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Research Article

Controllable Synthesis of Zn_2GeO_4 Nanorods for Photocatalytic Reduction of Aqueous Cr(VI) and Oxidation of Organic Pollutants

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Zn_2GeO_4 nanorods were successfully synthesized by a simple hydrothermal method. The composition, morphology, and optical properties of as-synthesized Zn_2GeO_4 samples were characterized by X-ray diffraction, scan electron microscopy, and UV-vis diffuse reflectance spectra. The photocatalytic properties of Zn_2GeO_4 nanorods were evaluated by the reduction of Cr(VI) and oxidation of organic pollutants in aqueous solution. The effects of solution pH on Cr(VI) reduction by Zn_2GeO_4 nanorods were studied in detail. The results indicated that the efficiency of Cr(VI) reduction was highest at pH 5.96. Moreover, Zn_2GeO_4 nanorods also showed excellent photocatalytic ability for the oxidation of organic pollutants such as rhodamine B and 4-nitrophenol.

1. Introduction

Cr(VI) is a frequent contaminant originating from industrial processes such as leather tanning, paint making, electroplating, and steel production. It is highly mobile in water and exhibits a high toxicity and carcinogenicity for environment and human beings [1, 2]. Its concentration in drinking water is restricted to be less than 0.05 mg/L by the World Health Organization. Therefore, the removal of Cr(VI)-containing wastewaters has attracted intense concerns. The reduction of Cr(VI) to the relatively nontoxic Cr(III) has become a key process. Moreover, Cr(III) can be easily precipitated as $Cr(OH)_3$ in neutral or alkaline solutions and removed as a solid waste [3]. Many conventional methods such as chemical precipitation, membrane separation, adsorption, and photocatalysis have been reported for the wastewater treatment [4–8]. Chemical precipitation needs high treatment cost for the consumption of reagents (ferrous sulfate or sodium bisulfite), and a large amount of toxic solid waste is generated. Membrane separation also needs high cost for the replacement of membrane after a certain of operation time. The main drawbacks of adsorption are the separation and regeneration of adsorbents. These drawbacks have hindered the applications for the Cr(VI) removal. Compared to the conventional reduction methods, semiconductor photocatalysis has now been considered as a promising method of treating Cr(VI)-containing wastewaters for its high performance, low cost, less solid wastes, and reusability [9–13].

Recently, Zn_2GeO_4 photocatalyst with d^{10} electronic configuration has attracted great research interest for its crystal cell and conduction bands of hybridized sp orbitals with large dispersion, which can promote the separation of electron-hole pairs upon photoexcitation [14, 15]. Great efforts have so far been made to synthesize one-dimensional (1D) nanostructures in the forms of rods [16–18], tubes [19–21], and belts [22, 23]. Compared to nanoparticles, 1D nanostructures not only allow the lateral confinement of electrons and guide the movement of electrons in the axial direction, but also enhance the light absorption and scattering because of the high length-to-diameter ratio of the 1D structures [24, 25].

To the best of our knowledge, there are no reports about photocatalytic reduction of aqueous Cr(VI) by Zn_2GeO_4 nanorods. In this work, Zn_2GeO_4 nanorods were synthesized by a simple hydrothermal method. The composition,

morphology, and optical properties of Zn_2GeO_4 nanorods were characterized by X-ray diffraction, scan electron microscopy, and UV-vis diffuse reflectance spectra. The photocatalytic properties of Zn_2GeO_4 nanorods were evaluated by the reduction of Cr(VI) and oxidation of organic pollutants in aqueous solution. A possible mechanism for the high photocatalytic performances of Zn_2GeO_4 nanorods was proposed.

2. Materials and Methods

All reagents were of analytical grade and used as received without any further purification. Deionized water was used throughout the experiments.

2.1. Preparation of Zn_2GeO_4 Nanorods. Zn_2GeO_4 nanorods were synthesized by a simple hydrothermal method. In a typical synthesis, 0.209 g GeO_2, 1.190 g $Zn(NO_3)_2{\cdot}6H_2O$, 1.502 g urea, and 0.018 g cetyltrimethylammonium bromide (CTAB) were added to 30 mL deionized water. The mixture was stirred for 20 min and then transferred to a Teflon-lined stainless steel autoclave of 25 mL capacity. The autoclave was sealed and heated at 140°C for 24 h, followed by cooling naturally to room temperature. The product was collected by centrifugation, washed thoroughly with alcohol and deionized water several times, and dried at 70°C for 12 h. A white Zn_2GeO_4 powder was finally obtained.

2.2. Characterization. The composition of Zn_2GeO_4 samples was analyzed by Bruker D8 Advance X-ray diffraction (XRD) with Cu Ka radiation (λ = 0.15406 nm). The accelerating voltage and emission current were 40 kV and 40 mA, respectively. The morphology of Zn_2GeO_4 samples was recorded by a FEI Quanta 200 scanning electron microscope (SEM), with an acceleration voltage of 25 kV. The UV-vis diffuse reflectance spectrum of Zn_2GeO_4 nanorods was measured by a UV-vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd.). $BaSO_4$ was used as a reflectance standard. The $^{\bullet}OH$ trapping photoluminescence spectra were recorded using an FLS920P Edinburgh analytical instrument equipped with a 450 W xenon lamp and a μF900H high-energy microsecond flash lamp as the excitation sources.

2.3. Photocatalytic Experiments. The photocatalytic activity of Zn_2GeO_4 sample was evaluated by the reduction of aqueous Cr(VI) (10 mg/L) and oxidation of rhodamine B (RhB, 10 mg/L) and 4-nitrophenol (4-NP, 10 mg/L) under UV light irradiation (300 W high-pressure mercury lamp). Prior to irradiation, an aqueous suspension (50 mL) containing sample (0.1 g) and pollutant (Cr(VI), RhB, and 4-NP) was magnetically stirred for 30 min in the dark to favor the adsorption-desorption equilibration. During irradiation, 5 mL aliquots were taken at a scheduled interval and centrifuged immediately to remove the particle. The residual concentration of Cr(VI) in the supernatant solution was measured by a 1,5-diphenylcarbazide spectrophotometric method with a spectrophotometer at 540 nm wavelength [26, 27]. The concentration of RhB and 4-NP aqueous solution was analyzed at maximum absorption of 554 nm and 317 nm, respectively.

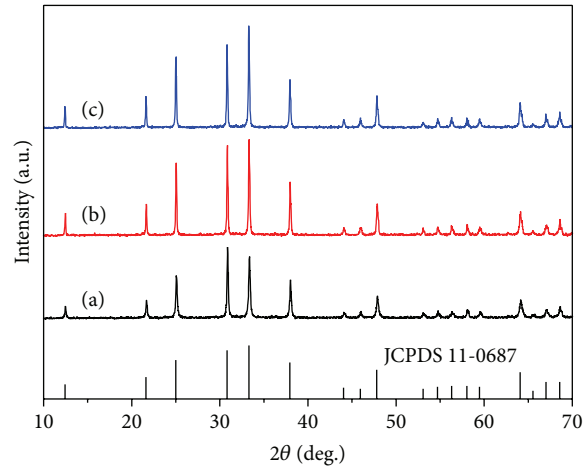

Figure 1: XRD patterns of the as-synthesized Zn_2GeO_4 samples with different CTAB content. (a) 0 g, (b) 0.018 g, and (c) 0.073 g.

3. Results and Discussion

3.1. Characterization of Zn_2GeO_4. The XRD patterns of Zn_2GeO_4 samples prepared in the presence of different CTAB content (0–0.073 g) are shown in Figure 1. All the samples displayed only the characteristic XRD peaks of hexagonal phase Zn_2GeO_4 (JCPDS card number 11-0687). XRD peak height indicated that the crystallinity of Zn_2GeO_4 can be effectively improved in the presence of CTAB. Moreover, no precipitation was obtained without the introduction of the urea in the hydrothermal process.

Comparative experiment was carried out to investigate the effect of CTAB on the formation of Zn_2GeO_4 nanorods (Figure 2). From Figures 2(a) and 2(b), it can be obviously seen that the Zn_2GeO_4 sample is composed of irregular microspheres. With the increase of CTAB content, agglomerate Zn_2GeO_4 nanorods were formed (Figures 2(c) and 2(d)). When the CTAB content was further increased to 0.073 g, uniformly dispersed Zn_2GeO_4 nanorods with lengths of 0.5–1 μm were prepared, as shown in Figures 2(e) and 2(f). Therefore, the amount of CTAB in the reaction system had a profound effect on the final morphology of the as-synthesized samples. The Zn_2GeO_4 nanorods were only formed in the presence of urea and CTAB. Our previous researches had discussed the formation mechanism of Zn_2GeO_4 microspheres in the presence of urea [28]. In fact, CTAB is often used as a "capping reagent" in the preparation of nanomaterials because it can adsorb on solid surfaces and selectively bind to some specific panels to control the velocity and direction of crystal growth [16]. But the correlative mechanism about the formation of Zn_2GeO_4 nanorods under the effect of urea and CTAB is not clear yet.

UV-vis diffuse reflectance spectrum of Zn_2GeO_4 nanorods is shown in Figure 3. The Zn_2GeO_4 nanorods exhibited strong absorption in the UV region. The absorption

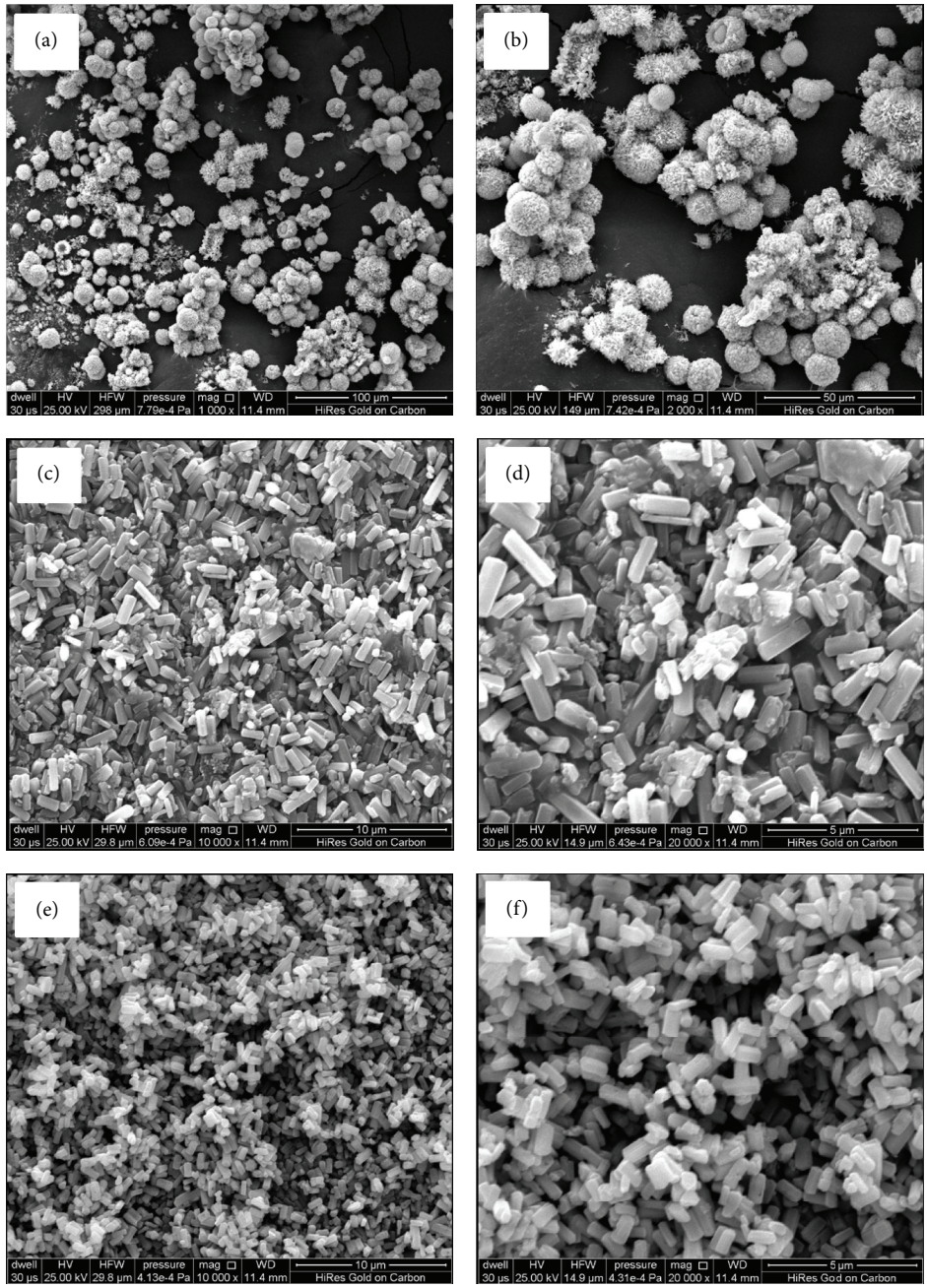

Figure 2: SEM images of the as-synthesized Zn_2GeO_4 samples with different CTAB content. (a, b) 0 g, (c, d) 0.018, and (e, f) 0.073 g.

edge of the Zn_2GeO_4 nanorods is about 275 nm. Thus, the band gap energy of the Zn_2GeO_4 nanorods estimated from the absorption edge is 4.5 eV based on

$$\alpha h\nu = A\left(h\nu - E_g\right)^{n/2}, \quad (1)$$

where a, ν, A, and E_g are the absorption coefficient, light frequency, proportionality constant, and band gap, respectively. Here n is equal to 1 as the Zn_2GeO_4 is a direct gap semiconductor [16]. The large band gap energy endows this photocatalyst with strong redox ability that efficiently improves photocatalytic reduction of Cr(VI).

3.2. Photocatalytic Experiments. Aqueous Cr(VI) was selected as a model pollutant to evaluate the photocatalytic performance of Zn_2GeO_4 nanorods. The initial solution pH is one of the most important parameters controlling the photocatalytic reduction in metal ions on semiconductor metal oxides. Figure 4 shows the photocatalytic reduction of aqueous Cr(VI) over Zn_2GeO_4 nanorods at different initial solution pH. From Figure 4, the initial pH plays an important role for the photocatalytic reduction of Cr(VI). In general, the Cr(VI) species may be in the form of $Cr_2O_7^{2-}$, $HCrO_4^-$, and CrO_4^{2-} in aqueous solution [29–31].

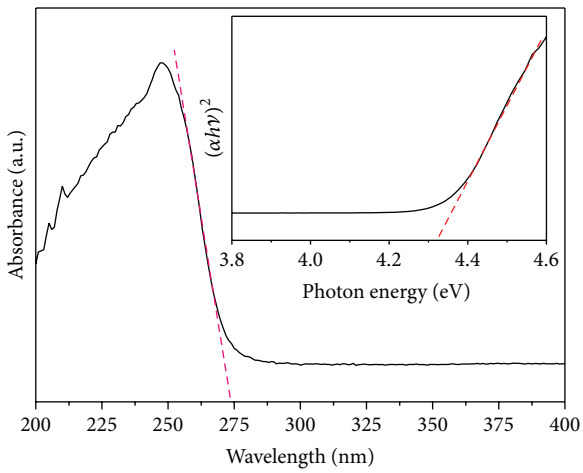

Figure 3: UV-vis diffuse reflectance spectrum of Zn_2GeO_4 nanorods.

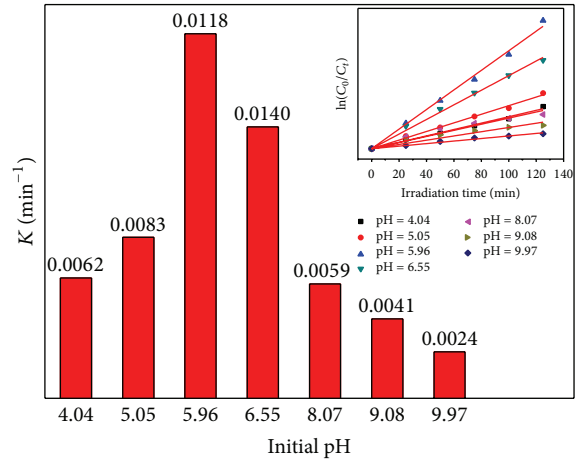

Figure 5: Kinetic studies of photocatalytic reduction of aqueous Cr(VI) by Zn_2GeO_4 nanorods at different initial pH.

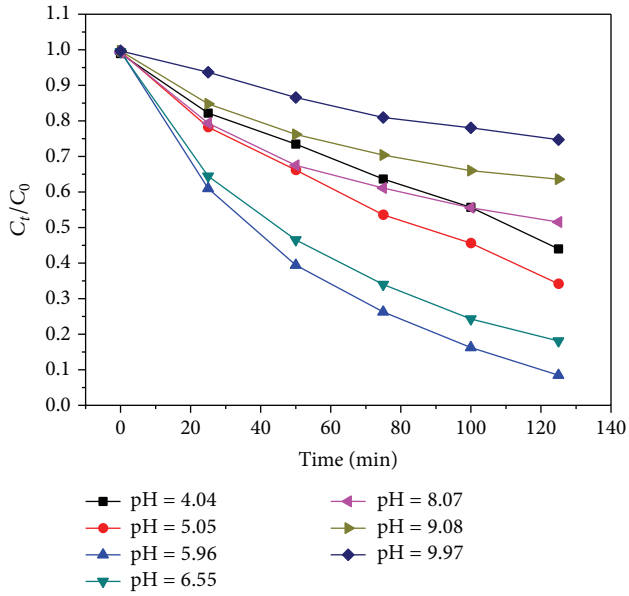

Figure 4: Photocatalytic reduction of aqueous Cr(VI) by Zn_2GeO_4 nanorods at different initial pH.

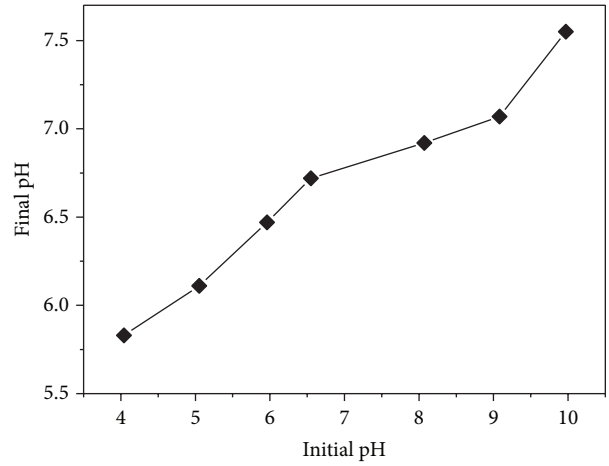

Figure 6: Variation of solution pH before and after photocatalytic reduction of aqueous Cr(VI).

The predominant form of Cr(VI) is $HCrO_4^-$ at a pH range from 2.0 to 6.0, while the major form was CrO_4^{2-} at pH above 7.0 [32, 33]. The main reactions for the photocatalytic reduction of aqueous Cr(VI) over the Zn_2GeO_4 nanorods may be given as follows:

$$HCrO_7^{2-} + 7H^+ + 3e^- \Longleftrightarrow Cr^{3+} + 4H_2O \quad (2)$$

$$CrO_4^- + 8H^+ + 3e^- \Longleftrightarrow Cr^{3+} + 4H_2O \quad (3)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \Longleftrightarrow 2Cr^{3+} + 7H_2O \quad (4)$$

From (2)–(4), it can be seen that H^+ was consumed in the reduction of Cr(VI) to Cr(III), so the reaction more easily occurred in the acidic solution. The efficiencies of aqueous Cr(VI) reduction were relatively low with the solution at pH of 4.04 and 5.05. The reason for this may be the decomposition of Zn_2GeO_4 nanorods. Meanwhile, the pseudo-first-order kinetic model for the reduction of aqueous Cr(VI) over the Zn_2GeO_4 nanorods was also investigated [34], as expressed by $\ln(C_0/C_t) = kt$, where k is the apparent rate constant, C_0 is the initial concentration of aqueous Cr(VI), and C_t is the concentration of aqueous Cr(VI) at the reaction time t. The linear plots of $\ln(C_0/C_t)$ versus t and the rate constants are shown in Figure 5. So it can be concluded that the efficiency of aqueous Cr(VI) reduction by the Zn_2GeO_4 nanorods is highest at pH 5.96.

Moreover, when the initial pH is 4–7, an obvious increase in final pH of solution was clearly observed in Figure 6, indicating that H^+ was consumed during the photocatalytic reduction of aqueous Cr(VI). However, the final pH was decreased when the initial pH is 8–10. The surprising result may be attributed to the formation of chromium in intermediate oxidation states such as Cr(III) and Cr(VI) [33].

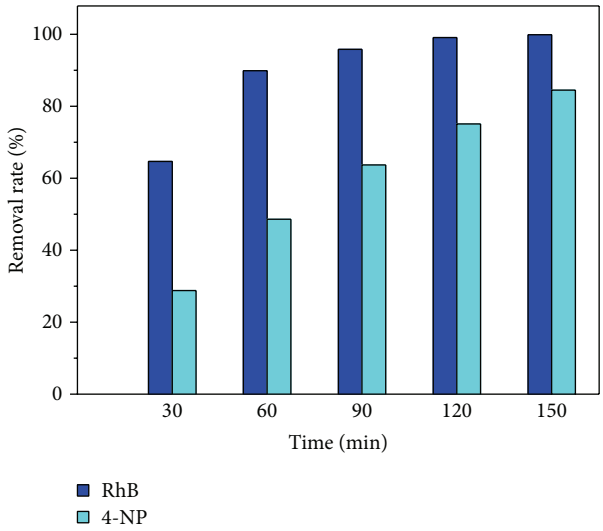

Figure 7: Photocatalytic degradation of 4-NP and RhB by Zn_2GeO_4 nanorods under UV light irradiation.

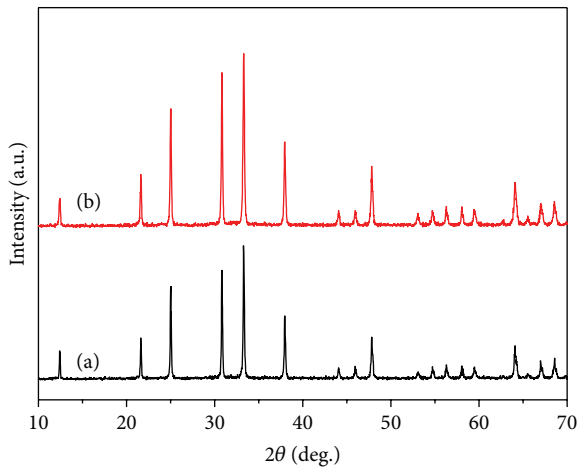

Figure 8: XRD patterns of the Zn_2GeO_4 nanorods (a) before and (b) after photocatalytic reduction of aqueous Cr(VI).

The Zn_2GeO_4 nanorods not only exhibited strong photocatalytic activity for the reduction of aqueous Cr(VI), but also showed excellent photocatalytic ability for the oxidation of organic pollutants (RhB and 4-NP). It can be seen from Figure 7 that the removal rates of RhB and 4-NP were increased with increasing irradiation time.

3.3. Photocatalytic Stability of Zn_2GeO_4 Nanorods. Since the stability of photocatalysts has always been a concern, it is important to investigate the stability of the Zn_2GeO_4 nanorods by the recycling experiment. After three recycles in the same reactions, the removal rate of Cr(VI) can still reach 75%. The sample collected after the third recycle was further characterized by XRD and SEM. XRD patterns (Figure 8) and SEM images (Figure 9) also show that there is no observable structural difference between the Zn_2GeO_4 nanorods before and after photocatalytic reduction of aqueous Cr(VI). These results indicated that the Zn_2GeO_4 nanorods were stable during the photocatalytic reduction of aqueous Cr(VI) process.

3.4. Possible Mechanism for Photocatalytic Reduction of Aqueous Cr(VI). A possible mechanism of the photocatalytic reduction of aqueous Cr(VI) by Zn_2GeO_4 nanorods is proposed (Figure 10). Under UV light irradiation, Zn_2GeO_4 nanorods were excited and photogenerated electrons (e^-) and holes (h^+) were generated. Considering the conduction band potential of −0.7 eV versus NHE is more negative than the standard reduction potential of Cr(VI)/Cr(III) (1.33 eV versus NHE), the photocatalytic reduction of Cr(VI) over Zn_2GeO_4 is thermodynamically allowed [22]. Thus, e^- in the conduction band of Zn_2GeO_4 can reduce Cr(VI) to Cr(III). In the absence of reducing agent, surface-adsorbed O_2 and H_2O accept h^+, producing $^{\bullet}OH$ radical. The $^{\bullet}OH$ can decompose the RhB and 4-NP. Moreover, $^{\bullet}OH$ radical in the photocatalytic process was detected by a photoluminescence (PL) method using terephthalic acid (TA) as a probe [35]. The PL emission spectra excited at 312 nm from TA solution (5×10^{-4} mol/L) were recorded at given time and the results are shown in Figure 11. From Figure 11, it can be seen that the intensity of PL emission spectra at about 426 nm increased with the increase of reaction time, indicating that $^{\bullet}OH$ radical existed in the photocatalytic process.

4. Conclusion

In summary, Zn_2GeO_4 nanorods were successfully synthesized by a simple hydrothermal method. The characterization results indicated that the amount of CTAB played an important role in the formation of Zn_2GeO_4 with different morphologies. Zn_2GeO_4 microspheres were formed without the introduction of CTAB. When the CTAB content was increased to 0.073 g, uniformly dispersed Zn_2GeO_4 nanorods with lengths of 0.5–1 μm were prepared. The Zn_2GeO_4 nanorods not only exhibited strong photocatalytic activity for

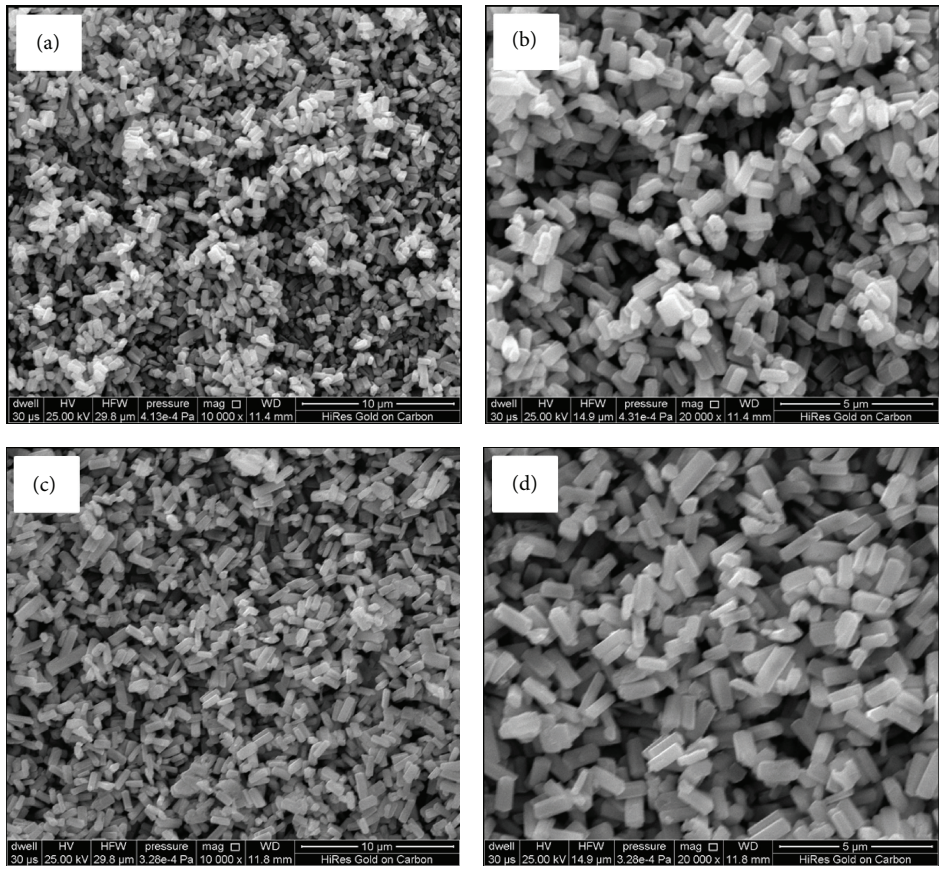

FIGURE 9: SEM images of the Zn_2GeO_4 nanorods (a, b) before and (c, d) after photocatalytic reduction of aqueous Cr(VI).

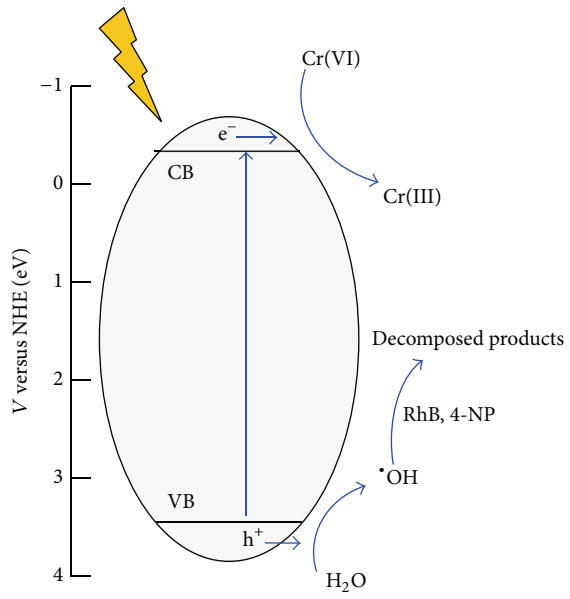

FIGURE 10: A schematic illustration of photocatalytic reduction of Cr(VI) and oxidation of organic pollutants by Zn_2GeO_4 nanorods under UV light irradiation.

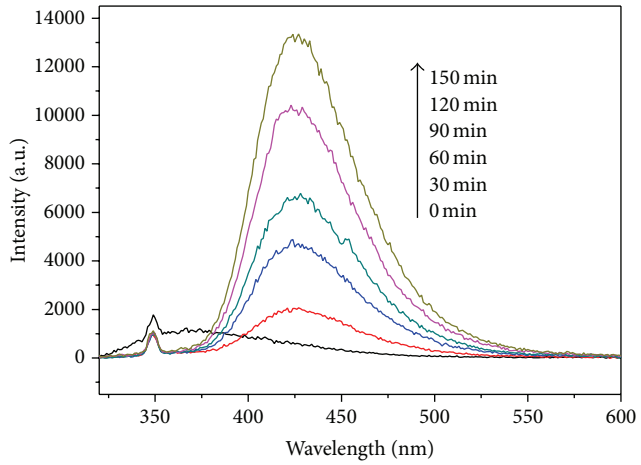

FIGURE 11: •OH trapping photoluminescence spectra of the Zn_2GeO_4 nanorods/TA suspension under UV light irradiation for different time.

the reduction of Cr(VI), but also showed excellent photocatalytic ability for the oxidation of organic pollutants such as

RhB and 4-NP. Recycling experiment proved that Zn_2GeO_4 nanorods possessed good photocatalytic stability. The novel Zn_2GeO_4 nanorods may find promising applications in the field of environmental photocatalysis.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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