Materials and Design 109 (2016) 634–643

Contents lists available at ScienceDirect

Materials and Design

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

Hydrothermal preparation of $MoS_2/TiO_2/Si$ nanowires composite with enhanced photocatalytic performance under visible light

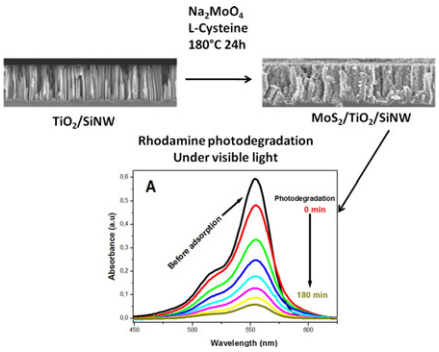
Abderrahmane Hamdi [a,b,c], Luc Boussekey [d], Pascal Roussel [e], Ahmed Addad [f], Hatem Ezzaouia [b,c], Rabah Boukherroub [a], Yannick Coffinier [a,*]

[a] Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, UMR CNRS 8520), Cité Scientifique, Université Lille1, Avenue Poincaré, BP 60069, 59652 Villeneuve d'Ascq, France
[b] Laboratory of Semi-conductors, Nano-structures and Advanced Technologies, Research and Technology Centre of Energy, Borj-Cedria Science and Technology Park, BP 95, 2050 Hammam-Lif, Tunisia
[c] Faculty of Science of Bizerte, University of Carthage, 7021 Zarzouna, Tunisia
[d] Laboratoire de Spectrochimie Infrarouge et Raman, CNRS UMR 8516, Cité Scientifique, Université Lille1, 59655 Villeneuve d'Ascq, France
[e] Unité de Catalyse et Chimie du Solide (UCCS), CNRS UMR 8181, Ecole Nationale Supérieure de Chimie de Lille, Cité Scientifique, Université Lille1, 59652 Villeneuve d'Ascq, France
[f] Unité Matériaux et transformations (UMET), UMR CNRS 8207, Université Lille1, Cité Scientifique, 59655 Villeneuve d'Ascq, France

HIGHLIGHTS

- Silicon nanowires synthesis by metal assisted chemical etching
- Simple method for MoS_2 hydrothermal synthesis and uniform deposition on silicon nanowires
- Composite material for photodegradation of rhodamine B under visible light
- Increase kinetic constant (K_{app}) for rhodamine degradation

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form 29 June 2016
Accepted 19 July 2016
Available online 20 July 2016

Keywords:
Silicon nanowires
Metal-assisted chemical etching
MoS_2
Hydrothermal method
Photocatalysis

ABSTRACT

In this paper, we report on a simple, low cost and environmentally friendly method for the synthesis of 3D hierarchical molybdenum disulfide (MoS_2) nano-sheets on TiO_2 coated Si nanowires (SiNW). The synthetic method has several advantages such as low temperature, short reaction time and does not require any additives or surfactants. Characterization of the obtained composite material was performed by using scanning electron microscopy (SEM), Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) patterns and high resolution transmission electron microscopy (HR-TEM). The photocatalytic activity of the as-prepared MoS_2 nanosheets was investigated for the degradation of Rhodamine B (RhB) under visible light irradiation. We found that $MoS_2/TiO_2/SiNW$ interface exhibited stable and good catalytic activity as compared to other MoS_2-based photocatalytic materials. The photocatalytic mechanism is believed to occur through photocatalytic and photosensitization processes.

* Corresponding author.
E-mail address: yannick.coffinier@univ-lille1.fr (Y. Coffinier).

http://dx.doi.org/10.1016/j.matdes.2016.07.098
0264-1275/

1. Introduction

Molybdenum disulfide (MoS_2), a transition metal dichalcogenide, gained a lot of attention due to its great chemical, electrical and optical properties offering great potential for many applications [1].

Among the various methods existing for the preparation of MoS_2 and MoS_2-based composites, the hydrothermal synthesis is becoming one of the most important and straightforward approach [1,2]. Indeed, many different MoS_2 structures or heterostructures (ZnO, TiO_2) have been obtained *via* this method such as nanospheres, nanoribbons, nanoparticles, nanosheets, nanoflowers, nanoplates, nanowalls, hollow cubic cage, nanopolyhedron [3–9]. The hydrothermal and solvothermal methods consist of mixing different precursors together (*e.g.* sodium molybdate and thiourea) at a certain temperature for a given time.

Nowadays several photocatalysts for the degradation of a wide range of contaminants in water under visible light have been developed. Among them, silicon nanowire (SiNW) substrates decorated or not by metallic or metal oxide particles have been successfully used for the degradation of organic dyes and toxic pollutants thanks to their high surface area, optical and electronic properties, low toxicity, surface tailorability and multifunctionality [10,11]. Recent studies described the use of MoS_2 particles decorating TiO_2 nanobelts or nanotubes, or other composite materials such as $MoS_2/Bi_2O_2CO_3$ and MoS_2/C_3N_4 composites and MoS_2 on Bi_2S_3 discoids [9,12,13] for photocatalytic purposes.

To date, only very limited studies have reported the deposition of MoS_2 on silicon nanowires. For example, Tran et al. reported a novel procedure to decorate SiNW (prepared *via* electroless method) by MoS_2 using a photo-assisted electrodeposition process to obtain SiNW@MoS_2 acting as a photocathode for H_2 generation [14].

In our present work, we report, for the first time, the deposition of MoS_2 sheets on TiO_2 coated SiNW using a simple hydrothermal method. The SiNW were fabricated by metal-assisted chemical etching (MACE) process of crystalline silicon in HF/$AgNO_3$ aqueous solution and then coated with a thin TiO_2 layer by atomic layer deposition. The structure and morphology of the samples were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and UV–vis spectroscopy. Then, we assessed the photocatalytic activity of MoS_2 nanosheets deposited on SiNW covered by TiO_2 layer for the degradation of rhodamine B (RhB) under visible light irradiation.

2. Experimental section

2.1. Materials and methods

Silicon wafers were purchased from Sil'tronix Silicon Technologies (Archamps, France). All cleaning and etching reagents were of VLSI grade. Sulphuric acid, 96% (H_2SO_4) from Technic (France), hydrogen peroxide 30% (H_2O_2) and nitric acid 65% (HNO_3) from Carlo Erba, hydrofluoric acid 50% (HF) was supplied by BASF. All chemicals were of reagent grade or higher and were used as received unless otherwise specified. Silver nitrate ($AgNO_3$), Rhodamine B (RhB), sodium molybdate (Na_2MoO_4), L-cysteine (L-Cys), ammonium oxalate (AO), benzoquinone (BQ), acetone, dichloromethane (CH_2Cl_2), methanol (MeOH), isopropyl alcohol (IPA) and ethanol (EtOH) were purchased from Sigma-Aldrich. Ultrapure water (Milli-Q, 18 MΩ·cm) was used for the preparation of the solutions and for all rinsing steps.

2.2. Preparation of silicon nanowires (SiNW)

The SiNW surfaces were synthesized by chemical etching of *p*-type ⟨100⟩ crystalline silicon wafer (with a resistivity of 0.009–0.010 Ω·cm) in HF/$AgNO_3$ aqueous solution. The silicon surface was first degreased in acetone and isopropyl alcohol, rinsed with MilliQ water, and then cleaned in a piranha solution (3/1 concentrated H_2SO_4/30% H_2O_2) for 20 min at 80 °C, followed by copious rinsing with Milli-Q water. The clean surface was placed in a sealed Teflon beaker containing HF (5 M)/$AgNO_3$ (0.035 M) aqueous solution and heated up to 55 °C for 30 min. The resulting surface was further dipped 3 times in HNO_3 for 5 min at room temperature to remove the electroplated metal. Finally, the surface was rinsed copiously with deionized water and dried under a gentle stream of nitrogen.

2.2.1. Safety considerations

The mixture H_2SO_4/H_2O_2 (piranha) solution is a strong oxidant. It reacts violently with organic materials. It can cause severe skin burns. It must be handled with extreme care in a well-ventilated fume hood while wearing appropriate chemical safety protection.

HF is a hazardous acid which can result in serious tissue damage if burns were not appropriately treated. Etching of silicon should be performed in a well-ventilated fume hood with appropriate safety considerations: face shield and double layered nitrile gloves.

2.3. Preparation of TiO_2/SiNW

TiO_2 films were deposited by atomic layer deposition (ALD). ALD allows the production of conformal coatings on substrates even on 1D objet such as SiNW. TiO_2 was deposited from $TiCl_4$ as the titanium source and H_2O vapor as the oxygen source. Nitrogen gas was used as the purge gas and the chamber temperature and pressure were 260 °C and 2.8 mbars, respectively. $TiCl_4$ and H_2O pulse durations were 250 ms for both precursors separated by 2 s of N_2 purge. Several thicknesses of TiO_2 were deposited: 5, 10, 20 and 30 nm by controlling the number of cycles.

2.4. Deposition of MoS_2 on TiO_2/SiNW

For the synthesis of molybdenum disulfide nanosheets, 0.035 g of sodium molybdate (Na_2MoO_4) and 0.07 g of L-cysteine ($C_3H_7NO_2S$) were used as Mo and S sources, respectively, and were dissolved together in 50 mL of deionized (DI) water at room temperature. After that, the mixture was ultra-sonicated for 15 min until a homogeneous solution was obtained. After sonication, 0.1 M of HCl was added to the mixture to acidify the solution, and then was transferred in a Teflon-lined stainless steel autoclave (100 mL) and heated-up at 180 °C in an electric oven. The duration of the hydrothermal reaction was varied from 3 to 24 h. Finally, the mixture was allowed to cool-down and the substrate was thoroughly washed several times with water and dried at 55 °C for 10 h in an oven.

2.5. Characterization

2.5.1. Scanning electron microscopy (SEM)

SEM images were obtained using an electron microscope ULTRA 55 (Zeiss) equipped with a thermal field emission emitter, three different detectors (EsB detector with filter grid, high efficiency In-lens SE detector, Everhart-Thornley Secondary Electron Detector) and an energy dispersive X-ray analysis device (EDX analysis).

2.5.2. Reflectivity measurements

The reflectance measurements were performed using a UV–vis spectrophotometer (Perkin-Elmer Lambda UV/vis 950 spectrophotometer) equipped with an integrating sphere. The scans were measured for wavelengths ranging from 250 to 800 nm at an incident light angle of 45° and at different locations on each scanned surface.

2.5.3. X-ray photoelectron spectroscopy (XPS)

For X-ray photoelectron spectroscopy (XPS) measurements (Type 5600, Physical Electronics Inc., Chanhassen, MN, USA), we used a monochromatic Al Kα X-ray source and an analyzer pass energy of 12 eV.