Materials Chemistry and Physics xxx (2015) 1–6

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

# Preparation of three dimensional graphene foam–$WO_3$ nanocomposite with enhanced visible light photocatalytic activity

R. Azimirad*, S. Safa

*Malek-Ashtar University of Technology, Tehran, Iran*

## HIGHLIGHTS

- 3D GF synthesized by CVD on a nickel foam as a highly porous conductive substrate.
- $WO_3$ nanoparticles coated on 3D GF by dip-coating.
- 3D GF–$WO_3$ shows an excellent photocatalytic degradation of Rhodamine B dye.
- Better photocatalytic properties assigned to the formation of W–C and W–O–C bonds.

## ARTICLE INFO

*Article history:*
Received 25 March 2015
Received in revised form
15 June 2015
Accepted 20 June 2015
Available online xxx

*Keywords:*
Composite materials
Nanostructures
Oxides
Semiconductors

## ABSTRACT

Three dimensional graphene foam (3D GF) was synthesized by chemical vapor deposition (CVD) on a nickel foam skeleton. After dissolving the nickel foam, the obtaining 3D GF was used as a highly porous conductive substrate for nucleation and growth of $WO_3$ particles. Scanning electron microscopy (SEM) and Raman spectroscopy was employed to ensure the quality of the prepared GFs and to judge about the 3D GF–$WO_3$ chemical structure. The $WO_3$ characteristic Raman peaks centered at 726, and 809 $cm^{-1}$ are slightly broadened and displaced to lower wavelength in the 3D GF–$WO_3$ nanocomposite, as compared to the corresponding peaks of the bare tungsten oxide. This phenomenon confirms the formation of W–C and W–O–C bonds in composite material which is important for faster transferring the photoexcited electrons to graphene 3D network as an exceptional electron acceptor. The 3D GF–$WO_3$ composite material was applied in photocatalytic degradation of Rhodamine B dye. It was observed that the annealed samples show an excellent photocatalytic performance relative to the as-prepared 3D GF–$WO_3$ samples and bare $WO_3$, which is ascribed to the lower electron/hole recombination through the formation of W–C and W–O–C bonds.

## 1. Introduction

Graphene (as a two dimensional sheet of sp2-hybridized carbon atoms arranged into a honeycomb lattice) with its extraordinary physical properties such as high electron mobility [1,2], superior thermal conductivity [3], high optical transparency [4] and extreme mechanical properties [5] has motivated enormous research efforts. Up to now, application of graphene and its derivatives have been investigated in many areas of technology [6–11]. For instance, the improvement in photocatalytic properties of semiconductor photocatalysts by graphene have been frequently reported [12–17]. In fact, graphene sheets with electron mobility exceeding ~15,000 $m^2\ V^{-1}\ s^{-1}$ at room temperature [18,19], and extremely high specific surface area (~2600 $m^2/g$) [20] can act as an excellent electron acceptor, and improve the lifetime and transfer of photogenerated charge carriers [21,22]. They can also increase the adsorption capacity for the reactants [23,24].

$TiO_2$ and ZnO are the most widely studied photocatalysts, which graphene is able to improve their photocatalytic properties [25–30]. They have large band gaps and need UV irradiation, while only 4–5% of solar spectrum lies in the UV region [31]. Graphene is also able to improve the photocatalytic performance of the tungsten oxide as a visible light driven photocatalyst but with lower photocatalytic activity than $TiO_2$ and ZnO. O. Akhavan et. al. have applied a Graphene–tungsten oxide composite thin films in photoinactivation of bacteriophage MS2 viruses under visible light irradiation, and reported an excellent visible light photocatalytic

---

* Corresponding author.
*E-mail address:* azimirad@yahoo.com (R. Azimirad).

http://dx.doi.org/10.1016/j.matchemphys.2015.06.043

Please cite this article in press as: R. Azimirad, S. Safa, Preparation of three dimensional graphene foam–$WO_3$ nanocomposite with enhanced visible light photocatalytic activity, Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.06.043

performance, as compared to bare tungsten oxide [32]. B. Weng et al. reported that, as compared to $WO_3$ nanorods, poly-(ethylenimine)–graphene–$WO_3$ nanorods with an appropriate addition ratio of graphene exhibit remarkably enhanced visible-light photoactivity toward the degradation of Rhodamine B [24]. H. Huang et al. investigated the photocatalytic activity of a composite of high-ordered mesoporous $WO_3$ and reduced graphene oxide [33]. There are few other reports on the photocatalysis using graphene–tungsten oxide composites [34–37]. However, all of these studies have used chemically derived graphene sheets, which due to the abundant existence of defects and oxygen-containing chemical groups show low conductivity. Moreover the chemically derived graphene sheets are not connected and do not comprise a monolithic structure.

Herein, we used graphene foam (GF), an interconnected three dimensional high quality robust structure of graphene sheets with very low density, high electrical conductivity and high accessible surface area (up to 850 $m^2\ g^{-1}$) [38], as a substrate for nucleation and growth of the tungsten oxide particles. The defect-free CVD-grown graphene and absence of inter-sheet junction-resistance in 3D GF can provide a highly conductive network. In addition, the porous nature and large specific surface area of this structure will increase the active sites for the photocatalytic reaction. The 3D GF–$WO_3$ nanocomposite was formed through the heat treatment of the as-prepared samples at 450 °C. To evaluate the photocatalytic activity of the 3D GF–$WO_3$ nanocomposites, degradation of Rhodamine B (as a well-known model contaminant) under visible light irradiation was examined. Decrease in the photocatalytic activity of the 3D GF–$WO_3$ nanocomposites after a long time utilization in the photocatalytic reaction, was also investigated. Finally, the reasons for the better photocatalytic activity of the annealed 3D GF–$WO_3$ composite compared to as prepared 3D GF–$WO_3$ and bare $WO_3$ have been discussed thoroughly.

## 2. Experimental details

### 2.1. Preparation of $WO_3$ nanoparticles on 3D graphene foam

The fabrication of the GF–$WO_3$ nanocomposites consists of two steps; preparation of the GFs and fastening of $WO_3$ nanoparticles on it.

### 2.1.1. CVD growth of the 3D graphene foam

The 3D graphene foams were grown by chemical vapor deposition method in a quartz tube with inner diameter of 22 mm, using the nickel foam as catalytic skeleton, as previously described elsewhere [38–41]. In a typical run, nickel foam (1.2 mm in thickness) were cut into 20 × 20 $mm^2$ pieces and heated to 1000 °C under Ar (500 sccm) and $H_2$ (200 sccm) flow in the quartz tube at ambient pressure. The samples were kept for 5 min in above condition to clean the nickel surfaces and afterwards, 7 sccm $CH_4$ (as the source of graphene) was charged to the mixed gas flow. After another 5 min, the $CH_4$ flow was stopped and the samples were cooled to room temperature at a rate of 100 °C $min^{-1}$ under Ar and $H_2$ flow. Finally the nickel substrates were etched away with a 3 M HCl solution at 70 °C for 6 h.

### 2.1.2. Synthesis of $WO_3$ sol

To synthesize peroxopolytungstic acid (PTA), 5 g tungsten wire (with purity of >99.9%) was cut down to small pieces and reacted with 20 ml hydrogen peroxide (30%). The mixture was stirred at room temperature until tungsten pieces was completely dissolved (~48 h), yielding a transparent colorless solution. Then 20 ml ethanol was added to the solution. To remove the excess $H_2O_2$, the obtained solution was heated at 60 °C for about 15 min, resulting to a transparent yellow-color solution.

The GF–$WO_3$ nanocomposite was provided through dip-coating of GF pieces (1 cm × 1 cm) with the peroxopolytungstic acid solution, for three times. After each dip-coating the sample was dried at 80 °C for 15 min. In this way, the weight ratio of graphene to tungsten oxide in the resulting samples was about 6%. Finally, the as-deposited samples were also annealed at 450 °C in air for 30 min. The same procedure was also carried out to prepare bare $WO_3$ onto glass substrates.

### 2.2. Photocatalyst test

The photocatalytic activity experiments on the prepared samples were studied by examining the photodegradation reaction of Rhodamine B as an organic pollutant. In each run, a 1 cm × 1 cm film of GF–$WO_3$ nanocomposite, $WO_3$ on the glass substrate, or freestanding GF was immersed in 40 ml of aqueous solution of Rhodamine B (0.1 mg $ml^{-1}$). After 30 min keeping the solution in dark in order to reach the adsorption–desorption equilibrium, it was irradiated by a 400 W Xenon lamp with a $\lambda < 400$ nm cut-off filter. At given time intervals (20 min), 3 mL of the sample was drawn from the reaction system and taken to a UV–visible spectrophotometer to measure the absorption spectrum, which is proportional to the concentration of Rhodamine B according to Beer's law. During the reaction, a water-cooling system was used to maintain the solution at room temperature.

### 2.3. Material characterization

The surface morphology of the samples was depicted using SE-4160 Hitachi scanning electron microscope (SEM) at an accelerating voltage of 15–30 kV. The SEM samples had been coated by gold thin film by desktop sputtering (Nanostructured Coating Co., Iran). Chemical composition of the GF samples were determined by Energy-dispersive X-ray analysis (EDX) in a TESCAN VEGA scanning electron microscope. Raman Spectroscopy was used to analyze the quality of the 3D GF samples. Raman spectra were measured by SENTERRA (BRUKER) Dispersive Raman Microscope with laser wavenumber at 785 nm of high-energy laser diodes as the excitation source.

## 3. Results and discussion

The structure and morphology of Ni foam (Fig. 1a) and GF after nickel etching (Fig. 1b) were studied by scanning electron microscopy. SEM images revealed a continuous three-dimensional structure, which copied and inherited the interconnected, highly porous 3D structure of the nickel foam template. High magnification SEM image (Fig. 1c) shows that a thin continuous layer of carbon atoms has covered the whole surface of nickel foam, which includes many micro and nano ripples and wrinkles. These ripples and wrinkles are probably formed in the fast cooling stage due to the different thermal expansion coefficients of nickel and graphene. The 3D highly porous structure of GF provides a large accessible surface area, which can be used as binding sites for $WO_3$ nanoparticles. Fig. 1d shows that the $WO_3$ nanoparticles are uniformly grown on the surface of the 3D GF. The higher magnification of the SEM image of the GF–$WO_3$ composite shown in the inset of the Fig. 4d reveals that the size of $WO_3$ particles is about ~160–180 nm in diameter.

EDX analysis was employed to confirm that the nickel foam substrate was completely removed after etching process. Fig. 2 shows EDX spectrum of a typical GF. The inset table in the figure represents the percentage of the various elements. The EDX data show that a very small amount of nickel is detectable in the GFs.

Please cite this article in press as: R. Azimirad, S. Safa, Preparation of three dimensional graphene foam–$WO_3$ nanocomposite with enhanced visible light photocatalytic activity, Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.06.043