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Spinel $ZnCO_2O_4$ Nanosheets - Modified SiNWs as Photocatalyst for Degradation of Organic Pollutant

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ABSTRACT

The photocatalytic degradation of azo dye RhB using spinel $ZnCo_2O_4$-modified silicon nanowires ($ZnCo_2O_4$/SiNWs) was investigated under visible light irradiation. Silicon nanowires (SiNWs) were elaborated by metal-assisted chemical etching and on which $ZnCo_2O_4$ was deposited by hydrothermal technique. The prepared samples were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The RhB photodegradation was monitored by UV-Vis spectrometry. It was revealed that $ZnCo_2O_4$/SiNWs exhibited higher phtocatalytic activity than unmodified SiNWs, and the phtocatalytic activity strongly depends on experimental parameters of SiNWs synthesis and $ZnCo_2O_4$deposition.

Keywords: silicon nanowires, spinel $ZnCo_2O_4$, hydrothermal, rhodamine B.

1 Introduction

Azo dyes represent a large class of synthetic colorants with a wide range of applicability in the textile, paper, wood, leather, cosmetic and food industries. These pollutants are considered toxic and carcinogenic, with negative impact on the aquatic ecosystem, environment and human health **[1-3]**, They need to be removed from wastewaters by different methods. Photocatalysis has been successfully used to oxidize many organic pollutants and particularly to decolorize dyes. Spinel compounds have been widely studied and have been found to possess advantages, including excellent visible light responsiveness (400–700 nm), ease of preparation, and strong resistance to light corrosion **[4]**. The unique structural features and abundant cations of these compounds cause them to have higher visible light absorption capacity than other similar catalysts **[5]**. Among them, $ZnCo_2O_4$ has normal spinel structure with trivalent Cobalt ions in octahedral voids and divalent Zinc ions in tetrahedral voids.

In this work, silicon nanowires SiNWs were elaborated by metal-assisted chemical etching (MACE) process and modified by $ZnCo_2O_4$ using hydrothermal technique in order to combine the interesting properties of SiNWs and $ZnCo_2O_4$ and tested them as new class of a strengthened photocatalyst for degradation of RhB under Visible-light irradiation.

2 Experimental

All reagents used in this work (Acetone, Ethanol, H_2O_2, $AgNO_3$, H_2SO_4, Zn $(NO_3)_2.6H_2O$, HNO_3, $CoCl_2.6H_2O$, CH_4N_2O were of analytical grade and purchased from Sigma- Aldrich. n-Si (100) samples of resistivity 5-10 Ω.cm and size 1.5x0.8 cm^2 were used in this work. SiNWs were elaborated by metal-assisted chemical etching and modified with zinc cobaltite ($ZnCo_2O_4$) by hydrothermal method. Different hydrothermal deposition temperatures (140- 160- 180 and 200°C) were experimented. The photocatalytic degradation reaction was carried out at room temperature by immersing the photocatalysts into a 3 mL aqueous solution of Rhodamine B (RhB) with an initial concentration of 5.10^{-6} M. The solution was irradiated with Visible light for 90 min.

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3 Results and Discussion

3.1 Morphology

The SEM images of silicon nanowires formed on Si surface by etching in aqueous solution are shown in Fig. 1.a. Cross-sectional SEM images shows the uniform formation of a large amount of silicon nanowires well vertically aligned on the surface with a length about 30 μm. Fig1.a shows that the nanowire tips stick together forming bundles due to van der waals' forces **[6]**.

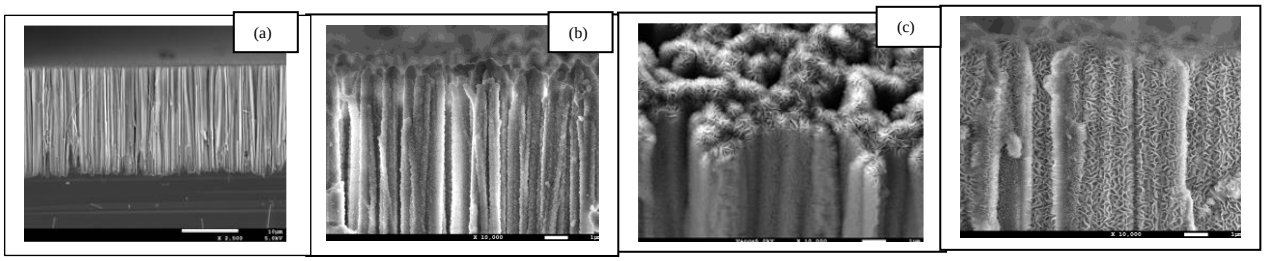

Figure 1: Cross-sectional of SiNWs (a) and cross-sectional SEM images of $ZnCO_2O_4$ coated SiNWs for different deposit temperature: (b) 140, (c) 180 and 200°C respectively.

Fig.1b, c and d reveals the morphology of nanowires after deposition of $ZnCo_2O_4$ by hydrothermal technique, indicating that the nanowires are completely covered with nanosheet of $ZnCo_2O_4$, meaning we have a conformal coating of $ZnCo_2O_4$.

3.2 Photocatalytic degradation-

Fig.2 depicts the variation of the ratio of the concentration (C/C0) as a function of irradiation time with different photocatalysts, where C0 is the initial concentration of RhB, and C is the concentration of RhB at irradiation time. A very slight improvement in the RhB degradation rate as the deposition temperature increases. For deposit temperatures of 140, 160, 180 and 200°C, degradation rates of 93%, 94%, 96% and 96%, were achieved, respectively. Which shows that the deposition temperature does not have a great influence on the degradation of RhB.

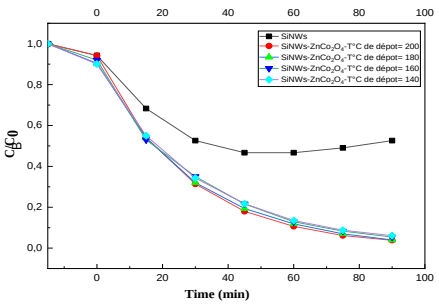

Figure 2: Variation of the RhB concentration versus time for different photocatalysts.

4 Conclusions

In this work a detailed study was carried out on the photocatalytic degradation of RhB using silicon nanowires modified by $ZnCo_2O_4$ as a photocatalyst under visible light irradiation. It found that a nanosheet of $ZnCo_2O_4$ was uniformly coated onto the entire silicon nanowires. The experimental results showed that the $ZnCo_2O_4$ hydrothermal deposition temperature have not a great influence on the degradation of rhodamine B.

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