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TiO_2 decoration of graphene layers for highly efficient photocatalyst: Impact of calcination at different gas atmosphere on photocatalytic efficiency

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ABSTRACT

Graphene based two-dimensional carbon nanostructures serve as a support to disperse TiO_2 nanoparticles. Here, a facile decoration of graphene oxide (GO) and reduced graphene oxide (G) sheets with TiO_2 nanoparticles at different contents (1–10%) has been demonstrated. Then the as-prepared TiO_2–GO samples were heat treated at 450 °C under oxidizing (O_2), inert (N_2) and (Ar) and reducing (N_2/H_2) conditions to obtain multi-layers TiO_2–GO and TiO_2–G nanocomposites. The findings indicated that the lattice fringes of TiO_2 anatase exhibit the typical distances of (101) (3.54 Å) with high crystallinity. HRTEM images show the multi-layers TiO_2–G sheets with thicknesses ~2.4 nm. The newly prepared multi-layers TiO_2–GO and TiO_2–G nanocomposites have been compared with a commercial photocatalyst P-25 by the determination of their photocatalytic efficiencies for degradation of methylene blue. It can be observed that when TiO_2–GO calcining in N_2/H_2, the produced TiO_2–G shows a higher photocatalytic activity than those treated in N_2 and O_2. Also, the photocatalytic degradation rates of MB by TiO_2–G are faster 6 and 2 times than that by P25 and TiO_2–GO respectively, which is due to the better contact between G and TiO_2 and the more effective charge transfer from TiO_2 to G multi-layers. From the economic point of view, the consumed amount of TiO_2–G sheets in photocatalysis process is one fifth of commercial photocatalyst P-25 without loss of photocatalytic performance. Incorporation of TiO_2 nanoparticles onto multi-layers graphene sheets provide greater versatility in carrying out photocatalytic processes.

1. Introduction

Graphene offer new opportunities to develop nanocomposites with unusual electronic catalytic properties [1]. Graphene is an atomic sheet of sp^2-bonded carbon atoms that are arranged into a honeycomb structure [2]. Apart from its unique electronic properties, the two dimensional (2D) planar structure material has several other excellent attributes, such as the large theoretical specific surface area [3] and the high transparency due to its one-atom thickness [4]. Moreover, the surface properties of graphene could be adjusted via chemical modification, which facilitates its use in composite materials [5,6]. 2D carbon nanostructures such as graphene can potentially serve as a support material with which to anchor semiconductor particles and improve the performance of optoelectronic and energy conversion devices. The development of semiconductor–graphene or metal nanoparticle–graphene composites provides an important milestone to develop energy harvesting and conversion strategies [7]. Incorporation of catalyst particles onto an individual graphene or reduced graphene oxide (G) sheet with good distribution can provide greater versatility in carrying out selective catalytic or sensing processes [7–11]. TiO_2 has a large-band-gap semiconductors, and it is photocatalytically active under UV irradiation. TiO_2 is capable of interacting with graphene oxide via carboxylic acid functional groups [12,13]. Thus, the combination of TiO_2 and graphene is promising to simultaneously possess excellent adsorptivity, transparency, conductivity, and controllability, which could facilitate effective photodegradation of pollutants [14]. It is evident that the individual graphene sheets are coupled to TiO_2 nanoparticles. These TiO_2 nanoparticles are likely to interact through charge–transfer interaction with carboxylic acid functional groups or simple physisorption on the graphene oxide sheets [12]. The previous published papers reported the enhanced photocatalytic activity by GO–TiO_2 composite for water splitting, antibacterial application, and the degradation of organic pollutions [15–25]. Sun et al., [16] synthesized GO–TiO_2 nanocomposites by

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simply covering the functionalized graphene with P25 nanoparticles by heterogeneous coagulation. A sol–gel method to prepare GO–TiO_2 composites using tetrabutyl titanate and GO as the starting materials was demonstrated, and enhanced water photocatalytic splitting than that of P25 has been observed [17]. Liang et al. reported the synthesis of the high-quality GO–TiO_2 composites with better control in the size and morphology of TiO_2 nanoparticles [18]. Zhang et al. [14] prepared P25-graphene composite from P25 and GO in ethanol solution using a hydrothermal method, where GO was reduced to G during the hydrothermal process [20]. Also, GO–TiO_2 nanocomposites have been prepared using RF magnetron sputtering [21]. P25 TiO_2 materials are aggregated nanoparticles, it is difficult to anchor all P25 nanoparticles onto GO sheets very well. The well connection between TiO_2 and GO sheets is essential for the effective charge transfer and effective charge separation during the photocatalytic process.

On the other hand, a variation of the number of graphene layers may result in a striking change of their electronic properties [1]. Accordingly, it is very important to explore the production of graphene with number of layers in large quantities for their further fundamental studies and extensive applications. Wu et al. [26] have been succeeded to prepare a specific number of layers by selecting suitable starting graphite with high electrical conductivity $\sim 1 \times 10^3$ S/cm, which is ~3 orders of magnitude higher than that of individual GO reduced by hydrazine or sodium borohydride [27,28]. However, the prepared of high-quality TiO_2–graphene with a number of layers still remains a significant challenge for efficient photocatalysis applications. From this window, herein, we report a facile synthesis of multi-layers TiO_2–GO and TiO_2–G nanocomposites at different TiO_2 contents with highly dispersed onto GO and G sheet using titanium isopropoxide. The as-prepared TiO_2–GO were heat treated at 450 °C under oxidizing (oxygen), inert (N_2) and (argon) and reducing (N_2/H_2) conditions to obtain multi-layers TiO_2–GO and TiO_2–G nanocomposites. The present method offers several advantages over the previously reported ones, including (i) there was no an extra reducing agent, (ii) the in situ growth of TiO_2 leads to the formation of uniform nanoparticles on G sheets, and (iii) TiO_2–G with multi-layers have been prepared for highly diffusion and adsorption of dyes. To the best of our knowledge, the measured photodegradation rate of MB in the current work is found to be among the highest values reported up to now.

2. Experimental work

2.1.1. Materials

Graphite powder and sodium nitrate ($NaNO_3$, 98%) was obtained from Koch-Light Laboratories Ltd. Sulfuric acid (H_2SO_4 95–97%) and potassium permanganate ($KMnO_4$, 99.5%) and ethanol solution (99.9%) were purchased from Fluka and BDH Chemicals Ltd. Hydrogen peroxide solution (30%, w/v) pure reagent for analysis and titanium (IV) isopropoxide 97% ($C_{12}H_{28}O_4Ti$) were obtained from Aldrich.

2.1.2. Synthesis of TiO_2–GO and TiO_2–G

The synthesis of TiO_2–GO and TiO_2–G involve three key steps, (i) oxidation of the starting graphite to synthesize GO, (ii) impregnation of TiO_2 into GO sheets (iii) calcination of the as-prepared TiO_2–GO at 450 °C under oxidizing (O_2), inert (N_2) and (Ar), and reducing (N_2/H_2) conditions to obtain multi-layers TiO_2–GO and TiO_2–G nanocomposites.

2.2. Synthesis of graphene oxide (GO)

The graphene oxide (GO) was synthesized according to the modification of Hummers' methods [29] and the process was described previously [26]. Hummer method was used to prepare graphene oxide using 2 g graphite powder, 1 g sodium nitrate and 46 ml sulfuric acid were mixed and stirred at 0 °C for 15 min. 6 g potassium permanganate added slowly to the above solution and cooled for 15 min. Then the suspended solution was stirred for 1 h and 92 ml H_2O was added slowly for 10 min. the suspension was diluted by 280 ml of warm water. Finally, titrate the solution with 10 ml of H_2O_2 (30%). The resulting suspension was filtered, washed with water and dried at 60 °C for 24 h.

2.3. Synthesis of TiO_2–GO and TiO_2–G sheets nanocomposites

The presence of oxygen functional groups makes GO sheets strongly hydrophilic; stable aqueous dispersions consisting almost entirely of sheets with a thickness of 1 nm can be obtained by a mild ultrasonic treatment of graphite oxide in water [30]. 0.2 g of GO was prepared from graphite powder by Hummer method as shown above, was dispersed in a mixed solution of H_2O (10 ml) and ethanol (5 ml) in ultrasonic for 1 h. Then the calculated amount of titanium isopropoxide was added to graphene oxide suspension and ultrasonicated for another 1 h to obtain 1, 3, 5 and 10 wt% TiO_2–GO. The product was isolated by filtration and washed with distilled water and ethanol. The as-prepared 10 wt% TiO_2–GO sample were heat treated at 450 °C under oxidizing (oxygen), inert (N_2) and (argon) and reducing (N_2/H_2) conditions nanocomposites (labelled TiO_2–GO, TiO_2–GN, TiO_2–GA and TiO_2–G) to obtain TiO_2–GO and TiO_2–G sheets nanocomposites with TiO_2 anatase form as high photoactive phase.

2.3.1. Characterization

Transmission electron microscopy (TEM) was conducted at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. Field emission-secondary electron microscope (FE-SEM) images were carried out with a FE scanning electron microanalyzer (JEOL-6300F, 5 kV). X-ray diffraction (XRD) data were acquired on a Bruker AXS D4 Endeavour X diffractometer using Cu $K\alpha_{1/2}$, $\lambda\alpha_1 = 154.060$ pm, $\lambda\alpha_2 = 154.439$ pm radiation. Raman spectroscopy was carried out using a WITEC CRM200 Raman system in the range from 500 to 2000 cm^{-1}. Infrared spectra were obtained on PerkinElmer Spectrun 100 FTIR-spectrometer in the range 350–5000 cm^{-1}. The samples were analyzed using the Thermo Scientific K-Alpha X-ray photoelectron spectrometer (Thermo Scientific, UK). The samples were mounted onto conductive tape and attached to a standard K-Alpha sample holder prior to introduction into the instrument. The XPS peaks for C1s and O1s were fitted to deconvolve the chemical states. A Shirley background was subtracted and peaks were fitted using Gaussian–Lorentzian shapes, where the Gaussian and Lorentzian functions were convolved to give the final peak envelope. Peaks were fitted using Thermo Scientific Avantage software. Photoluminescence (PL) spectra were measured by using RF-5301) fluorescence spectrophotometer with scan range from 220 to 900 nm and excitation wavelength at 280 nm. GO, 1 wt% TiO_2–GO, 10 wt% TiO_2–GO composites were dispersed in DI water for PL test.

2.4. Photocatalytic activity tests

The photocatalytic tests were performed in an aqueous solution using methylene blue (MB) (Aldrich, $\lambda_{max} = 664$ nm) as the probe molecule. A quartz photoreactor was filled with 200 cm^3