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Photocatalytic degradation of Methylene blue by modified porous silicon nanowires

N. Brahiti[a], T. Hadjersi[b], H. Menari[b]

[a]*Université Mouloud MAMMERI de TiziOuzou*

Département de physique, Nouvelle Ville, BASTOS, Algeria

[b]*Centre de recherche en technologie des semiconducteurs pour l'énergétique (CRTSE)*

2 Bd. Frantz Fanon, B.P. 140 Alger-7 Merveilles, Alger, Algeria

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Abstract

In this paper, the effect of the time deposition of metal nanoparticles on the photodegradation of methylene blue is studied. The modified silicon nanowires were used as heterogeneous photocatalysts for the decomposition of methylene blue under UV light irradiation. The above reactions were monitored by UV–Vis spectrophotometer which shows the positive effect of the time deposition of metal nanoparticles on the photodegradation of methylene blue. 91% of the degradation was observed with the hydrogen terminated porous silicon nanowires and the degradation is about 95% for the modified porous silicon nanowires with Au (80min) and the same degree was obtained with Pt (120min) at 200 minutes of irradiation. The rate of the degradation reaches 100% at 90min of illumination with the decorated porous silicon nanowires with Pd nanoparticles.

Keywords: *silicon nanowires, chemical etching, photocatalysis, organic polluants.*

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 platinized n-type crystalline silicon and silicon powder are good photocatalysts for formic acid decomposition [3]. More recently, Chen et al. used one dimensional hydrogen-terminated silicon nanowires (SiNWs), prepared by oxide-assisted-growth, under ultrasonic agitation for the degradation 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 [4]. 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 the modified SiNWs by metal nanoparticles (Au, Pt and Pd) with different time's deposition have an important effect on the photodegradation of methylene blue under UV light irradiation.

2. Experimental

2.1 Synthesis of porous silicon nanowires

n-Type (100) substrates with a resistivity of 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 20 min 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. The SiNWs were decorated with metal nanoparticles by electroless deposition method.

2.2 Photocatalytic Experiment

The methylene blue solution with first concentration of 10^{-4}M was prepared by dissolving methylene blue powder (Aldrich, 99.99%) in DI water. The dilute solution of the dye (10^{-6}M) was prepared by diluting the mother solution with DI water with a magnetic stirrer at room temperature for 10 minutes. The experience of the photodegradation was carried out in a vat exposed to UV light irradiation in dark for 200 minutes; the measurement of the absorbance is effectuated each 20 minutes of illumination. The photocatalytic performance was measured by the decay of the absorption of the dye as a function of irradiation time.

3. Results and discussions

3.1. Morphological characterization

The SEM plan and cross section images of silicon nanowires were showed in figure.1.

The SEM images show that the silicon nanowires are porous, vertically aligned to the surface and reveal a length of 15 µm approximatively and a diameter range of 50-200nm. The nanowire bundles were observed due to agglomeration at their tops-ends because of the von der waals force [5].

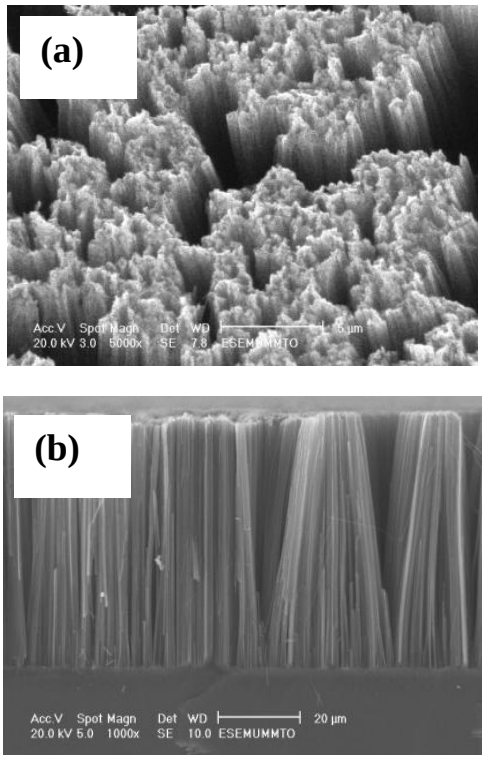

Figure1. Plan (a) and cross section (b) image of silicon nanowires.

3.2. Photocatalytic degradation of methylene blue

In this communication, we report on the high efficiency of hydrogen terminated porous silicon nanowires and decorated porous SiNWs with gold, platinium and palladium nanoparticles for the photodegradation of methylene blue under UV light irradiation. The photocatalytic degradation reaction was carried out at room temperature by immersion of the substrate into 4 mL aqueous solution of methylene blue. The photocatalytic performance was measured by the decay of the absorption of the dye as a function of irradiation time. Fig. 2 exhibits UV/vis spectra of methylene blue before and after UV light irradiation in the presence of a hydrogen-terminated silicon nanowires (H–SiNWs) substrate. The characteristic absorption band of methylene blue at 663 nm decreased significantly with increasing irradiation time. We have further examined the photocatalytic activity of oxidized SiNWs (SiNWs–Ox) and SiNWs loaded with Au, Pt and Pd nanoparticles substrates at different concentrations under UV light irradiation.

Figure3. shows the comparison between the photolysis of methylene blue and the photocatalysis of the dye using oxidized silicon substrate (Ox-Si), oxidized porous silicon nanowires (Ox-SiNWs) and hydrogen terminated porous silicon nanowires (H-SiNWs), the results indicate that the photolysis presents a degradation of 29% of the dye at 200min, 40% of degradation is obtained with Ox-Si. The photocatalytic degradation with Ox-SiNWs substrate is much lower than that of the hydrogenated sample; the rates of the degradation are respectively 58% and 91%. Loading the porous silicon nanowires with Au, Pd and Pt nanoparticles at different concentrations show a positive effect on the performance of the photocatalyst. However, when the concentration of the metal nanoparticles NPs was significantly increased, a significant increase in the photoactivity was obtained. The degree of the degradation for SiNWs–Au (10min) is about 60% in comparison to 61% for Au (15min), 70% for Au (20min), 78% for Au (30min) and 95% for Au (80min) after 200 min of irradiation (Figure.4).

As seen in figure 5, the photodegradation using the platinum decorated porous silicon nanowires displays a degradation of about 65% for Pt (60min) and 95% for Pt (120min). The degradation with Pd decorated porous silicon nanowires is about 95% with Pd (120min) at 200 min and reaches 100% with Pd (180min) at 90 min of illumination under UV light (Figure.6).

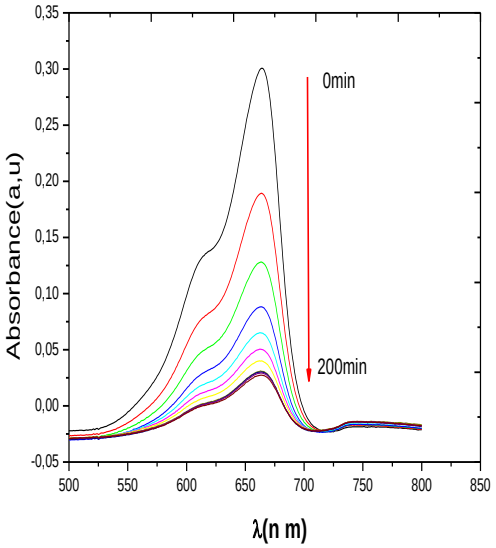

Figure2. UV/vis absorption spectra of methylene blue before and after UV light irradiation in the presence of the hydrogen terminated SiNWs substrate as a function of irradiation time.

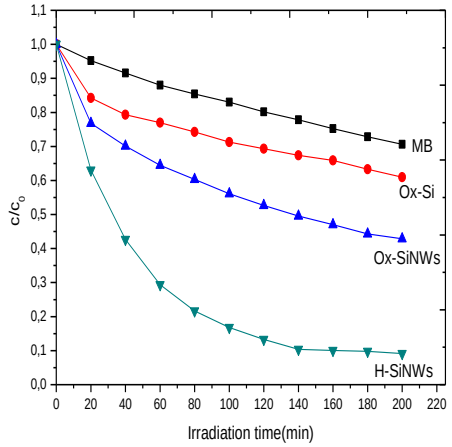

Figure 3. comparison between photolysis and photocatalysis of methylene blue using Ox-Si, Ox-SiNWs and H-SiNWs.

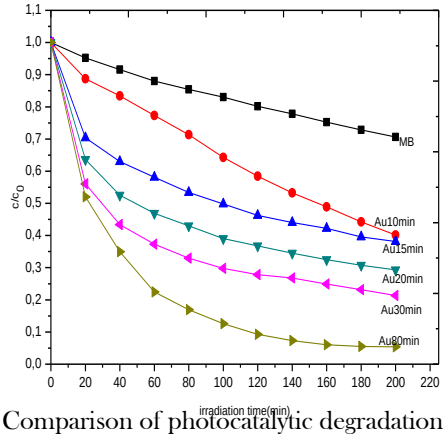

Figure 4. Comparison of photocatalytic degradation of methylene blue for different concentrations of Au nanoparticles as a function of time under UV light irradiation.

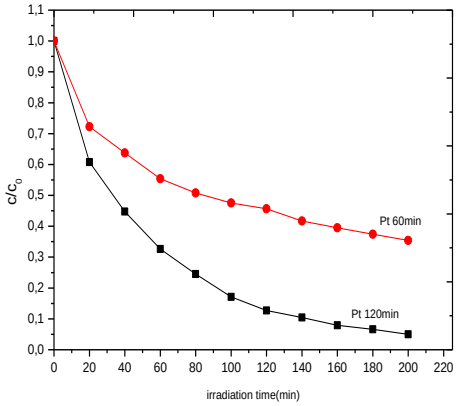

Figure 5. Comparison of photocatalytic degradation of methylene blue for different concentrations of Pt nanoparticles as a function of time under UV light irradiation.

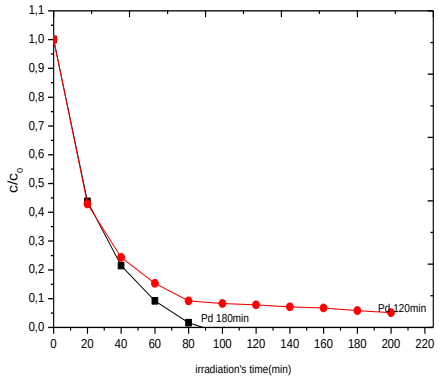

Figure 6. Comparison of photocatalytic degradation of methylene blue for different concentrations of Pd nanoparticles as a function of time under UV light irradiation.

Incorporating metal nanoparticles onto semiconductor photocatalysts can enhance the photocatalytic activity because the difference in their Fermi levels can introduce a Schottky barrier between the metal and the semiconductors. The increase of the concentrations of metal nanoparticles deposited onto porous silicon nanowires induces the increase on the electron trappers and in consequence reduces the rate of the recombinaison between the electrons and holes which is favorable for the photocatalytic activity.

The degree of the degradation with Au (80min) is about 95% and it is similar to the rates of the degradation with Pt (120min) and Pd (120min), this can be attributed to the fact that the Au nanoparticles can be deposit easily onto silicon nanowires at room temperature in comparison with Pd and Pt nanoparticles which require a higher time to deposit onto porous silicon substrates and which is effectuated at 50°c under magnetic stirrer.

For Pd (180min) the degaradation is achieved at 90min of illumination because the concentration of the nanoparticles of palladium is very important so therefore the trappers of electrons are numerous.

4. Conclusion:

In this study, porous silicon nanowires were investigated with electroless chemical etching in HF/H_2O_2 solution and were decorated with noble metal nanoparticles by electroless chemical deposition. We have examined the net effect of the time deposition of gold, platinium and palladium nanoparticles onto porous silicon nanowires on the photodegradation of methylene blue under UV light irradiation. We have concluded that the photocatalytic activity of modified porous silicon nanowires increases with the concentration of metal nanoparticles, and the porous SiNWs -Au (80min), Pt(120min) and Pd(180min) exhibit better photocatalytic activity for the degradation of the methylene blue in comparison with porous H-SiNWs.

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