Journal of Industrial and Engineering Chemistry 36 (2016) 184–193

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Enhanced visible light photocatalytic activities of template free mesoporous nitrogen doped reduced graphene oxide/titania composite catalysts

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ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form 29 January 2016
Accepted 31 January 2016
Available online 8 February 2016

Keywords:
Nitrogen doped TiO_2
Reduced graphene oxide
Visible light irradiation
Photocatalyst
Mesoporous catalyst

ABSTRACT

We report a new photocatalytic material to address the twin issues namely recombination of electron/hole pairs and visible light inactivity of the titania based photocatalysts. A template free hydrothermal method was adapted to synthesize mesoporous nitrogen doped reduced graphene oxide/titania composite catalysts (N-[x% rGO-TiO_2] where x = 2.5, 5, 7.5 and 10%). The detailed physicochemical studies of the catalysts were done and correlated with their photocatalytic activities. Simultaneous nitrogen doping on both reduced graphene oxide and titania was confirmed by X-ray photoelectron spectroscopy (XPS). The photocatalytic activities of the synthesized composite catalysts were evaluated towards the photodegradation of organic dyes namely methylene blue and congo red under visible light irradiation. Among them, the composite N-[5% rGO/TiO_2] showed the highest photocatalytic activity. Doping of nitrogen makes graphene a better charge transporter whereas nitrogen in TiO_2 lattice makes it visible light active (red shift).

Introduction

The untreated effluents from textile industries cause a great damage to the environment [1,2]. Although several methods such as coagulation, flocculation and aerobic processes were reported to mitigate the problem of pollution, they have inherent limitations [3–7]. However, advanced oxidation processes (AOP) involving semiconductor oxides hold great promise in the purification of polluted water resources [8]. The best studied semiconductor for the detoxification work is titania due to its excellent activity, stability against corrosion, non-toxicity and low cost [9–12]. Unfortunately, TiO_2 is a wide band gap semiconductor (E_g = 3.2 eV) and hence only active under UV light (<400 nm) [13–15]. The use of UV light makes TiO_2 based photocatalytic technology an expensive affair. Despite several efforts, the development of a cheap, highly active and visible light driven photocatalyst still remains a great challenge for the researchers all over the world. Several strategies such as doping, impregnation or anchoring metals or non-metals in to the crystal lattice of TiO_2 were reported for the synthesis of visible light active photocatalysts [16–21]. The present authors also adapted such strategies and obtained good photocatalytic activity and they attributed the photocatalytic activity in the visible region to the prevention of recombination of the excitons by the doped metals (e^- traps) and reduction of the band gap [22–25].

Carbon-titania composite photocatalysts have received great attention due to their considerable efficiency for separating electron–hole pairs. Among the various carbon materials, graphene is an attractive and significant material owing to its two-dimensional nanostructure with remarkable properties specifically, excellent mobility of charge carriers, and large specific surface area. The sp^2 hybridized carbon honey comb structure with delocalized π electron clouds make graphene an excellent support for visible light photocatalysis [26–30]. Due to its outstanding features of graphene, recently numerous efforts have been paid to combine graphene with semiconductor photocatalysts to enhance the catalytic performance [31–35]. Additionally, doping of nitrogen into graphene increases the transfer rate of electron from the conduction band of the semiconductor whereas, the doping of nitrogen into titania creates an additional donor level above the valence band of titania thereby reducing the energy requirement for the excitation of electron from valance band (VB) to conduction band (CB) of titania.

In the present investigation, we have successfully demonstrated the synthesis of mesoporous nitrogen doped reduced graphene

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http://dx.doi.org/10.1016/j.jiec.2016.01.042
1226-086X/

oxide-TiO_2 catalyst via a simple one-step hydrothermal method for the first time. Here, a simultaneous doping of nitrogen on reduced graphene oxide and TiO_2 lattice, and reduction of graphene oxide also achieved through single step. To the best of our knowledge, there is no report found in literature using this procedure or method. The effect of nitrogen doping on the photocatalytic activity was investigated by degradation of industrial dyes namely methylene blue (MB) and congo red (CR) under the visible-light illumination. 5% rGO/TiO_2 composite with nitrogen doping showed the highest photocatalytic activity.

Experimental

Materials

Titanium isopropoxide (TIP) from Spectrachem, graphite flakes from Alfa Aesar, methylene blue and congo red from S.D. fine chemicals, sodium nitrate, potassium permanganate, hydrogen peroxide, concentrated sulfuric acid and urea from Merck were obtained. All the chemicals and reagents used in this experiment were of analytical grade and used without any further purification. Millipore water was used for the entire study.

Synthesis of graphene oxide

Graphene oxide (GO) was prepared by modified Hummer's method [36]. 1 g of graphite flakes, 0.5 g of $NaNO_3$ and 23 mL of conc. H_2SO_4 were added into a 250 mL three necked round-bottom (RB) flask, stirred at room temperature for 1 h and kept in an ice bath. To this mixture 3 g of $KMnO_4$ was added slowly over a period of 1 h and stirred vigorously. Ice bath was removed and stirred further for 4 h. Then the mixture temperature was raised to 35 °C using water bath and stirred for another half an hour. The suspension was poured into 250 mL of deionized water and heated to 70 °C. Then the suspension was allowed to stir for 15 min. The unreacted compounds were removed by the addition of 30% hydrogen peroxide solution. The graphene oxide was obtained through repeated centrifugation and washing with 5% HCl solution. Finally, the slurry was dried in a vacuum oven at 70 °C overnight.

Synthesis of nitrogen doped rGO-TiO_2 composites

In a typical synthesis, 10 mL of titanium isopropoxide and 30 mL of ethanol were taken in a beaker and stirred for 30 min. To this dispersion, required amounts of GO (with respect to Ti amount) dispersed in ethanol were added to synthesize 2.5, 5, 7.5, 10% rGO-TiO_2 composite catalysts. For nitrogen doping, all the above solutions were mixed with 20 mL aqueous solution containing 5 g urea and stirred vigorously for 2 h. Then the mixture was transferred into a 100 mL autoclave kept at 180 °C for 24 h and allowed to cool to attain room temperature. The grey coloured mass was rinsed with water followed by ethanol and dried at 60 °C in a hot air oven. Finally, the mass was annealed at 400 °C under nitrogen atmosphere for 2 h. For comparison, N-TiO_2 and 5% rGO-TiO_2 were also synthesized by adopting the same procedure without adding GO and urea, respectively.

Characterization of catalysts

Phase purity and crystallinity of the catalysts were investigated by powder X-ray diffraction (XRD) on a Rigaku diffractometer using Cu Kα radiation. Raman spectra were recorded using Raman spectrometer (WITec alpha 300) with an excitation source of Nd:YAG laser (532 nm). Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer IR spectrophotometer in the range of 400–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was obtained from ESCALAB 250, Thermo Scientific Ltd. Scanning electron microscope (SEM) images and energy dispersive spectrum (EDS) were obtained using a Hitachi SU-4800 SEM instruments. High resolution transmission electron microscope (HR-TEM) analysis was performed by a JEOL JEM-2100F field emission electron microscope operated at an acceleration voltage of 200 kV. N_2 adsorption–desorption isotherms were constructed using Belsorb mini (BEL-Japan). UV–vis diffuse reflectance spectra (DRS-UV-vis) were recorded using Jasco V650 Spectrophotometer with $BaSO_4$ as reference. Electrochemical measurements were carried out on a CHI VMP3B-20 electrochemical workstation (Biologic Science Inst.) using standard three-electrode system (a working electrode, a platinum wire as a counter electrode and a standard Ag/AgCl in saturated KCl as reference electrode). Coating method was adopted for the preparation of working electrode. The mixture of active material and binder were taken in 9:1 weight ratio. In this method, 25 mg of catalyst was dispersed in 0.3 mL of n-butyl carbitol and 0.166 mL of teflon to prepare a slurry which was then brush coated on to a 2 cm × 1.5 cm GDL carbon paper MGL 370 (10% PTFE coated). The coated carbon papers were dried at room temperature and sintered at 400 °C for 1 h to maintain uniform thickness of the coating between 0.5 and 1 mm. The electrochemical impedance measurements were recorded with open circuit potential. The amplitude of the sinusoidal wave was 10 mV, frequency was ranged from 1 MHz to 100 MHz and the electrolyte was 0.5% H_2SO_4. Inert atmosphere was maintained by purging nitrogen gas into the electrolyte before and during the measurements.

Photocatalytic activity tests

The photocatalytic activities were evaluated towards the photodegradation of two different dyes namely methylene blue (MB) and congo red (CR). A 350 W tungsten lamp was used as visible light source. 50 mg of catalyst was suspended in 100 mL of aqueous dye (3.12×10^{-5} M) and was stirred for 30 min to reach adsorption–desorption equilibrium under dark conditions. During photodegradation, 2 mL of reaction solution was withdrawn at definite time intervals and analyzed using UV–vis spectrophotometer. The photocatalytic reaction temperature was controlled by an external cooling system.

Results and discussion

XRD analysis

XRD patterns of pure GO, N-TiO_2, 5% rGO-TiO_2 and nitrogen doped rGO-TiO_2 composite catalysts are shown in Fig. 1. The characteristic peak located at $2\theta = 10.5°$ in the GO pattern, assigned to the characteristic (002) plane of GO. The absence of peak at $2\theta = 10.5°$ for 5% rGO-TiO_2 and nitrogen doped rGO-TiO_2 composite catalysts confirms that the graphene oxide (GO) was completely reduced and no separate peaks for reduced graphene oxide were detected [37,38]. In all the titania based catalysts, the observed peaks at $2\theta = 25.6°$, 38.8°, 48.1°, 53.9°, 55.0°, 62.8°, 69.4°, 70.5° and 75.1° can be indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes, respectively. The obtained peaks were exactly matched with pure anatase phase of TiO_2 (JCPDS card No: 73-1764). Sharpness of all the peaks indicates that TiO_2 is highly crystalline.

The average crystalline size was determined using Scherrer's equation and given in Table 1

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$