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Synthesis of Cu_2O/graphene/rutile TiO_2 nanorod ternary composites with enhanced photocatalytic activity

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ABSTRACT

A ternary composite of Cu_2O, graphene and rutile TiO_2 nanorods was prepared using $Cu(CH_3COO)_2 \cdot H_2O$, graphene oxide and $TiCl_4$ as the starting materials and its enhanced photocatalytic performance was demonstrated. Graphene/TiO_2 nanorod composites (GT) were obtained by a simple hydrothermal method and then, Cu_2O was coupled onto the surface of graphene/rutile TiO_2 to form Cu_2O/graphene/rutile TiO_2 nanorod (CGT) composites *via* a chemical bath deposition process. The as-prepared sample was characterized by X-ray diffraction (XRD), emission field scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), specific surface area analyzer (BET), Raman spectroscopy and ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS). It is found that the introduction of graphene and Cu_2O has little effect on the morphology of TiO_2 nanorods with average dimensions of 140 nm (length) × 30 nm (diameter) (L/D ratio ≈5). A red shift of light absorption edge and more absorption in the visible light region were observed for the resulted ternary samples compared with TiO_2 and graphene/TiO_2 composites. The photocatalytic activity was evaluated by the photodegradation of methylene blue under visible light irradiation, which showed 2.8 times corresponding enhancement of the degradation efficiency for the ternary composites compared with TiO_2. This work provides a new strategy to improve the visible light response of TiO_2 and facilitate its application in environmental remediation.

1. Introduction

In past few years, photocatalytic decomposition of organic pollutants in waste water or air using semiconductors has attracted much attention [1,2]. Titanium dioxide (TiO_2) has been considered to be one of the most promising photocatalysts because of its chemical stability, non-toxicity, low cost and superior activity [3–6]. However, the large energy band gap of TiO_2 (3.2 eV) indicates only UV light (about 4% of the solar energy) can activate this materials. Furthermore, the rapid recombination of photoinduced electrons and holes in TiO_2 also hampered its full potential application. Thus, improving its utilization efficiency of solar energy has generated considerable scientific interest. Up to now, numerous strategies have been developed to promote the photocatalytic activities of TiO_2, such as doping TiO_2 with metal [7,8] and nonmetal [9–11] or coupling TiO_2 with narrow band gap semiconductors [12,13]. Among these, modification of TiO_2 with narrow band gap semiconductors has been reported as one of the best options for achieving high efficient utilization of solar energy in photocatalysis [14–16].

Many different reports have described visible band gap semiconductors for modification [12–17]. Alternatively, cuprous oxide (Cu_2O), a p-type semiconductor with a direct band gap of about 2.0 eV, is a promising material for the conversion of solar energy into electrical or chemical energy [18–20]. Recently, Cu_2O and TiO_2 composites have been studied for improving the photocatalytic activity of TiO_2. Cheng et al. [21] developed Cu_2O decorated TiO_2 *via* chemistry bath process and demonstrated that the hydrogen evolution rate over the as-prepared composites was one order of magnitude higher than that of commercial P25 TiO_2. The Cu_2O can serve as an electron–hole separation center to promote H_2 evolution. Wang et al. [13] prepared Cu_2O/TiO_2 p-n heterojunction photoelectrodes by an ultrasonication-assisted sequential chemical bath deposition. They confirmed that the obtained composites possessed enhanced photocurrent, more effective photoconversion capability and superior photoelectrocatalytic activity in the degradation of Rhodamine B. The narrow band gap Cu_2O

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nanoparticles act as sensitizers to promote the charge transfer to TiO_2, leading to efficient photogenerated charge carrier separation.

Previous reports have shown that graphene have certain beneficial effects on the photocatalytic activity of semiconductors [22], such as increasing the light absorption and charge transport. More recently, graphene have been widely studied to incorporate into semiconductor materials (such as TiO_2 [23,24], ZnO [25], and so on) to obtain photocatalysts with superior catalytic performance. Graphene, a two-dimensional sp^2-hybridized carbon material, possesses many excellent properties such as high electrical conductivity, flexible structure, large theoretical specific surface area, unique mechanical strength and superior transparency [26,27]. Due to the introduction of graphene, the band structure and the interfacial charge transfer of semiconductor were modified, leading to an improvement in their photocatalytic performance [28,29]. Lu et al. [30] synthesized graphene–TiO_2 composites *via* a solvothermal process and reported excellent photocatalytic activity for the degradation of methylene orange under visible light. Sang et al. [31] prepared reduced graphene oxide/TiO_2 nanobelt by an in situ photochemical reduction method. The as-prepared sample exhibited remarkable visible light driven photocatalytic activity in photodegradation of methylene orange and hydrogen production by water splitting. Our recent studies also revealed that TiO_2 nanorods modified with graphene showed high performance in photocatalytic degradation of organic pollutants [32]. Furthermore, we also demonstrated the sensitizing effect of graphene oxide on the photoelectron chemical and photocatalytic properties of the TiO_2 nanotube arrays under visible light [33].

The multivariate perturbation in a multi-element composite of TiO_2 can provide synergistic effects to further enhance the photocatalytic activity of TiO_2. Recently, there has been growing interests about the multiple modification methods, such as co-dopings [34,35], co-couplings [36–38] or doping-coupling [39] hybrid modification of TiO_2. Aragaw et al. [35] confirmed the highest saturated photocurrent density of Sn and C codoped TiO_2 nanowires and 60%, 94%, and 100% efficiency improvements of the maximum solar energy conversion efficiency compared to undoped, Sn doped, and C doped TiO_2 nanowires. The improvement is attributed to the synergetic effects of Sn and C codopants which can lower recombination and enhance life time of photogenerated charge-separated carriers on the surface states. Wang et al. [38] prepared TiO_2 loaded CuS and NiS by hydrothermal approach and proved that CuS and NiS can act as effective dual co-catalysts to enhance the photocatalytic H_2 production activity of TiO_2. Luo et al. [40] synthesized Cu_2O/N–TiO_2 *via* a two-step route and demonstrated its extended absorption edge and markedly enhanced photodegradation efficiency of methyl orange solutions under both the visible and full-spectrum light irradiation in comparison with TiO_2 and Cu_2O/TiO_2. It was observed that the trapping of electrons and the charge carrier life time enhancement of Cu_2O/N–TiO_2 are more effective than that of TiO_2 and Cu_2O/TiO_2, which was attribute to the formation of p–n heterojunction and intraband deep localized states.

It is worth noting that one-dimensional (1D) TiO_2 nanorods are especially appealing for applications in various areas due to their high surface area, efficient light harvesting, photoinduced charge separation and transport [41]. Besides, they can also avoid agglomeration in the photocatalysis compared with TiO_2 anon-powder [42]. Furthermore, rutile TiO_2 have also attracted considerable attention for photocatalysis because of thermodynamically stable phase and an excellent combination of physical properties such as exceptional light-scattering efficiency, high refractive index, opacity, and chemical inertness [43,44]. Herein, we developed a feasible fabrication approach for a ternary nanocomposite of Cu_2O, graphene and rutile TiO_2 nanorods. Their enhanced visible light response and improved photocatalytic activity for the degradation of methylene blue were demonstrated. To the best of our knowledge, little information has been reported on such ternary composite and its photodegradation performance [45].

2. Experimental

2.1. Materials and reagents

All chemicals were analytical grade and used without further purification. Sodium hydroxide (NaOH, 98.0%), cupric sulfate ($Cu(CH_3COO)_2 \cdot H_2O$, 99.95%), glucose ($C_6H_{12}O_6 \cdot H_2O$, 99.9%) and titanium tetrachloride ($TiCl_4$, 99%) were purchased from Aladdin industrial corporation.

2.2. Synthesis of graphene/TiO_2 rutile nanorod composites

Graphene oxide (GO) was synthesized using Hummer's method [46], and the GO aqueous solution was obtained by ultrasonic treatment of graphene oxide in deionized water. GT composites were fabricated by a simple hydrothermal reaction process. Typically, 7 mL of 0.5 mg/mL GO solution was transferred to 60 mL of deionized water and stirred for 60 min. Subsequently, 3 mL of $TiCl_4$ solution was dropped gradually to the above solution followed by stirring for another 40 min. The obtained suspension was placed into a Teflon-sealed autoclave of 100 mL capacity and maintained at 180 °C for 6 h. After centrifuging, the solid products were sequentially washed with deionized water and absolute ethanol for several times and dried at 60 °C for 2 h.

2.3. Fabrication of Cu_2O/graphene/TiO_2 rutile nanorod composites

The combination of Cu_2O nanoparticles onto the surface of the GT were carried out *via* a chemical bath deposition process. In detail, the obtained GT composites (0.3 g) were added into pre-prepared ethanol solution of $Cu(CH_3COO)_2 \cdot H_2O$ with a desire concentration (0.001, 0.0025, 0.005 and 0.01 M) and dispersed by ultrasound irradiation for 1 h to allow the adsorption of Cu ions onto the surface of the composites. Subsequently, the powders were collected by centrifugation and put into a NaOH solution (10 mL, 0.1 M). Ultrasound irradiation was again applied to disperse the powders. The well-dispersed suspension was maintained at 60 °C in water bath and an aqueous solution of glucose (10 mL, 0.1 M) was gradually added into the above suspension with continuous stirring for a reaction time of 10 min. Finally, the precipitate was rinsed twice with deionized water and ethanol and dried overnight at 60 °C to afford the ternary composites of CGT. The obtained sample was noted as CGT *x*M, where *x* represents the concentration of $Cu(CH_3COO)_2 \cdot H_2O$ ethanol solution.

2.4. Characterizations of the resulted samples

The crystallinity and phase composition of the as-prepared samples were characterized by XRD (PANalytical X'Pert, Holland) using Cu Kα radiation operated at 40 kV and 40 mA. The morphologies and microstructures of the samples were obtained using TEM (FEI Tecnai F20, USA) and SEM (JEOL JSM-7000F, Japan). The UV–vis DRS were obtained by UV–vis spectrophotometer (Shimadzu UV 3600, Japan) in a region of 200–800 nm. Raman spectra were recorded with the excitation of a 325 nm He–Cd laser guided by a Raman spectrometer (Renishaw, UK). The specific surface area of the samples were determined by N_2 adsorption-desorption analysis conducted at 77 K (Micromeritics ASAP 2020 V4.01, USA).