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Enhanced photocatalytic degradation of methylene blue by metal-modified silicon nanowires

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ABSTRACT

Silicon nanowires (SiNWs) modified with Au, Pt and Pd nanoparticles were used as heterogeneous photocatalysts for the photodegradation of methylene blue in water under UV light irradiation. The modification of SiNWs was carried out by deposition of metal nanoparticles using the electroless metal deposition (EMD) technique. The effect of metal nanoparticles deposition time on the photocatalytic activity was studied. It was found that the photocatalytic activity of modified SiNWs was enhanced when the deposition time of metal nanoparticles was increased. In addition of modified SiNWs with Pt, Au and Pd nanoparticles, oxidized silicon substrate (Ox-Si), oxidized silicon nanowires (Ox-SiNWs) and hydrogen-terminated silicon nanowires (H-SiNWs) were also evaluated for the photodegradation of methylene blue.

1. Introduction

Photocatalysis has attracted much interest because of its potential application in clean energy sources to degrade organic pollutants from water [1,2]. Semiconductors are commonly used as photocatalysts because of their wide ranging band gaps. In particular, TiO_2 was studied the most because of its exceptional stability towards chemical and photochemical corrosion [3]. Silicon is a low cost and environmental friendly semiconductor, which prevails in integrated microelectronics. However, it is not used in pollution control because its valence band is not positive enough to oxidize pollutant species [4]. Nevertheless, it has been reported by Yoneyama et al. that platinized *n*-type crystalline silicon and silicon powder are good photocatalysts for formic acid decomposition [5,6]. Also, Chen et al. used one dimensional hydrogen-terminated silicon nanowires (H-SiNWs), prepared by oxide-assisted-growth for the degradation of methyl red [7]. More recently, Shao et al. investigated the performance of H-SiNWs and noble metal-modified (Pt, Pd, Au, Rh, Ag) SiNWs substrates prepared by the VLS method for the degradation of Rhodamine B and oxidation of benzyl alcohol to benzoic acid under visible light irradiation. It was found that H-SiNWs exhibited better photocatalytic activity than Pd-, Au-, Rh- or Ag-modified SiNWs for the degradation of Rhodamine B [8]. In addition, Megouda et al. reported the high performance of H-SiNWs and SiNWs coated with metal (Ag, Cu) nanostructures for the photodegradation of Rhodamine B under UV and visible light irradiation [2]. Liu et al. used SiNWs elaborated by metal-assisted electroless etching in a solution containing HF/H_2O_2 as photocatalysts for the photodegradation of Rhodamine B. Different concentrations of H_2O_2 were experimented and they found that a concentration of 20% gives the best photocatalytic activity; a degradation of 35% was obtained after 5 h of irradiation under Xe arc lamp [9]. Qu et al. show that unmodified and Pt-modified porous silicon nanowires can be used as effective photocatalysts for the degradation of organic dyes and toxic pollutants under visible irradiation [10]. In addition, Pan et al. found that Cu-modified silicon nanowires show enhanced catalytic activity for the coupling reaction of benzene halides (iodobenzene, bromobenzene, and chlorobenzene) and aniline [11]. Also, Tsang et al. show that Au- and Cu-modified Si nanowires are superior catalysts for selective oxidation of hydrocarbons [12]. In this study, we show that SiNWs modified by metal nanoparticles (Au, Pt and Pd) with different concentrations have a significant effect on the photodegradation of methylene blue under UV light irradiation. The SiNWs were elaborated by a simple method termed metal-electroless etching and modified by the electroless metal deposition (EMD) technique.

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2. Experimental

2.1. Materials

Methylene blue powder ≥95% pure was purchased from FLUKA Analytical and was used without further purification. Silicon obtained from Siltronix was used to elaborate the photocatalysts. All chemicals used in this study such as gold(III) chloride (99.99%), palladium(II) chloride (99.99%), platinum oxide (99.99%), hydrogen fluoride (50%), oxygen peroxide (30%), nitrates of silver (≥99.8%), acetone (98%), ethanol (≥99.8%), sulfuric acid (95–97%) and nitric acid (65%) were obtained from Sigma–Aldrich.

2.2. Samples preparation

n-Type FZ-Si (100) substrates of resistivity of 0.019–0.024 Ω cm were used in this study. The silicon substrates were first cleaned by ultrasonication in ethanol, acetone and deionized water (5 min each). The cleaned silicon pieces were then immersed into a beaker containing a piranha solution for 20 min at room temperature, followed by a dip in 10% HF aqueous solution for 1 min at room temperature to remove the native oxide. Ag electroless chemical deposition was carried out in a solution containing 0.005 M $AgNO_3$ and 4.8 M HF for 1 min at room temperature [13]. The Si pieces with deposited silver were rinsed with deionized water and then immediately immersed into an etching bath containing 4.8 M HF and 0.4 M H_2O_2 for 60 min [13,14]. The silver metal was removed from the nanowires by immersing the Si pieces in the concentrated nitric acid for 5 min. Three metal types were used for the modification of SiNWs namely: Au, Pd and Pt. For this purpose, three chemical solutions were used:

1. 0.15 M HF:1 mM $AuCl_3$
2. 0.15 M HF:1 mM $PdCl_2$:HCl
3. 0.15 M HF:1 mM PtO_2:HCl

Au nanoparticles were deposited at room temperature in the first solution, whereas the deposits of Pd and Pt were made in the second and the third solution at 50 °C under magnetic stirring, respectively. For each deposited metal type, a set of samples was prepared by varying the deposition time.

2.3. Characterization

Scanning electron microscopy (SEM) images were obtained using a PHILIPS XL30 electron microscope with an accelerating voltage of 20 kV. The absorption spectra of the methylene blue solutions in quartz cuvettes with an optical path of 10 mm were recorded using a CARY 500 "VARIAN" UV–vis spectrophotometer. The wavelength range was 500–800 nm.

2.4. Characterization of silicon nanowires

Fig. 1a shows that the SiNWs are uniformly distributed on the surface of the substrate. The cross section SEM image shows that the SiNWs are vertically aligned to the surface and the interface between nanowires and substrate is clearly distinguished thus indicating that the etching is uniform (Fig.1b). The length of SiNWs is about 62 μm. In addition, it can be observed that the nanowire tips aggregate to form bundles which are caused by van der Waals forces [15]. Au and Pd nanoparticles were deposited on silicon nanowires by electroless metal deposition (EMD) process in aqueous HF solutions containing a metal salt. The used metal salts $AuCl_3$ and $PdCl_2$ dissociate in the solution to produce the metal ions Au^{3+} and Pd^{2+}, respectively, whereas Pt nanoparticles were deposited on silicon nanowires with the same process in a solution containing HF, HCl and platinum dioxide (PtO_2).

The electroless deposition of Au, Pd and Pt occurs according to the following cathodic reactions, respectively [16]:

$$Au^{3+} \rightarrow Au + 3h^{+} \quad (1)$$

$$Pd^{2+} \rightarrow Pd + 2h^{+} \quad (2)$$

$$Pt^{2+} \rightarrow Pt + 2h^{+} \quad (3)$$

Since the electronegativity of these metals is higher than that of Si, metallic ions in the vicinity of the sample surface are believed to capture electrons from silicon. The deposited metal atoms first form nuclei and then nanoclusters to give nanoparticles [16,17]. The decoration of SiNWs with Au nanoparticles for 20 min is low as can be observed in Fig. 2a. The cross section SEM image (Fig. 2b) reveals that the Au nanoparticles have a spherical shape and their concentration is more important on the surface than in the depth. Moreover, it is worth to point out that the length of nanowires is decreased to 36 μm. The Au concentration increases with deposition time as can be observed in Fig. 2c and e. Indeed, Au dendrites were formed for deposition times of 80 min and 180 min with a higher concentration for the longer time. In addition, it can be seen that the length of SiNWs decreases progressively with increasing of deposition time. It is reduced from 31 μm to 29 μm as time is increased from 80 min to 180 min (Fig. 2d and f). The diminution of nanowires length can be attributed to the etching of their tips during the Au deposition. The involved mechanism is that

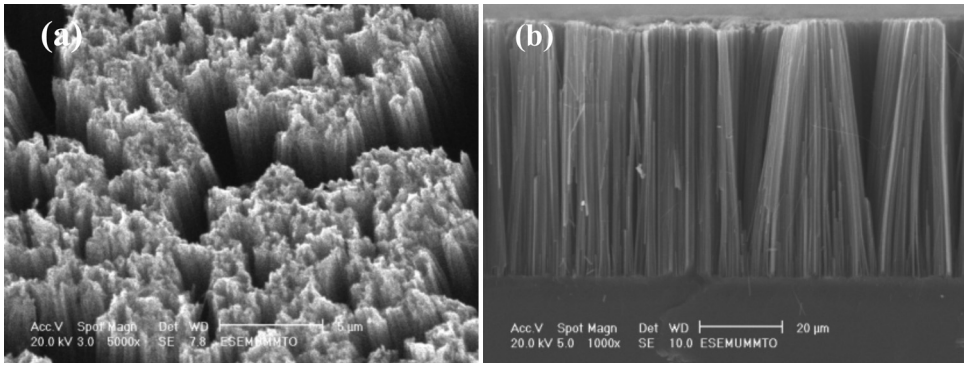

Fig. 1. Plan (a) and cross section (b) SEM images of silicon nanowires elaborated in HF (4.8 M): H_2O_2 (0.4 M) at room temperature for 60 min.