Applied Catalysis B: Environmental 130–131 (2013) 270–276

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

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

# One-pot synthesis of gold nanoparticle/molybdenum cluster/graphene oxide nanocomposite and its photocatalytic activity

Alexandre Barras[a], Manash R. Das[b], Rami Reddy Devarapalli[c], Manjusha V. Shelke[c], Stéphane Cordier[d], Sabine Szunerits[a], Rabah Boukherroub[a,*]

[a] Institut de Recherche Interdisciplinaire (IRI, USR CNRS 3078), Université Lille 1, Parc de la Haute Borne, 50 Avenue de Halley, BP 70478, 59658 Villeneuve d'Ascq, France
[b] Materials Science Division, CSIR-North East Institute of Science and Technology, Jorhat 785 006, Assam, India
[c] Physical and Materials Chemsitry Division, CSIR-National Chemical Laboratory, Pune 411 008, India
[d] Université de Rennes 1, Institut Sciences Chimiques de Rennes, UR1-CNRS 6226, Equipe Chimie du Solide et Matériaux, Campus de Beaulieu, CS 74205, 35042 Rennes Cedex, France

ARTICLE INFO

*Article history:*
Received 24 July 2012
Received in revised form 9 November 2012
Accepted 12 November 2012
Available online 24 November 2012

*Keywords:*
$[Mo_6Br_8(N_3)_6]^{2-}$ cluster
Graphene oxide
Gold nanoparticles
Nanohybrid
Rhodamine B
Photodegradation
Visible light

ABSTRACT

The paper reports on a facile one-pot synthesis of a tri-component gold nanoparticle/molybdenum cluster/graphene oxide (AuNPs@Mo–GO) nanohybrid composite. The synthetic methodology consists on direct UV irradiation of an aqueous solution containing graphene oxide (GO), $Na_2[Mo_6Br_8(N_3)_6]$, $HAuCl_4\cdot 3H_2O$ and isopropanol at room temperature in air using a UV fiber lamp. The composite material exhibits very high photocatalytic activity for the degradation of rhodamine B under visible light irradation. The resulting nanohybrid material was characterized using Raman spectroscopy, UV–vis spectrometry, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

## 1. Introduction

The use of synthetic dyes in many fields of applications such as textiles, papers, leathers, additives, food and cosmetics is continuously increasing. Due to their extensive applications, large-scale production and chemical stability, these pollutants can cause significant environmental pollution [1].

A wide range of methods such as photocatalysis have been developed and extensively studied for the removal of hazardous chemical compounds from water wastes to decrease their impact on the environment. Even though much work in heterogeneous photocatalysis has been focused on semiconductor materials such as $TiO_2$, ZnO, $Fe_2O_3$, $WO_3$, $Ta_2O_5$, ZnS and CdS, these materials often display large bandgaps, which require UV light irradiation and thus limiting the efficient utilization of solar energy [2].

Recently, we have demonstrated the high photocatalytic performance of the molybdenum cluster compound, $Na_2[Mo_6Br_8(N_3)_6]$, for the degradation of organic pollutants under visible and solar light irradiation [3]. Molybdenum atom octahedral clusters are nanosized molecular units that exhibit a large absorption window from UV to visible and a large emission window from red to infrared due to the delocalization of valence electrons on all metal centers [4–6].

Graphene oxide (GO), obtained by chemical treatment of graphite powder with strong chemical oxidants, has found widespread applications in various fields [7–9]. In the last years, there has been a huge interest in the literature to integrate metal nanoparticles onto GO and reduced graphene oxide (rGO) surfaces for the preparation of graphene-based nanohybrid materials [10]. The resulting nanocomposites have shown excellent properties and improved functionalities due to the synergetic effects between GO and the inorganic components. For example, Zhang et al. [11] reported that GO can be reduced via a direct redox reaction in the presence of $Sn^{2+}$ and $Ti^{3+}$ cations to form rGO–$SnO_2$ and rGO–$TiO_2$ composites with a good photocatalytic performance for the degradation of rhodamine B under visible light irradiation. Xiong et al. [12] demonstrated that rGO-gold nanocomposites displayed an excellent visible-light photocatalytic activity for the degradation of rhodamine in water.

The aim of the present work is to take advantage of the exceptional properties of GO and the excellent photocatalytic performance of $Na_2[Mo_6Br_8(N_3)_6]$ for the preparation of a new class of composite materials. Herein, we report on a simple and facile synthetic methodology for the preparation of a tri-component

---

[*] Corresponding author. Tel.: +33 3 62 53 17 24; fax: +33 3 62 53 17 01.
*E-mail address:* rabah.boukherroub@iri.univ-lille1.fr (R. Boukherroub).

0926-3373/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2012.11.017

AuNPs@Mo–GO nanohybrid. In this method, an aqueous solution containing GO, $Na_2[Mo_6Br_8(N_3)_6]$, $HAuCl_4 \cdot 3H_2O$ and isopropanol was irradiated at room temperature in air using a UV fiber lamp. The tri-component material was found to exhibit high photocatalytic activity for the degradation of rhodamine B under visible light irradiation.

## 2. Experimental part

### 2.1. Preparation of $Na_2[Mo_6Br_8(N_3)_6]$

500 mg of $NaN_3$ were introduced in an Schlenk container with 20 mL of methanol at 55 °C. After dissolution of $NaN_3$, 1 g of $MoBr_2$ was added to the solution. After one night of reaction, a clear solution was obtained. After filtration and evaporation of methanol, $Na_2[Mo_6Br_8(N_3)_6]$ was separated from excess of $NaN_3$ and NaBr by 3 successive extractions with dry acetone. Yield: 74%. EDS Na: 12; Mo: 41; Br: 47 (theo: 12.5/37.5/50). The presence of $N_3$ on the cluster was confirmed by IR analysis [13].

### 2.2. Preparation of AuNPs@Mo–GO nanocomposite

GO nanosheets investigated in this work are prepared by the modified Hummer's method from natural graphite powder according to recently published work [14–17].

In a typical procedure, an aqueous solution of GO (600 μL, 1.5 mg mL$^{-1}$), $Na_2[Mo_6Br_8(N_3)_6]$ (600 μL, 1 mM), $HAuCl_4 \cdot 3H_2O$ (600 μL, 1.5 mM), and isopropanol (4 μL) was irradiated at $\lambda = 365$ nm (power intensity = 0.5 W cm$^{-2}$) for 30 min at room temperature in air using a UV fiber lamp (Spot Light Source 300–450 nm, L9588-01, Hamamatsu, Japan). The AuNPs@Mo–GO material was separated from the solution by centrifugation (14 000 rpm for 20 min). The product was washed with water several times and resuspended in water at a concentration of 1 mg mL$^{-1}$.

### 2.3. Photodegradation of RhB under visible light irradiation

The catalytic properties of the AuNPs@Mo–GO nanocomposite have been evaluated for the photocatalytic degradation of rhodamine B (RhB) in an aqueous solution. The photocatalytic degradation reaction was carried out in a 1 cm spectrometric quartz cuvette containing 2 mL of 10 mg L$^{-1}$ or 1 mg L$^{-1}$ of RhB and the photocatalyst at different catalyst/RhB ratios. The RhB aqueous solution was irradiated under visible light irradiation without stirring at room temperature in air through with a cut off filter ($\lambda = 420$ nm, to suppress the light with wavelength shorter than 420 nm) using a visible fiber lamp (Spot Light Source 400–700 nm, L9566-03, Hamamatsu, Japan). The intensity of the light was measured using a PM600TM Laser Fiber Power Meter (Coherent Inc., USA) and was determined as being 0.5 W cm$^{-2}$. The whole quartz cuvette was directly transferred at different irradiation time intervals in a UV–vis spectrophotometer. The concentration of RhB was determined by monitoring the changes in the absorbance maximum at ca. 554 nm.

### 2.4. Instrumentation

#### 2.4.1. UV–vis spectrometry

Absorption spectra were recorded using a Perkin-Elmer Lambda UV-vis 950 spectrophotometer in a spectrometric quartz cuvette with an optical path of 10 mm. The wavelength range was 400–800 nm.

#### 2.4.2. Raman spectroscopy

The sample for the Raman analysis was prepared by dispersing AuNPs@Mo–GO in ethanol by sonication. 50 μL of the sample was drop casted on a cleaned silicon wafer and dried. Raman analyses were performed on an HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) using 632.8 nm green laser (NRS1500 W).

#### 2.4.3. Transmission electron microscopy

High resolution transmission electron microscope (HRTEM) images were taken by using Icon analytical 300 keV microscope.

#### 2.4.4. X-ray photoelectron spectroscopy

The initial GO and AuNPs@Mo–GO were deposited as thin films on clean p-type (1 0 0) silicon wafers by casting 50 μL of the respective suspension and removal of water by drying the substrates on a heating plate at 70 °C in air. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 220 XL spectrometer from Vacuum Generators featuring a monochromatic Al Kα X-ray source (1486.6 eV) and a spherical energy analyzer operated in the CAE (constant analyzer energy) mode (CAE = 100 eV for survey spectra and CAE = 40 eV for high-resolution spectra), using the electromagnetic lens mode. No flood gun source was needed due to the conducting character of the substrates. The angle between the incident X-rays and the analyzer is 58°. The detection angle of the photoelectrons is 30°. Fitting was made using CasaXPS 2.3.16Dev37 software using Gaussian Lorentzian shape GL(30) curves.

## 3. Results and discussion

Fig. 1 displays the strategy for the preparation of AuNPs@Mo–GO nanocomposite. GO nanosheets investigated in this work are prepared by the modified Hummer's method from natural graphite powder [14]. In a typical procedure, an aqueous solution of GO (600 μL, 1.5 mg mL$^{-1}$), $Na_2[Mo_6Br_8(N_3)_6]$ (600 μL, 1 mM), $HAuCl_4 \cdot 3H_2O$ (600 μL, 1.5 mM), and isopropanol (4 μL) was irradiated at $\lambda = 365$ nm (power intensity = 0.5 W cm$^{-2}$) for 30 min at room temperature in air using a UV fiber lamp. The AuNPs@Mo–GO material was separated from the solution by centrifugation (14 000 rpm for 20 min). The product was washed with water several times and resuspended in water at a concentration of 1 mg mL$^{-1}$.

Fig. 2a exhibits UV–vis absorption spectra of the starting GO and AuNPs@Mo–GO nanocomposite. No obvious absorption band in the wavelength range of 400–800 nm can be seen from GO. In contrast, the UV–vis spectrum of the AuNPs@Mo–GO nanocomposite displays an absorption peak at ~540 nm due to the plasmonic band of the Au NPs of 10–20 nm in diameter, suggesting the formation of AuNPs on the surface of GO sheets. Moreover, the initial brown color of the nanocomposite dispersion turned to purple brown during the irradiation process, indicating the formation of AuNPs. Fig. 2b shows the Raman spectrum of the as-synthesized material. The Raman shifts at 1322 cm$^{-1}$ and 1586 cm$^{-1}$ are the characteristic D- and G-bands of the GO, respectively, where the D-band is the breathing mode of κ-point phonons of $A_{1g}$ symmetry due to the local defects and disorder at the edges of the GO and the G-band is due to $E_{2g}$ phonon of sp$^2$ C atoms [18,19]. The Raman shift at 867 cm$^{-1}$ is most likely due to the asymmetric stretching mode of the terminal Mo═O bond [20].

Transmission electron microscopy (TEM) measurements were performed to characterize the morphology of the as-synthesized AuNPs@Mo–GO nanocomposite material. GO displays sheets with chiffon-like wrinkles as shown in Fig. 3a. It clearly shows the presence of spherical AuNPs with a mean diameter of 16 ± 9 nm (see inset, dark particles), and amorphous molybdenum clusters