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Gold nanoparticles coated silicon nanowires for efficient catalytic and photocatalytic applications

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ABSTRACT

This work is focused on the elaboration of gold (Au) nanoparticles supported silicon nanowires (SiNWs) for catalytic and photocatalytic applications. The SiNWs investigated in this study are synthesized by metal-assisted chemical etching technique, while the gold nanoparticles (AuNPs) are loaded on SiNWs through the redox reaction between $HAuCl_4$ and HF-treated SiNWs. Scanning electron microscopy (SEM), energy dispersive X-ray (EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), and photoelectron spectroscopy (XPS) were used to characterize the morphology, composition and chemical states of the fabricated samples. The catalytic activity of the SiNWs loaded with AuNPs was investigated for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with sodium borohydride ($NaBH_4$). The photocatalytic activity of SiNWs-AuNPs under visible light irradiation was assessed using Rhodamine B (RhB) as a representative organic dye. The course of the above reactions was monitored by UV–vis spectrophotometry. Our results showed that the SiNWs-AuNPs samples could catalyze the reduction of 4-NP and degradation of RhB with excellent efficiency and stability.

1. Introduction

During recent years, metal nanoparticles (MNPs) have been intensively used in various fields thanks to their unique properties in various fields [1,2]. The range of applications for MNPs is increasing widely and involves various catalytic processes and photocatalytic elimination of environmental pollutants [3–6].

In this regard, multifunctional MNPs-support systems with good stability and high efficiency are extensively desirable. Until now, various supports have been used for MNPs including silicon nanowires (SiNWs). SiNWs based supports are used as host matrices to load and disperse MNPs having catalytic and photocatalytic applications [7–9]. The developed SiNWs-MNPs exhibited remarkable properties such as efficient low cost, high surface area and good catalytic [10]. Several techniques and methods have been adopted to produce homogenous SiNWs such as stain etching, thermal evaporation, laser ablation, and metal-assisted chemical etching (MACE) [11].

SiNWs decorated with MNPs (Pt, Ag, Cu, Ni, Au…) [12,13] are widely studied and the resulting materials have been investigated to elaborate composite materials with enhanced sensing performance or for heterogeneous catalysis studies [10,14–16]. Of all of these MNPs, gold nanoparticles (AuNPs) coated silicon nanowires (SiNWs-AuNPs) have proved to be effective nanocomposite materials for catalysis applications [17,18]. The catalytic performance of synthesized SiNWs-AuNPs has been assessed for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with sodium borohydride ($NaBH_4$) at ambient temperature. The degradation reaction of 4-NP to 4-AP represents an important chemical transformation, because nitrophenols are considered as the principal toxic pollutants (announced by U.S Environmental Protection) and are widely used in the production of pesticides and dyes [19–21]. In contrast, the reduced product, 4-AP, is in great demand for the fabrication of pharmaceutical products like paracetamol and analgesics [22,23]. Many Au nanoparticles supported on various catalysts have been used for the reduction reaction of 4-nitrophenol with $NaBH_4$. Indeed, Hanani et al. [24] investigated the performance of Au NPs supported on titania for the reduction of *p*-

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nitrophenol and found that the catalytic activity is largely influenced by the size of the Au NPs: the smaller the better. In fact, the smaller Au NPs can easily aggregate and hence result in a considerable increase in catalytic activity. However, the results of Huan et al. [25] demonstrated that small gold nanoparticles (Au NPs) on mesoporous SiO_2 supported reducible oxides like Fe_3O_4 are more effective catalysts for the degradation of *p*-nitrophenol with $NaBH_4$. Independently, Bhowmk et al. showed that ultra-small gold nanoparticles supported on carbon nitride exhibit high catalytic activity for the reduction of nitrophenol [26].

Currently, several photocatalysts have been studied for the degradation of toxic pollutants using visible or UV light irradiation. Among them, SiNWs decorated with MNPs, such as Ag, Cu, Pd, Pt, and Au have been investigated for the decomposition of organic dyes [17,27]. For instance, Brahiti et al. [17] synthesized SiNWs decorated with gold nanoparticles and examined their activity for the photodegradation of methylene blue (MB). They have concluded that increasing the metal nanoparticles deposition time led to a significant enhancement of the photodegradation activity of methylene blue under UV light irradiation. Megouda et al. [27] reported on the high performance of hydrogen-terminated (H-SiNWs) and SiNWs decorated with metal (Ag and Cu) nanostructures for the photodegradation of Rhodamine B (RhB) under UV and visible light irradiation. The results showed that H-SiNWs photocatalysts exhibited high catalytic activity of RhB under UV or visible light irradiation, and decoration of SiNWs with Cu NPs enhanced considerably their photocatalytic activity for the same photocatalytic process. Recently, Bhowmk et al. [26] demonstrated that carbon nitride modified with ultra-small Au nanoparticles could degrade many organic dyes under UV, visible or sunlight irradiation such as MB, RhB, and methyl orange (MR).

We report herein on the fabrication of silicon nanowires capped with gold nanoparticles (SiNWs-AuNPs) substrates and evaluation of their catalytic and photocatalytic activities. The SiNWs investigated in this study were obtained by using the well-known metal-assisted chemical etching (MACE) technique, while Au NPs deposition was achieved using electroless deposition. The catalytic performance of SiNWs-AuNPs was assessed for the reduction of 4-NP with $NaBH_4$ to produce 4-AP, while the photocatalytic activity was investigated by conducting RhB decomposition using visible light irradiation. Possible mechanisms describing the enhanced catalytic and photocatalytic reactions are discussed briefly. The improvement of these reactions could be easily monitored by UV–vis absorption spectroscopy. Our results show that the gold nanoparticles supported on silicon nanowires can be used as an effective photocatalyst for the photodegradation of RhB under visible light irradiation, and for the catalytic reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$.

2. Experimental section

2.1. Materials

Silicon wafers were purchased from Siltronics. All cleaning and etching reagents were of VLSI grade. Hydrofluoric acid 48% (HF) was supplied by Amplex. All chemicals and reagents used for experiments and analyses were of analytical grade. Chloroauric acid ($HAuCl_4$), acetone, 4-nitrophenol, sodium borohydride ($NaBH_4$) and Rhodamine B were purchased from Sigma-Aldrich. Milli-Q water (18 MΩ) was used for all experiments.

2.2. Sample preparation

2.2.1. Preparation of silicon nanowires (SiNWs) substrates

In the present study, the investigated SiNWs were synthesized following the procedure reported in [14]. Double side polished (100) oriented p-type silicon wafers (boron-doped, 1–10 $\Omega\,cm^{-1}$ resistivity) were sequentially cleaned in acetone, isopropanol and deionized water in an ultrasonic bath. The clean surface was first hydrogenated by immersion in 5% HF aqueous solution for 3 min at room temperature. The hydrogenated sample was then 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 rinsed with deionized water and then dipped three times in nitric acid (HNO_3) for 5 min at room temperature to remove the silver nanoparticles and dendrites deposited on the silicon nanowires during the chemical etching.

2.2.2. Preparation of SiNWs decorated with gold nanoparticles (SiNWs–AuNPs)

Gold nanoparticles deposition was carried out by immersion of the SiNWs substrate into an aqueous solution of $HAuCl_4$ (0.001 M)/HF (0.15 M) for 4 min at room temperature. The resulting interface was rinsed with water and dried under a gentle stream of nitrogen.

2.2.3. Catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP)

The catalytic application of our elaborated samples was evaluated for the catalytic reduction of 4-nitrophenol to 4-aminophenol. Briefly, the SiNWs-based catalyst was dipped into 3 mL of freshly prepared aqueous solution of 4-NP (0.1 mM) and 300 µL of $NaBH_4$ (0.1 M). The progress of the catalytic reaction was monitored by UV–vis spectroscopy through the decrease of the absorption band of 4-NP at 398 nm and the increase in absorption band of 4-AP at 298 nm.

2.2.4. Photocatalytic reduction of Rhodamine B (RhB)

For the photocatalytic degradation experiments, the SiNWs-AuNPs sample was placed into a quartz cuvette containing 3 mL aqueous solution of RhB with an initial concentration of 5×10^{-6} M. Before irradiation and in order to complete the dye adsorption, the cuvette was covered with aluminum paper and kept for 10 min in the dark. Then, the aluminum is removed and the whole cuvette was irradiated by visible-light lamp ($\lambda > 420$ nm, power = 1 W), in the presence of SiNWs-AuNPs, for 240 min. The measurement of the absorbance is performed each 30 min of irradiation. The photocatalytic conversion was investigated by the decrease in absorption band of the RhB dye located at 553 nm as a function of time.

2.3. Sample characterization

The structural characterization of the prepared samples was recorded on a Bruker D8 Advance diffractometer using Cu-Kα (1.5406 Å) wavelength.

The morphology of the fabricated samples was assessed using scanning electron microscopy (SEM, Model: ULTRA 55 (Zeiss)). The size of the gold nanoparticles and their morphology were analyzed by transmission electron microscopy (TEM) using a CM 30 Philips operating at 300 kV and equipped with an Energy Dispersive X-ray spectroscopy (EDX) detector. High resolution TEM (HRTEM) images were recorded on FEI Tecnai G2-20 twin operating at 200 kV.

The chemical composition of the elaborated samples was estimated by energy dispersive X-ray spectroscopy (EDX). In order to make a quantitative interpretation, X-ray photoelectron spectroscopy (XPS) analysis of the fabricated samples was studied using an ESCALAB 220 XL spectrometer equipped with a monochromatic Al-Kα X-ray source.

The reflectance measurements were performed using an UV − vis spectrophotometer (Perkin- Elmer Lambda UV/vis 950 spectrophotometer, with Universal Reflectance Accessory Snap-on module), equipped with an integrating sphere. Reflectance was measured in the 200 – 800 nm range at an incident light angle of 45°.

The UV–vis absorption measurements were recorded by using a Perkin Elmer Lambda UV–vis 950 spectrophotometer in a spectrometric quartz cuvette with an optical path of 10 mm.

High performance liquid chromatography (HPLC) analysis was carried out on a Shimadzu LC2010-HT (Shimadzu, Tokyo, Japan) using a 5 µm C_4 QS Uptisphere® 300 Å, 250 × 4.6 mm column (Interchim,