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PHOTOCATALYTIC HYDROGEN EVOLUTION FROM WATER ON SiC UNDER VISIBLE LIGHT IRRADIATION

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Abstract

A kind of green SiC fine powder was characterized by XRD and UV-Vis diffuse reflectance, and studied in the photocatalytic splitting of water. The results showed that the green SiC fine powder can absorb visible light and split water with the formation of hydrogen under visible light irradiation. The activity is affected significantly by the initial pH of solutions and the types of cheap reagents, where the addition of OH⁻ or S²⁻ leads to a remarkable increase in the activity.

Keywords: SiC, visible light, water splitting, hydrogen evaluation

INTRODUCTION

Because of the physical and chemical properties of hydrogen, it is accepted as a nearly ideal energy carrier for the future. Since the pioneering work of Fujishima and Honda in 1972 [1], the photocatalytic production of hydrogen from water using semiconductors has been extensively investigated. In the past 30 years, various photocatalysts have been found. However, most of these catalysts can absorb only UV light. The development of visible-light-driven

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photocatalysts has been urged for utilizing solar energy effectively, and many effective catalysts have been reported, such as CdS, Cu₂O, Ta₃N₅, TaON, H₂Ti₄O₉, BaCr₂O₄, ZnFeO₄, In-Ta containing compounds, *etc.* [2-8].

SiC has been used to reduce carbon dioxide under UV light irradiation in the field of photocatalysis [9, 10]. Nariki *et al.* [11] produced ultra fine SiC powder from bulk SiC by arc-plasma irradiation, and found that the SiC powder could split pure water under UV light irradiation with wavelengths of 260 to 410 nm. The activity per unit surface area was estimated to be almost the same order of magnitude as that of conventional photocatalysts such as Pt/TiO₂. However, the author did not report whether the SiC powder is active or not under visible light irradiation.

In this letter, we report that a kind of green SiC fine powder, which is used as an abrasive material, is an active photocatalyst for the splitting of water under visible light irradiation. The green SiC fine powder was characterized and the effect of the initial pH of the solutions, the types of sacrificial reagents, *etc.* on the reaction rates were studied.

EXPERIMENTAL

Pretreatment of catalyst

SiC powder (particle size 400~500 nm; SiC, 98.46 wt.%; C, 0.11 wt.%; SiO₂, 0.12 wt.% with negligible amounts of metals) was obtained from Shenzhen Weina Ultra Fine Materials Co., China. The powder was first calcined in air at 700°C for 3 h to remove any organic residues, etched in a 2% HF solution for 5 h to remove the surface layer of SiO₂ and trace amounts of metals, thoroughly washed with deionized water and dried at 120°C for 12 h.

Characterization

X-ray powder diffraction (XRD) pattern was recorded by a Rigaku D/max v/pc diffractometer (Cu K_α radiation). UV-Vis diffuse reflectance spectrum was recorded on a JASCO V-570 spectrophotometer with BaSO₄ as a reference. FT-IR spectra were obtained using a Nicolet MAGNA 560 spectrometer with KBr pellets containing 1 wt.% of sample.

Photocatalytic reaction

Photocatalytic reactions were conducted in a gas-closed Pyrex reactor with a side flat window of 7 cm². The photocatalyst powder (0.05 g) was dispersed in deionized water or aqueous solution (40 mL). High purity nitrogen was bubbled

through the suspension before the reaction to remove oxygen. A 150 W xenon lamp was used to irradiate the reactor under magnetic stirring. The UV light in the beam was removed through a 1 M NaNO₂ solution. The gases collected were analyzed by gas chromatography (TCD, TDX column with N₂ as carrier gas).

RESULTS AND DISCUSSION

Characterization results

The X-ray diffraction pattern of the pretreated green SiC powder is given in Fig. 1. It is seen that all peak positions are consistent with those of standard hexagonal SiC (6H-SiC). The intense peaks of the SiC sample indicated its good crystallinity. In the XRD pattern, the presence of cubic SiC (3C-SiC) cannot be ruled out due to the significant overlap of its Bragg reflections with those of 6H-SiC.

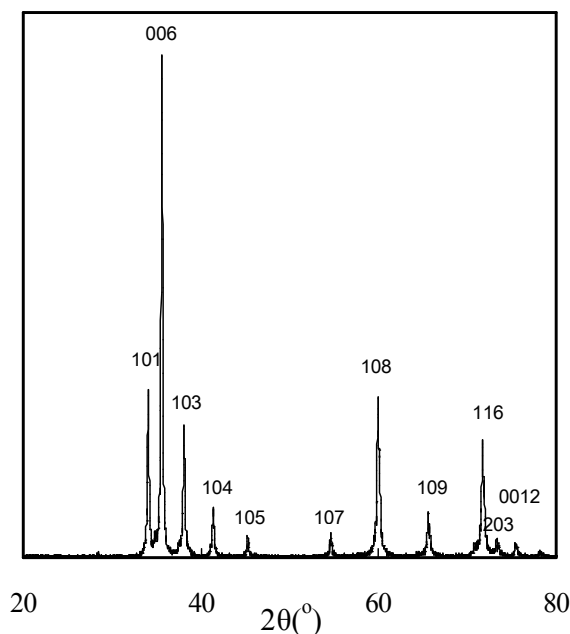


Fig. 1. XRD pattern of green SiC powder

The UV-Vis diffuse reflectance spectrum of the pretreated green SiC powder is shown in Fig. 2. The absorption edge of this SiC powder starts at about 550 nm, with the band gap estimated at about 2.3 eV [12]. In fact, the green color indicates

that it can absorb visible light. It was reported that 6H-SiC and 3C-SiC have the band gap of 3.0 and 2.2 eV, respectively. The UV-Vis diffuse reflectance spectrum indicates that the green SiC powder might contain some 3C-SiC phase.

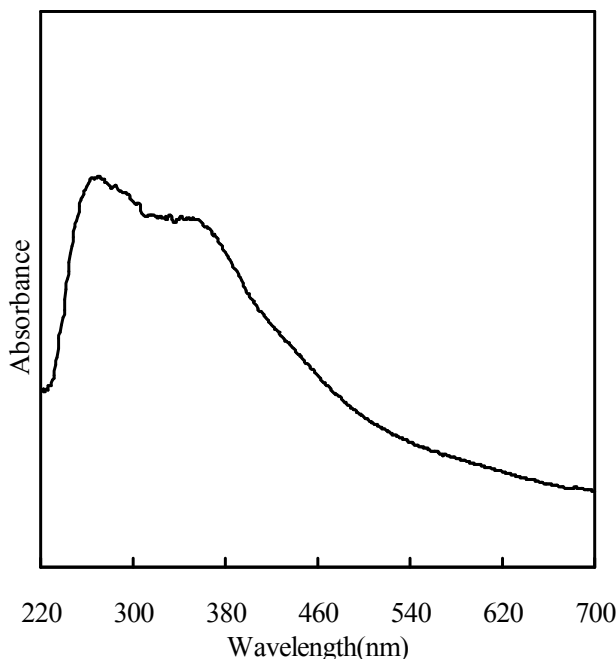


Fig. 2. UV-Vis diffuse reflectance spectrum of green SiC powder

Photoactivity of SiC

Photocatalytic H₂ evolution results from pure water or aqueous solutions containing Na₂S, CH₃OH and EDTA as sacrificial reagents under visible light irradiation are shown in Fig. 3. Figure 3 shows that this kind of SiC powder can split pure water under visible light irradiation. The average rate of H₂ generated in 10 h was 24.9 $\mu\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. The conduction band of SiC is much more negative (-1.4 eV, vs. SHE) than the reduction potential of water to form H₂ (0 eV), and it can absorb visible light. This fact may explain why the green SiC powder is active in splitting pure water.

Figure 3 also shows that the addition of Na₂S enhanced the activity remarkably, whereas the effect of CH₃OH was not appreciable, while EDTA completely suppressed the activity. However, Galinska *et al.* [13] reported that Na₂S, CH₃OH, and EDTA were all effective cheap reagents in the Pt/TiO₂ photocatalytic system and deduced that these reagents could trap the

photogenerated hole and thus increase the photoactivity. This difference between Pt/TiO₂ and the present green SiC powder may be explained by the different band structure of TiO₂ and SiC. The potential of the valence band of SiC is less positive than that of TiO₂, therefore photogenerated holes from SiC are less oxidative than those of TiO₂. Thus, under visible light irradiation, SiC can only oxidize S²⁻, but not CH₃OH and EDTA. Instead, the adsorbed EDTA molecules on the SiC surface might prevent the absorption of light, and suppressed the water splitting.

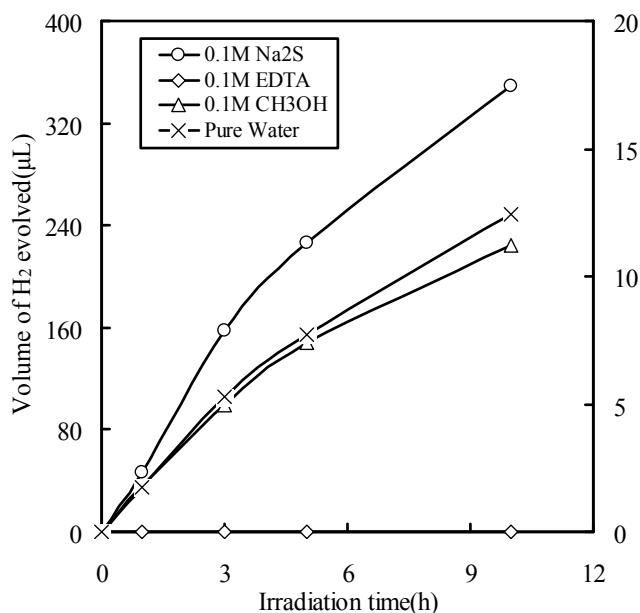


Fig. 3. Photocatalytic H₂ evolution from various aqueous solutions under visible light irradiation: (A) 0.1M Na₂S (O); (B) 0.1M EDTA (◊); (C) 0.1M CH₃OH (Δ); (D) Pure Water (×)

Reaction conditions: solution 40 mL, catalyst 0.05 g

Effect of the initial pH of the solution on the photoactivity is shown in Fig. 4. The activity was affected significantly by the pH of the solution. Addition of OH⁻ led to a remarkable increase in the activity. The volume of H₂ evolved from the pH = 12 solution was about 50 times of that from pure water under the same reaction conditions. It was reported that two equilibria exist on the SiC surface in aqueous solution [14]:

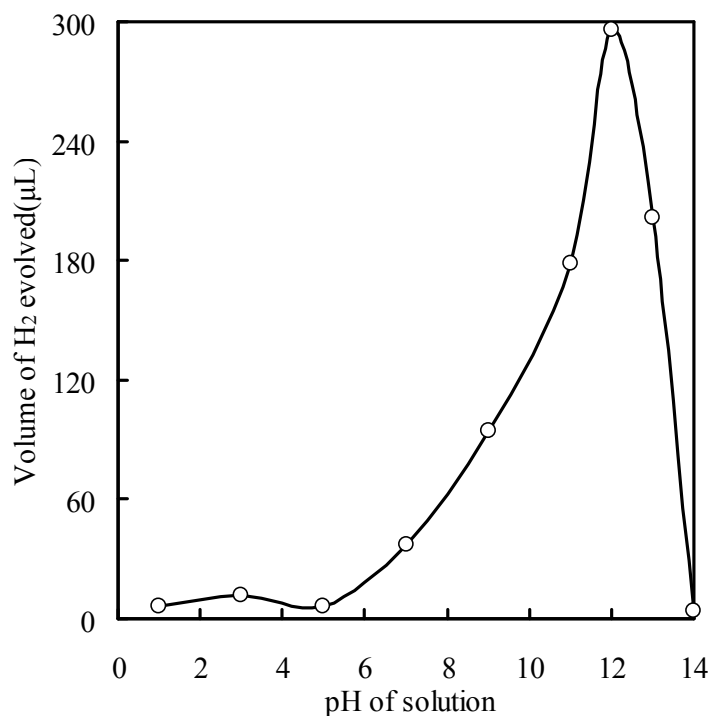
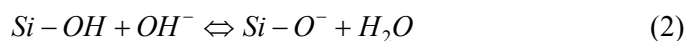
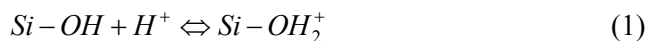


Fig. 4. Effect of initial pH of the solution on water splitting.
Reaction conditions: solution 40 mL, catalyst 0.05 g, irradiation time 5 h, pH adjusted with H₂SO₄ or NaOH

At high pH values more H⁺ ions would be adsorbed on the SiC surface, and hence the possibility for the reduction of H⁺ to H₂ by electrons in the conduction band would also be higher. Similar trends were also found on other photocatalysts [15, 16]. However, it is a surprise to find that the activity increase is so sharp with the increase of pH. It was reported that the pH change of a photocatalytic system shifts the position of the valence band and the conduction band edge, which in turn affects the ability of photo-oxidation or photo-reduction of the semiconductors [17]. However, the conduction band of SiC is much more negative than the reduction potential of water to form H₂. So, this effect on the activity can be ignored. This suggests that the adsorption of H⁺ plays a vital role in the photocatalytic reaction on SiC. The life span of photogenerated electron-hole pairs might be long enough to reduce H⁺ adsorbed.

The abrupt decrease of photoactivity above pH 12 might be related to the dispersion of SiC powder in the solution. In fact, a remarkable aggregation was observed at pH above 12.

Oxygen was not detected in either of the experiments, even in splitting of pure water. The infrared spectra of SiC powder before and after photocatalytic splitting of pure water indicated that the absorption peak attributable to the stretching vibration of Si-O at 1100 cm^{-1} considerably increased after the reaction (the results are not shown here). This is consistent with the result of Nariki's work [11]. In one experiment, 0.5 g pretreated SiC was dispersed in 40 mL solution at pH = 12 and irradiated until the catalyst deactivated, then the suspension was centrifuged. It was found that the pH value of the clear solution was 10.1, and white silicic acid colloids were generated in the solution after a HCl solution of 0.1 M was added. The results suggest that the photogenerated holes oxidize the SiC to form SiO_2 on the surface. However, after etching in HF aqueous solution, the activity could not be regenerated. The reasons why no oxygen was released need to be studied further.

In conclusion, the green SiC micropowder can split pure water to produce hydrogen under visible light irradiation. The activity was affected significantly by initial pH of the solution and the type of sacrificial reagents. The addition of OH^- or S^{2-} led to a remarkable increase in the activity.

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