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Effect of the concentration of Au nanoparticles on photodegradation of methylene blue by silicon nanowires

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***Abstract*—Modified silicon nanowires by metal nanoparticles were used as heterogeneous photocatalysts for the decomposition of methylene blue under UV light irradiation. The above reactions were monitored by UV–Vis spectrophotometer. The effect of the concentration of Au nanoparticles deposited onto silicon nanowires on photodegradation of methylene blue is studied.**

***Keywords*— photocatalysis, silicon nanowires, 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 bandgaps. Among them TiO_2 has been studied the most because of its exceptional stability towards chemical and photochemical corrosion. Silicon is a low cost semiconductor and environmental friendly, which dominates integrated microelectronics. Although silicon displays a small energy band gap (1.1 eV), it is not used in pollution control because its valence band is not positive enough to oxidize pollutant species. However, earlier reports by Yoneyama et al. showed that platinizedn-type crystalline silicon and silicon powder are good photocatalystsfor formic acid decomposition[3,4]. More recently, Chen et al. used one dimensional hydrogen-terminated silicon nanowires (SiNWs), prepared by oxide-assisted-growth, under ultrasonic agitation for thedegradation of methyl red. Independently, Shao et al. investigated the performance of hydrogen-terminated SiNWs and noble metal-modified (Pt, Pd, Au, Rh, Ag) SiNWs substrates for the degradation of rhodamine B and oxidation of benzyl alcohol to benzoic acid under visible light irradiation. It was found that hydrogen-terminated SiNWs exhibited better photocatalytic activity than Pd-, Au-, Rh- orAg-modified SiNWs in the degradation of rhodamine B[5].Also, Megouda et al. reported 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.

In this study, we show that gold nanoparticles can be loadedontoSiNWs by metal electroless deposition at different times of deposition and demonstrate that the modified silicon nanowires can be used as effective photocatalysts for the photodegradation of methylene blue under UV light irradiation.

2. EXPERIMENTAL

2.1 Synthesis of porous silicon nanowires

n-TypeSi (100) substrates of resistivity 0.0019–0.024Ω cm were used in this study. The silicon substrates were first cleaned by ultrasonication in ethanol, acetone and deionized water (30 min each), The cleaned silicon pieces were immersed into a beaker contained piranha solution for 20min at room temperature, followed by disoxidation in HF10% for 1 min to remove the native oxide just before the Ag electroless chemical deposition in a solution containing 0.005M $AgNO_3$ and 4.8M HF for 1 min at room temperature. The silver-deposited Si pieces were rinsed with de-ionized water to remove extra silver ions and then immediately immersed into an etching bath containing 4.8MHF and 0.4M H_2O_2 for 60 min. The silver metal was removed from the nanowires by immersing the Si pieces in the concentrated nitric acid for 10 minutes.Fig.1exhibits plan and cross SEM images of the investigated SiNWs. One clearly sees that the SiNWs are vertically aligned to the surface and are uniformly formed.

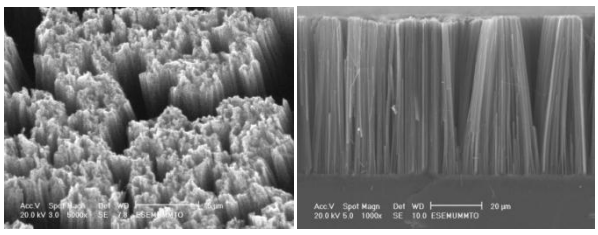

Fig1. Plan (a) and cross section (b)SEM image of p-SiNWs

2.2 Photocatalytic reactions

The silicon nanowires were decorated with gold nanoparticles by electroless chemical deposition in a solution containing 0.15M HF and 1mM $AuCl_3$ at room temperature. The effect of the concentration of nanoprticles deposited onto silicon nanowires is studied by modifying the time of deposition.The photocatalytic degradation reaction was carried out at room temperature by immersion of the substrate into 4mL of diluated aqueous solution of methylene blue with a concentration of 10^{-6} M. The photocatalytic performance was measured by the decay of the absorption of the dye as a function of irradiation time. The methylene blue solution is was prepared by dissolving methylene blue powder (Aldrich, 99.99%) in DI water.We have examined thephotocatalytic activity of oxidized SiNWs (Ox-SiNWs),hydrogen terminatedSiNWs (H-SiNWs) and modified SiNWs loaded with Au nanoparticles substrates at differentstime'sdeposition underUV light irradiation (Fig. 2).

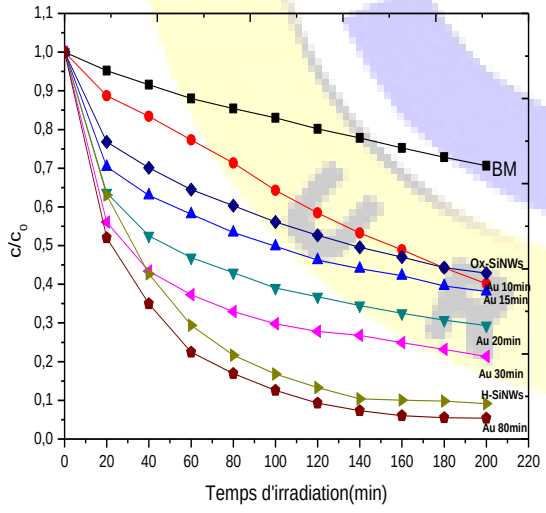

Fig 2. Comparison of photocatalytic degradation of methylene blue for different photocatalytic systems as a function of time under UV light irradiation. The initial concentration of methylene blue is 10^{-6} M.

The results indicate that the photolysis of methylene blue under UV light irradiation present a degradation of 29% only of the dye at 200 minutes of irradiation. The photodegradation yield of the oxidized silicon nanowires (Ox-SiNWs) is much lower than that of the hydrogen-terminated silicon nanowires (H-SiNWs), the rates are 57% and 91% respectively.Loading the SiNWs with gold nanoparticles at different times of deposition shows positive effect on the performance of the photocatalyst. The degree of degradation for SiNWs–Au(10min) is about 60% in comparison to 62% for SiNWs -Au(15min), 71% for SiNWs -Au(20min), 78% for SiNWs -Au(30min) and 95%for SiNWs -Au(80min).Fig.3 shows the UV–Vis spectra of the methylene blue solution throughout the photocatalytic decomposition by SiNWs -Au (80min).The methylene blue peak at 663 nm decreases gradually with the time of irradiation.The degradation of methylene blue is following the usually proposed mechanism[6]:

1. Absorption of efficient photons ($h\nu \geq E_G$)

$$Si + hv(\geq E_g) \rightarrow h^+_{BV} + e^-_{BC} \quad (1)$$

2. Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to -1/2)

$$O_2)_{ads} + e^-_{CB} \rightarrow O^{\bullet -}_2 \quad (2)$$

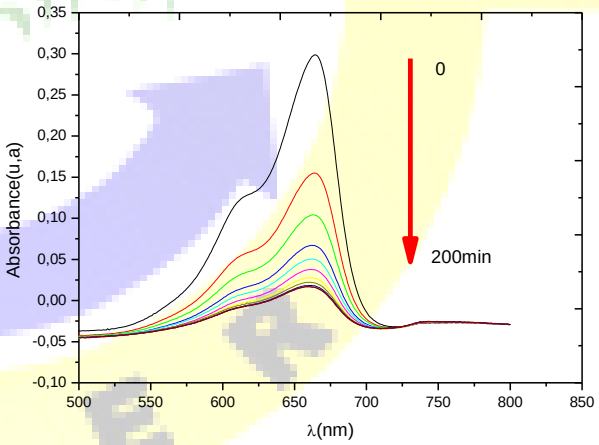

Fig. 3 UV/vis absorption spectra of methylene blue before and after UV light irradiation in the presence of the porous SiNWs-Au(80min) substrate as a function of irradiation time

3. Neutralization of OH^- groups by photoholes which produces $OH^{\bullet}$radicals

$$(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h^+_{VB} \rightarrow H^+ + OH^{\bullet} \quad (3)$$

4. Neutralization of $O_2^{\bullet -}$ by protons

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \quad (4)$$

5. Transient hydrogen peroxide formation and dismutation of oxygen

$$2HO_2^{\bullet -} \rightarrow H_2O_2 + O_2 \quad (5)$$

6. Decomposition of H_2O_2 and second reduction of Oxygen

$$H_2O_2 + \bar{e} \rightarrow OH^{\bullet} + OH^- \quad (6)$$

7. Oxidation of the $OH^{\bullet}$ organic reactant via successive attacks by radicals

$$R + OH^{\bullet} \rightarrow R'^{\bullet} + H_2O \quad (7)$$

8. Direct oxidation by reaction with holes

$$R + h^+ \rightarrow R^{+\bullet} \rightarrow \text{degradation products} \quad (8)$$

As an example of the last process, holes can react directly with carboxylic acids generating CO_2

3. CONCLUSION

We have examined the net effect of the time deposition of gold onto porous silicon nanowires on the photodegradation of methylene blue under UV light irradiation. We have concluded that the photocatalytic activity of modified silicon nanowires increase with the concentration of gold nanoparticles, and the SiNWs -Au (80min) exhibits the best rate of degradation in comparison with porous H-SiNWs.

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