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Original Article

Influences of ZnO Nanorod Arrays on Photocatalytic Activity of n-ZnO Nanorods/p-Si Heterostructure

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Abstract: Zinc oxide is known as an excellent material for biosensors, solar cells, semiconductors and photocatalysts. In this work, n-ZnO nanorods/p-Si heterostructures were successfully fabricated by a hydrothermal method at different baking temperatures. The n-ZnO nanorods/p-Si heterostructures show good photocatalytic ability at high baking temperature. The concentration of Rhodamine B can be decreased up to 97% after 150 min treated by the n-ZnO nanorods/p-Si heterostructures grown at 80 ^{o}C. This result indicates that the n-ZnO nanorods/p-Si heterostructures are capable of being used in the decomposition of organic compounds.

Keywords: Photocatalytic, ZnO/Si, hydrothermal method, heterostructure, nanostructure

1. Introduction

Nowadays, in parallel with continuous developments of industries, the problem of water pollution is becoming increasingly important, greatly affecting human life. The main cause of this situation is the use of dyes in the textile industry, the tanning and manual bleaching industries, the paper industry, etc. and the toxic and untreated toxic substances directly discharged into the environment. Therefore, the removal of organic contaminants is essential. Techniques have been used for recycling, concentrating and treating waste water such as distillation technique [1], membrane [2], chemical oxidation [3], photocatalytic technique [4], etc. In which, the photocatalytic one is attracting scientists interest in solving environmental problems, especially in treating dyes from industrial waste water because it can completely mineralize organic dyes to H_2O, CO_2 and inorganic acids without causing secondary pollution [5]. Some metal semiconductor materials such as TiO_2 [6], ZnO [7], Fe_2O_3 [8], etc. were used

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as optical catalysts because they are cost-effective, non-toxic, and environmentally friendly [9]. In particular, ZnO exhibits a higher photocatalytic efficiency compared with TiO_2, and is likely to be widely applied in the future to treat environmental pollutants [10, 11]. ZnO material has a direct energy band structure, a band gap as wide as 3.37 eV with high exciton binding energy at room temperature. However, with a wide band gap, the ZnO material can only absorb light in the ultraviolet region. In the energy spectrum of sunlight, the ultraviolet region accounts for only about 5% of the total energy of the spectrum [6]. In addition, due to the structure of the direct energy band, the electron-hole pairs lifetime is short (~ ns). Therefore, the efficiency of ZnO material in photocatalytic activity is still low. To improve the photocatalytic efficiency of ZnO materials, noble materials such as Ag, Au, Pt or some kinds of semiconductor oxide were combined to create electron traps that reduce recombination, increasing electron lifetime, expanding optical absorption band, and electron-hole separation by heterogeneous contacts of composite materials. Si semiconductor material has narrow and indirect band gap (1.12 eV). Therefore, combining Si material with ZnO material has the ability to expand the light absorption band of composites. In addition, using p-type Si semiconductor material to form the n-ZnO/p-Si heterogeneous transition layer could reduce the recombination rate of the electron-hole pair, expanding the light absorption band, increasing the lifetime of the electrons and therefore, resulting in the improvement of photocatalytic efficiency of the ZnO materials. Furthermore, the photochemical catalytic performance can also be improved by increasing the effective surface area of the ZnO material. Moreover, the fabrication of n-ZnO/p-Si structure in the form of films for recovery and reuse is relatively simple in the application for environmental treatment [12-14]. Therefore, in this work, n-type ZnO nanorods were grown on p-type Si substrates by a hydrothermal method. The influences of n-type ZnO nanorods structures on n-ZnO nanorods/p-type Si heterostructures were also investigated for photocatalytic application.

2. Experimental Details

2.1. The Process of Fabricating n-Zno Nanorods/p-Si Heterostructure

The p-type silicon substrates were soaked in 500 ml of 1.5M NaOH solution for 10 minutes, then were cleaned by distilled water and dried by N_2 gas. 0.438 g $Zn(COOCH_3)_2.2H_2O$ was diluted in 20 ml of IPA solution and stirred for 30 minutes to obtain a transparent solution. The solution was spin-coated on p-type silicon substrate and then annealed at 500 °C for 1 hour. After this process, an ZnO nano seed layer was formed on the Si substrate. Hydrothermal solution was created by diluting 1.782 g $Zn(NO_3)_2.6H_2O$ and 0.84 g $C_6H_{12}N_4$ in 300 ml of DI water. The ZnO nano seed layer/p-Si substrates were placed in an autoclave with 100 ml hydrothermal solution. The prepared autoclave was baked at 60 °C ÷ 100 ^oC for 2 hours. After 2 hours of baking, the autoclave was allowed to cool down naturally. Finally, the n-ZnO nanorods/p-Si heterostructures were cleaned ultrasonically in ethanol and DI water for 30 min for several times and then dried at 60 ^oC for 12 h in an oven under the atmospheric conditions to remove organic residuals and evaporate the remaining DI water. To change the structure of n-ZnO nanorods array, the hydrothermal temperature was varied from 60 to 100 ^oC. Other hydrothermal parameters such as baking time, concentration of hydrothermal solution, etc. were kept as constants.

2.2. Photocatalytic Activity Measurement

The photocatalytic ability of the n-ZnO nanorods/p-Si heterostructure was studied by the decomposition of Rhodamin B (RhB) under visible light radiation. The n-ZnO nanorods/p-Si heterostructure (2x2 cm^2) was placed in 50 ml of 20 ppm RhB solution. A 300 W Xenon lamp was used

as a source of light. After each 30 min radiation, the concentration of RhB solution was analyzed by an UV-vis spectrometer (Jasco, V-670) with RhB peak at a wavelength of 554 nm.

3. Results and Discussion

The crystal structure of ZnO nanorods fabricated by hydrothermal method was investigated through X-ray diffraction and shown in Figure 1. The diagram of X-ray diffraction showed that the produced ZnO nanorods possess a Wurtzite structure with polycrystalline but single phase structure. Diffraction peaks of (100); (002); (101); (102); (110); (103) observed on the diffractogram belong to the diffraction peaks of ZnO material, therefore, in the fabricated sample there is no appearance of any impurities. In addition, the diffraction peak (002) has the greatest intensity. This indicates that the ZnO nanorods have a strong orientation in the c-axis that was perpendicular to the substrate surface.

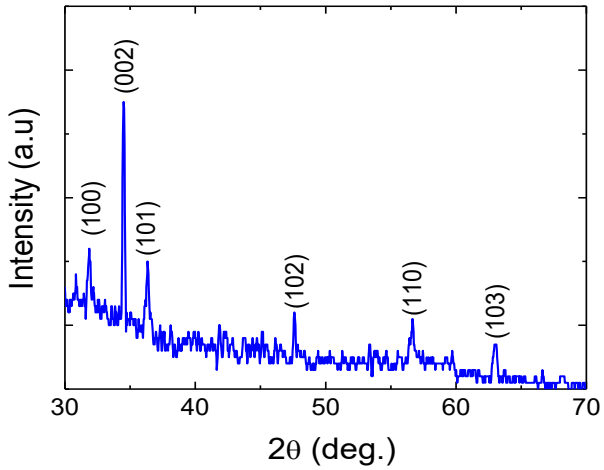

Figure 1. X-ray diffraction of ZnO nanorods array.

Surface morphology of the ZnO nanorods fabricated at different temperatures was observed through scanning electron microscope (SEM) and was presented in Figure 2. SEM surface morphology images of the fabricated samples showed that the cross-sections of the ZnO nanorods had a hexagonal structure and a diameter of 40 nm, high uniformity in size, and a tendency to orientation perpendicular to the surface. The rod diameter and length tend to increase proportionally with the baking temperature. This can be explained based on the reaction speed as well as the growth rate of the crystal, which strongly depends on the baking temperature.

The optical absorption spectrum of the ZnO nanorods is shown in Figure 3a. The ZnO nanorods show a very clear absorbance edge at about 370 nm. To determine the band gap of the ZnO nanorods, the first derivative of the absorbance by photon energy was determined and presented in Figure 3b. The results show that the band gap of the ZnO nanorods does not change significantly and is constant at 3.35 eV. This indicates that the ZnO nanorods fabricated by hydrothermal method have the optical band gap regardless of fabrication temperature. In addition, the optical absorption results show that the transmittance of samples in the visible light depends quite strongly on the baking temperature, the higher the temperature is, the lower the optical transmission is. This can be explained through the thickness of the ZnO nanostructures when the fabrication temperature is high, which leads to the interference of light when passing through the structure.

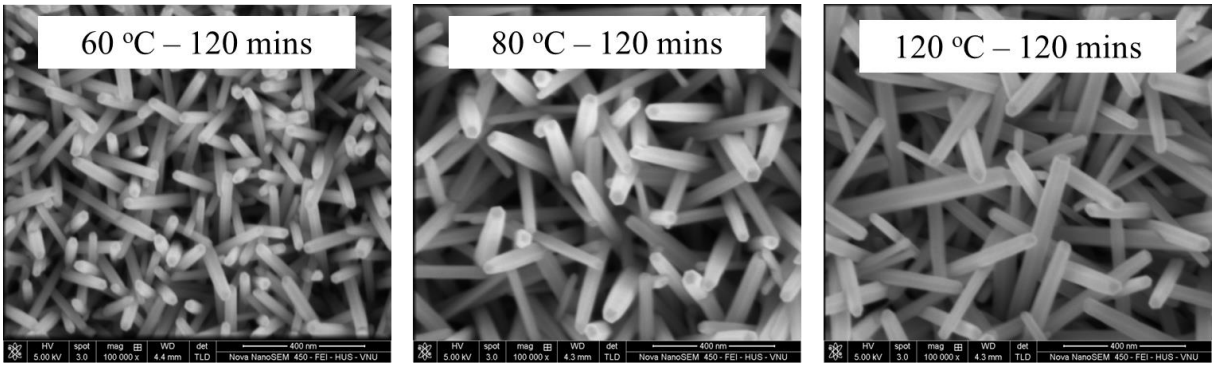

Figure 2. SEM images of ZnO nanorods fabricated by hydrothermal method at different temperatures.

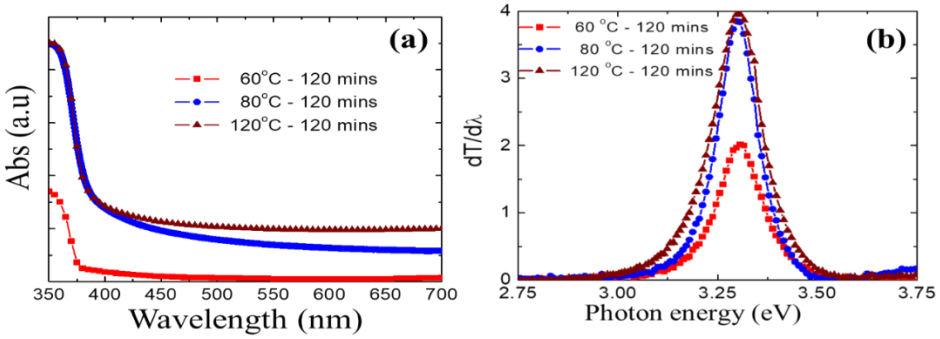

Figure 3. (a) Optical absorption spectra and (b) the first derivative of the absorbance by photon energy of the ZnO nanorods.

The photocatalytic activities of the n-ZnO nanorods/p-Si heterostructures were investigated based on the ability to decompose organic Rhodamine B (RhB). Initial organic matter concentration is 10 ppm. During the photocatalytic process, the n-ZnO nanorods/p-Si heterostructures were excited by the Xenon lamp. After every 30 minutes of irradiation, 3 ml of RhB solution is taken for analysis. Results of RhB organic decomposition after 150 minutes by the n-ZnO nanorods/p-Si heterostructures are shown in Figure 4.

The absorption spectra show the absorption peak of RhB at a wavelength of 553 nm. The concentration of RhB in the solution gradually decreased with the photocatalytic treatment time. The speed of decline is quite fast during the first 90 minutes of irradiation. After a period of 150 minutes of irradiation, the RhB concentration decreased to over 90%.

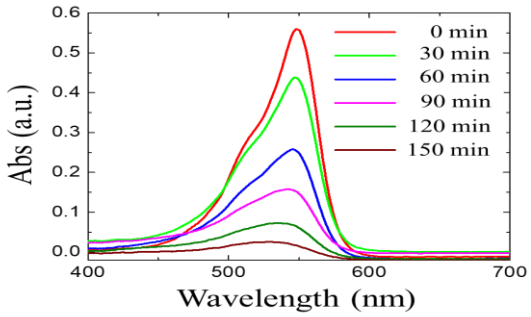

Figure 4. Absorption spectra of RhB solution after every 30 minutes of photocatalytic treatment.

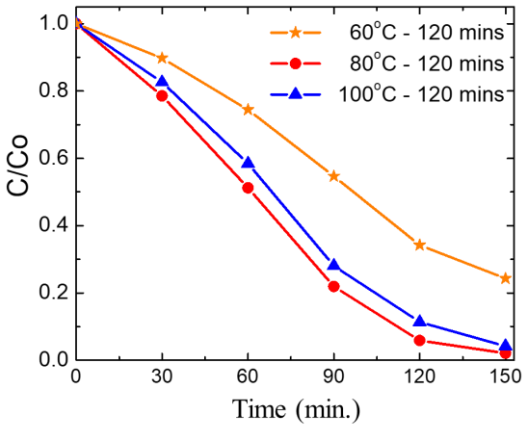

Figure 5. The photocatalytic activity of the n-ZnO nanorods/p-Si heterostructures.

Figure 5. shows the photocatalytic activity of the n-ZnO nanorods/p-Si heterostructures fabricated by different baking temperature. Co and C are the initial concentration (no photo-catalytic treatment) and concentration after the photocatalytic treatment for different time periods. The concentration of RhB decreased with the photocatalytic processing time with the rate of reduction in an exponential form. After 150 minutes of irradiation, the concentration of RhB decreased to about 78%, 97%, 95% when the baking temperatures were 60 °C, 80 °C, and 120 °C, respectively. The results indicate that the n-ZnO nanorods/p-Si heterostructures with a higher baking temperature will have higher photocatalytic activities.

4. Conclusion

The n-ZnO nanorods/p-Si heterostructures were successfully fabricated by a hydrothermal method at different baking temperatures. The n-ZnO nanorods/p-Si heterostructures showed good photocatalytic ability at higher baking temperature. The concentration of RhB decreased up to 97% after 150 min treated by the n-ZnO nanorods/p-Si heterostructures that were grown at 80 °C. This result indicates that the n-ZnO nanorods/p-Si heterostructures are capable of being used in the decomposition of organic compounds.

Acknowledgments

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