via centrifugation at 8000 rpm for 30 min and then washed repeatedly with deionized water for 5 times before drying at 60 °C for 12 h. To make the expression simpler, all the products are denoted by *a*Ti-*b*GO-*c*C-*d*U, where Ti, GO, C and U represent $TiCl_3$, GO nanosheets, CTAB and urea while *a*, *b*, *c* and *d* represent the contents (volume or concentration) of the above four variables, respectively.

2.2.3. Photocatalytic growth of silver nanostructures on TiO_2/rGO nanocomposite

The synthesized composite powder (1 mg) was added in ethanol (10 mL), dispersed via ultrasonication, and the resultant suspension was then dripped onto a $\sim 4 \times 4$ mm^2 silicon wafer slide. After drying in the air, the slide was immersed in 3 mL of a 0.1 M $AgNO_3$ solution placed in a petri dish (36 mm in diameter). The dish was then irradiated with 5 mW/cm^2 UV light for 45 min. The UV light, composed of the wavelengths of 296, 365, 424 and 474 nm at intensity ratio of 0.82/1.0/0.37/0.30, was generated by a 200 W high-stability mercury-xenon lamp (A type, San-Ei Electric Co., Ltd., Osaka, Japan) using a UV-curing system (model UVF-204S, San-Ei Electric Co., Ltd.). After the irradiation, the slide was gently washed with water and ethanol followed by air drying.

2.3. Characterization techniques

Phase identification was preformed via micro-Raman spectroscopy (model Jobin Yvon T64000, Horiba Co. Ltd., Tokyo) and X-ray diffractometry (XRD, model RINT 2200 V/PC, Rigaku Co., Tokyo). The Raman signals were acquired using an excitation source of 50 mW Ar^+ laser (514 nm), with a total acquisition time of 20 s (two accumulations). The X-ray diffractometry was performed at 40 kV/40 mA, using nickel-filtered Cu Kα radiation and a scanning speed of 0.5° 2θ/min. The phase constituents of the TiO_2 polymorphs were calculated from the integrated intensities of the anatase (101), brookite (121), and rutile (110) XRD peaks [47]. Sample morphologies were observed via field-emission scanning electron microscopy (FE-SEM, model S-5000, Hitachi Co. Ltd., Tokyo) operated at 10 kV and transmission electron microscopy (TEM, model FEM-3000F, JEOL Ltd., Tokyo) under an acceleration