

Research Article

Highly Branched Sn-Doped ZnO Nanostructures for Sunlight Driven Photocatalytic Reactions

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Ultralong, highly branched Sn-doped zinc oxide (ZnO) nanostructures were fabricated using a simple substrate-free chemical vapor deposition (CVD) method. The nanostructures exhibited efficient photocatalytic activities in degradation of methylene blue (MB) under natural sunlight. 100% of MB with the concentration of 10 mg/L could be completely removed within 36 minutes. Possible reasons for the enhanced photocatalytic effect were analyzed.

1. Introduction

Energy and environment issues are two severe problems we face today. Utilizing solar energy is considered as one of the major strategies to solve the energy and environmental problems. Photocatalytic effect is a perfect interpretation, which can complete renewable energy generation and environmental remediation without any harmful materials. However, there are two major drawbacks for traditional photocatalytic materials. First, the recombination of photogenerated electrons and holes is too fast, which results in low quantum efficiencies and limits the photocatalytic potentials. Second, the utilization of solar energy is limited, which greatly hinders the commercialization of such technology. Great efforts have been made to overcome these two issues. Cocatalysts such as noble metals [1, 2], grapheme [3], and semiconducting quantum dots [4] have been proved to be effective in reducing the probability of carrier recombination. In order to expand the band of solar energy adsorption, we can either tune the bandgaps of semiconducting photocatalysts or use composite photocatalytic materials [5, 6]. On the other hand, to increase the effective areas for solar energy absorption and photocatalytic reaction, the surface areas of the photocatalysts are expected to be as large as possible.

Among all the photocatalysts, ZnO is considered to be very competitive due to its nontoxic nature, low cost, high reactivity, and good conductivity. Moreover, one-dimensional ZnO nanostructures have the most abundant

morphologies; thus the surface to volume ratio (S/V) can be tuned in a wide range. ZnO hollow structures [7], nanoflowers [8], and nanosheets [9] are proved to have enhanced photocatalytic efficiency than ZnO nanoparticles due to the large S/V . On the other hand, doping ZnO with other elements such as Sn, Al, and Ti has been proved to be effective in adjusting the bandgap, resulting in enhanced light adsorption in the visible wavelength range [10–12].

In this work we report a simple substrate-free, catalyst free, high-yield growth method for fabricating highly branched Sn-doped ZnO nanostructures. The products can be synthesized in large scale if only the precursors are sufficient. The ZnO nanostructures exhibited excellent photocatalytic activities in the degradation of methylene blue (MB) in aqueous solution under natural sunlight irradiation. The superior photocatalytic behaviors can be attributed to the combined effects of large S/V , abundant surface defects, and enhanced visible light adsorption. Scanning electron microscope (SEM) was used to characterize the morphologies. Photoluminescence (PL), Raman, and X-ray diffraction (XRD) were carried out to examine the defects and crystal structures.

2. Experimental

2.1. Synthesis of Sn-Doped ZnO Nanostructures. Sn-doped ZnO nanostructures were synthesized using a single-tube

chemical vapor transporting and condensation system equipped with Lindberg blue furnace. The diameter of the tube is 2.54 cm and the length is 65 cm. Prior to nanostructure growth, the temperature inside the furnace was carefully calibrated using a K-type thermocouple (TES 1310, Taiwan). Zinc oxide (Alfa Aesar 99.99%) and tin oxide (Alfa Aesar, 100%) mixed with equal amount of graphite (200 mesh, Alfa Aesar 99.99%) were calibrated using a K-type thermocouple (TES 1310, Taiwan). Zinc oxide (Alfa Aesar 99.99%) and tin oxide (Alfa Aesar, 100%) mixed with equal amount of graphite (200 mesh, Alfa Aesar 99.99%) powders were placed in a quartz tube with appropriate position directly which was positioned in the furnace during growth. The weight ratio of ZnO and SnO₂ precursors is kept at 95%:5%. High purity argon (Ar, 99.999 + %) and oxygen (O₂, 99.999 + %) with different ratios were used as the carrier gas at a constant total flow rate of 50 sccm. During the experiment, the targeted temperature of the inside of the furnace was 900°C with heating rate 30°C/minute, and the holding time was 25 minutes for all the samples under environmental conditions.

2.2. Sample Characterization. The morphologies of the samples were characterized using a field-emission SEM (FE-SEM, FEI, Quanta FEG). The crystal structures of as-prepared sample were tested using X-ray diffraction (XRD, Bruker, D8 Advance). Room temperature PL spectra were collected using FS 920 type spectrometer (Edinburgh) at the exciting wavelength of 325 nm. Raman spectra of ZnO nanostructure were examined using Raman station 400 F machines (PerkinElmer). The light absorbance spectra were obtained by spectrometer with UV-Vis-2550.

2.3. Photocatalytic Reactions. The photocatalytic activities of samples were examined using methylene blue (MB) as the indicator. Different weights of Sn-doped ZnO photocatalysts were added into a bottle containing 40 mg MB aqueous solution with the concentration of 10 mg/L. Then the photocatalysts were magnetically stirred in the dark for 30 minutes to reach adsorption-desorption balance. The photodegradation experiments were carried out under natural sunlight (the power intensity was measured to be 1.8 mW/cm²). The solutions were sampled at intervals of 6 minutes and centrifuged at 8000 rpm, then analyzed by recording variations in the absorption band (664 nm) in the UV-Vis spectra of MB using UV-Vis-2550.

3. Results and Discussions

The growth process of Sn-doped ZnO branched wires is schematically illustrated in Figure 1(a). According to thermal analysis results (see Figure S1 in Supplementary Material available online at <http://dx.doi.org/10.1155/2014/381819>), Sn will be evaporated at a relatively low temperature. The Sn vapor condensed at the surface of the precursor powders. Because of the low melting point of Sn metal, droplet will form at the surface of the powders, which will serve as the active sites for the subsequent Zn vapor deposition. Therefore the growth is a substrate-free self-catalyzed process, which

is cost-effective and suitable for large scale production. Figures 1(b) and 1(c) show the low magnification and high magnification SEM images of the as-synthesized samples. From Figure 1(b), it can be seen that the wires are extremely long with highly branched nanorods. The length of the stem is up to several millimeters which can be obtained from optical microscope image inset of the Figure 1(b). The lengths and the width branched nanorods are in the range of 5–10 μm and 0.4–0.8 μm, respectively. From the XRD pattern in Figure 1(d), it is obvious that the sample has typical wurtzite crystal structures with four characteristic peaks. The strong peaks located at 32.28°, 34.96°, 36.62°, and 57.03° are corresponding to the miller index of (100), (002), (101), and (110) phases of ZnO. No peaks related with SnO₂ were detected, demonstrating that the Sn atoms were completely dissolved in the ZnO lattices.

Figure 2 summarized the optical properties of the Sn-doped ZnO nanostructures. For comparisons, pure ZnO were also measured. Figure 2(a) is the Raman spectra of Sn-doped ZnO and undoped ZnO nanowires. Wurtzite ZnO belongs to P6₃mc space group and crystal symmetry is C6V₄. The center of the Brillouin is $\Gamma_{\text{opt}} = A_1 + 2B_1 + E_1 + 2E_2$, where A_1, E_1 are polarity mode which is infrared and Raman active, E_2 is nonpolar and Raman active only, B_1 is static with nothing. 333 cm⁻¹, 383 cm⁻¹, 438 cm⁻¹, 577 cm⁻¹, and 1151 cm⁻¹ can be attributed to $2E_2, A_1$ (TO), E_2 (high), A_1 (LO), and $2E_1$ (LO) mode, respectively. The strongest peak at 438 cm⁻¹ was usually associated with crystalline quality and the peaks at 383 cm⁻¹ and 577 cm⁻¹ usually correspond to oxygen deficiency. It can be seen that the increase in visible emission intensity for the Sn-doped ZnO compared with that of the pure could be attributed to intrinsic defects, which are created only when Sn diffused in the ZnO host matrix. The photoluminescence spectra of as-prepared Sn-doped ZnO nanostructures and undoped samples are shown in Figure 2(b). While undoped ZnO nanowires only show strong intrinsic emission, Sn-doped sample has significant visible peak centered at 500 nm, which can be attributed to the defect related emission. The light emission in the visible range demonstrates the formation of the many intermediate energy levels in the bandgaps of ZnO. The defects may contribute to the photocatalytic efficiency in two ways. First, the decrease of bandgap will facilitate the visible light absorption. Second, surface oxygen deficiencies can serve as electron capture centers, which could reduce the recombination rate of photogenerated electrons and holes. Otherwise, their UV emission broadens towards longer wavelengths which could be attributed to the decrease of the bandgap when ZnO is doped Sn. We believe that luminescence of the Sn-doped ZnO is related not only to intrinsic defects but also to the nature of Sn ions present in the ZnO host lattice, which need further study. The optical absorption characters of the samples were examined using UV-Vis diffuse reflectance spectrum, as is shown in Figure 2(c). Obviously, the samples show significant adsorption in the visible range compared with pure ZnO [13] and commercial TiO₂ [14], which is related with the reduced bandgap width caused by Sn doped. Figure 2(d) shows the transient photocurrent response of the samples. It

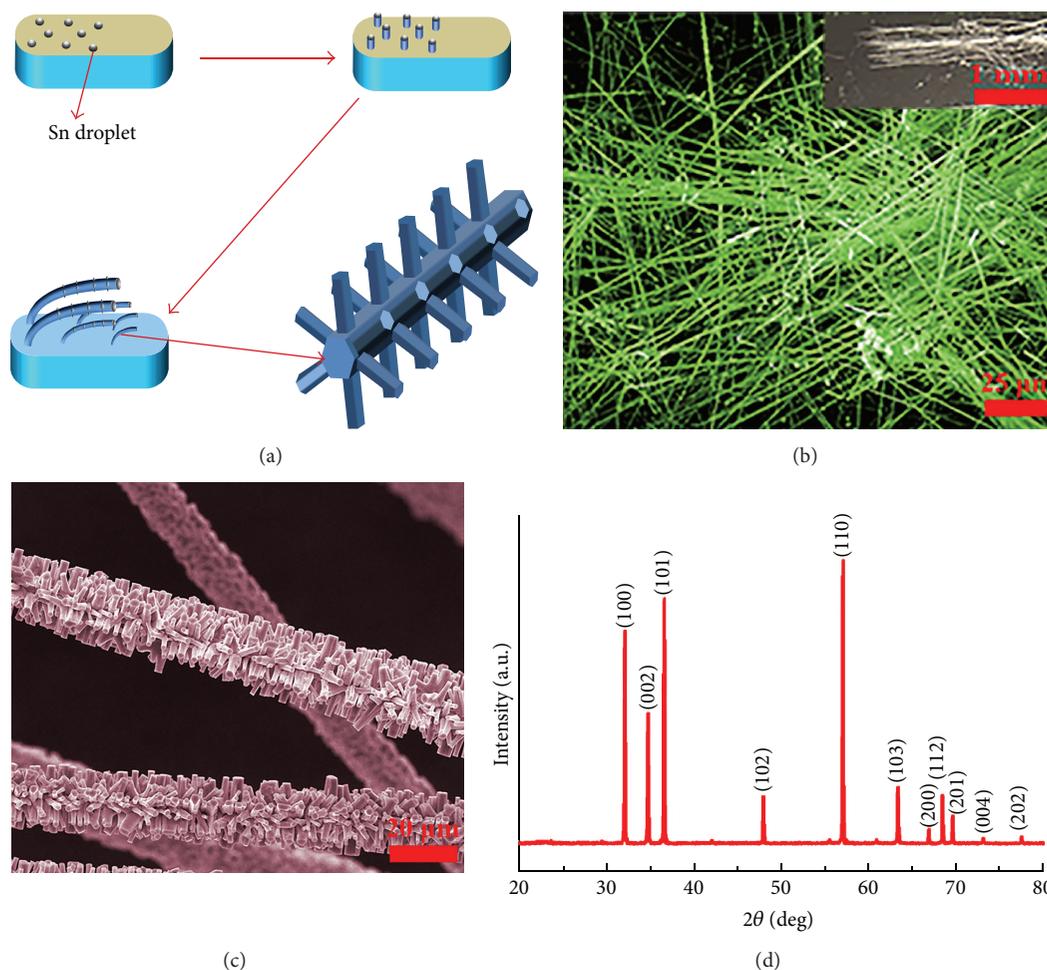


FIGURE 1: Morphologies and structures of as-synthesized samples. (a) Schematic diagram of the growth process. (b) Low-magnification SEM image. Inset: optical microscope image of the aligned samples. (c) High-magnification SEM image. (d) XRD pattern.

can be seen that the photocurrent increased eight times under the irradiation of sunlight. The photocurrent was greatly improved compared with undoped ZnO, indicating that the charge separation rate was enhanced.

The photocatalytic activity of these ZnO nanostructures was examined using methylthionine chloride (MB) as the indicator. Natural sunlight was used as the light source. The reaction process is monitored spectrophotometrically by measuring the degradation of MB, which exhibits a distinct spectral profile with an adsorption maximum at 664 nm. From Figure 3(a), it is clear that the concentration of MB decreases dramatically while catalyzed using Sn-doped ZnO nanostructures. 60% of the MB dyes can be decomposed in 6 minutes. The MB dyes can be completely removed in 36 minutes. In comparison, the photocatalytic efficiency of undoped ZnO is obviously lower. In 36 minutes, only 60% of MB can be decomposed. The C/C_0 curves as a function of time were plotted in Figure 3(c), both pure ZnO and the Sn-doped ZnO photocatalysts can effectively remove the MB. Moreover, the Sn-doped ZnO catalysts exhibit higher photocatalytic activity compared with pure ZnO. The kinetic curve shows linear relationships with time and can be fitted

using the kinetic equation $\ln(C/C_0) = -kt$, demonstrating that the photodegradation reaction of MB can be considered as a pseudo-first-order reaction. Kinetic value is an important parameter for the photocatalyst. Figure 3(c) shows the bar graph of rate constants which could reach 0.11 min^{-1} when catalyzed by Sn-doped ZnO, which is almost 4 times higher than that of pure ZnO. Also, it is much higher than the values reported in the literatures [15–18], suggesting that Sn-doped branched nanowires have superior photocatalytic effects.

The superior photocatalytic efficiency of Sn-doped ZnO branched nanostructures can be schematically illustrated in Figure 4. When the photocatalysts were irradiated by sunlight with the photon energy $h\nu$ that matched or exceeded the bandgap energy (E_g) of ZnO (3.37 eV), electrons could be excited from the valence band (VB) to the conduction band (CB), simultaneously leaving the same number of holes behind in the VB. The holes and electrons would react with H_2O and oxygen dissolved in water which were adsorbed at the surface of ZnO nanostructures and generated hydroxyl radicals ($\cdot\text{OH}$) and superoxide anions radicals (O_2^-), respectively, with extremely high oxidation properties. These OH radicals and superoxide anion radicals could decompose MB

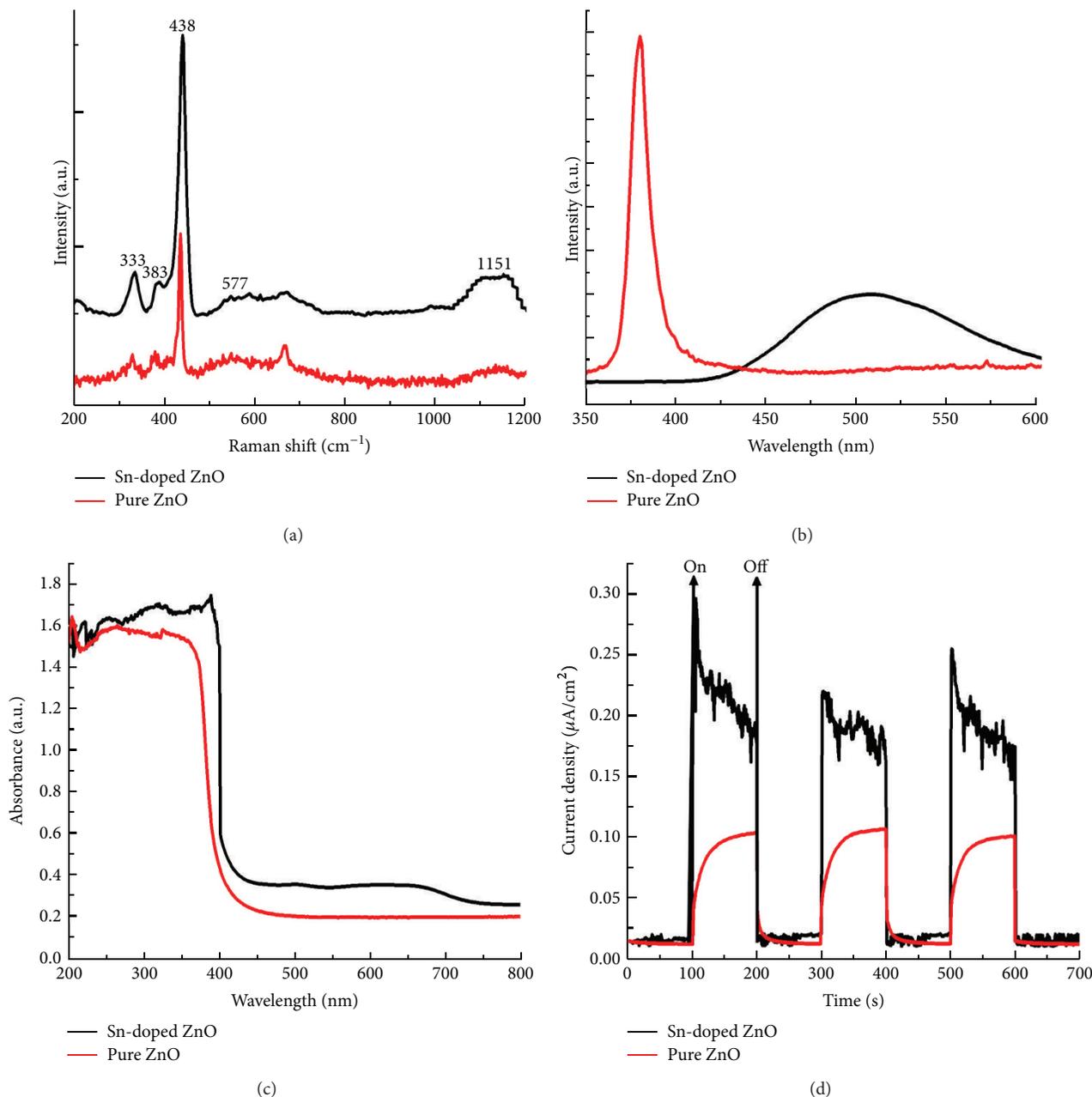


FIGURE 2: (a) Raman spectra. (b) PL spectra. (c) UV-Vis absorbance curve. (d) Transient photocurrent response of as-synthesized samples and pure ZnO.

dye into dioxide and water, resulting in the mineralization of organic dyes in the aqueous solution. The superior photocatalytic activity of Sn-doped ZnO branched wires must be related with their unique morphologies and abundant surface defect states. Branched ZnO nanostructures have large S/V , which could facilitate the light adsorption, increase the concentration of photo generated carriers, and enlarge the effective area of photodegradation reaction. Countless branches of the microwires will significantly decrease the light reflection and enhance the sunlight utilization rate. Besides, surface defects of the samples were also considered to be a critical factor for enhancing photocatalytic

activity. A bunch of defects states were formed during the synthesis of ZnO nanostructures, which was confirmed by PL spectra (Figure 2(b)) and Raman spectra (Figure 2(a)). These defects could trap photogenerated holes by forming shallow levels and therefore the recombination probability of electrons and holes could greatly be restrained. On the other hand, surface defects will cause many intermediate energy levels in the bandgaps of ZnO, which will enhance the light adsorption in the visible range (Figures 4 and 2(c)). Therefore the photocatalytic efficiency could be greatly improved. The band structure in Figure 4 illustrates that many intermediate energy formed because of the deficiency

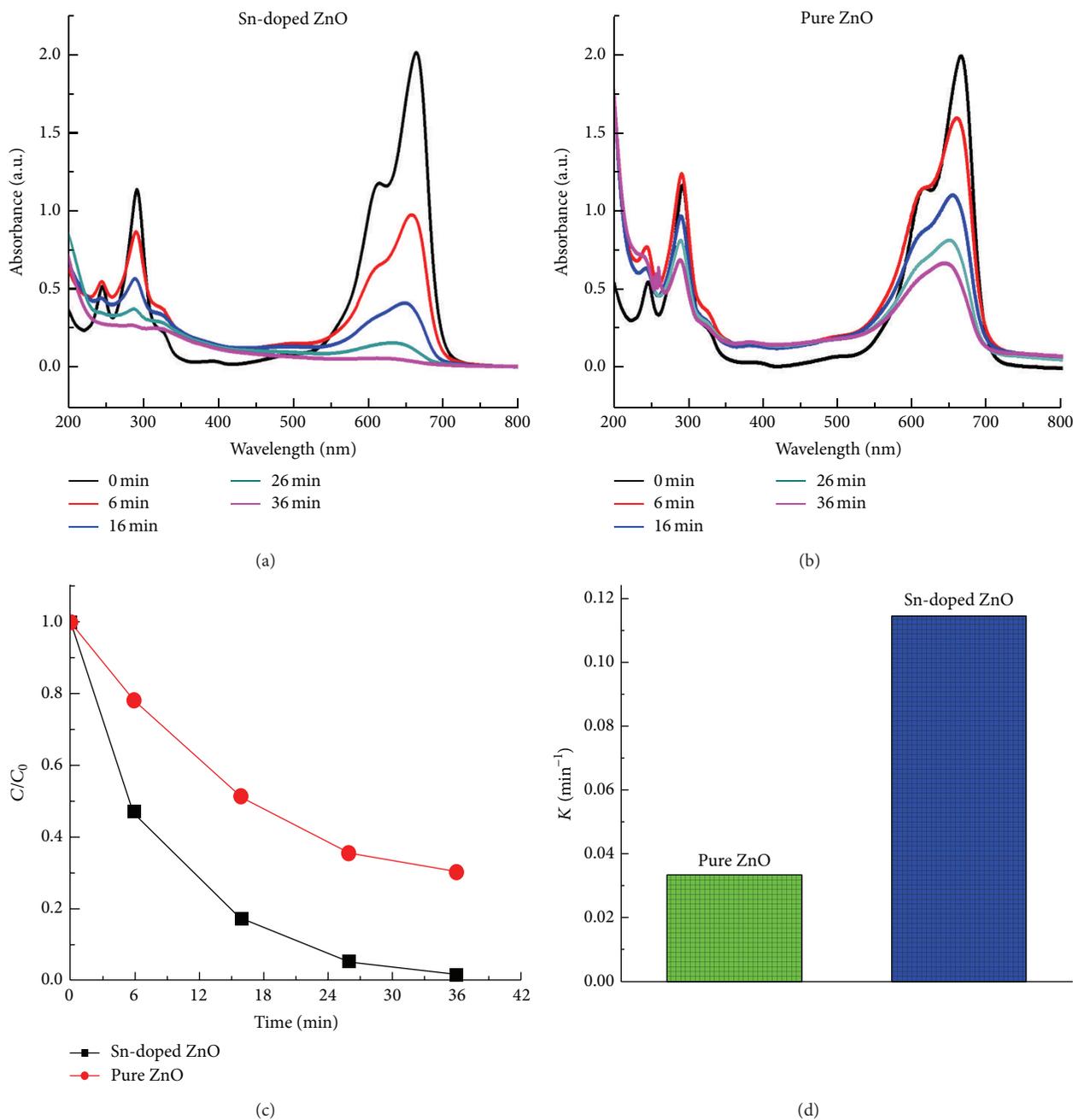


FIGURE 3: (a)-(b) Absorption spectra of MB solution at different time after irradiating under the natural solar light using Sn-doped ZnO nanostructures and pure ZnO as the photocatalyst. (c) The C/C_0 versus time curves of MB. (d) Rate constants of Sn-doped and pure ZnO photocatalyst.

which will significantly increase the light absorption in the visible range.

4. Conclusions

In summary, Sn-doped ZnO nanostructures were successfully synthesized using simple, substrate-free, and catalyst-free CVD method. The nanostructures are highly branched and have abundant surface defects, which are desirable for the application of photocatalysts. Photocatalytic performances of

these nanostructures were evaluated using MB solution as the indicator under the natural sunlight. The results demonstrated that the photocatalysts are very efficient. 100% MB was decomposed in 36 minutes. The superior photocatalytic behavior can be attributed to the synergetic effect of large S/V and rich surface oxygen states. Our research provided a simple yet efficient way to fabricate ZnO based photocatalysts in large scale. Also, the “superlong” nature of Sn-doped ZnO nanostructures suggests that the photocatalysts are recyclable, which is also critical for the commercial use.

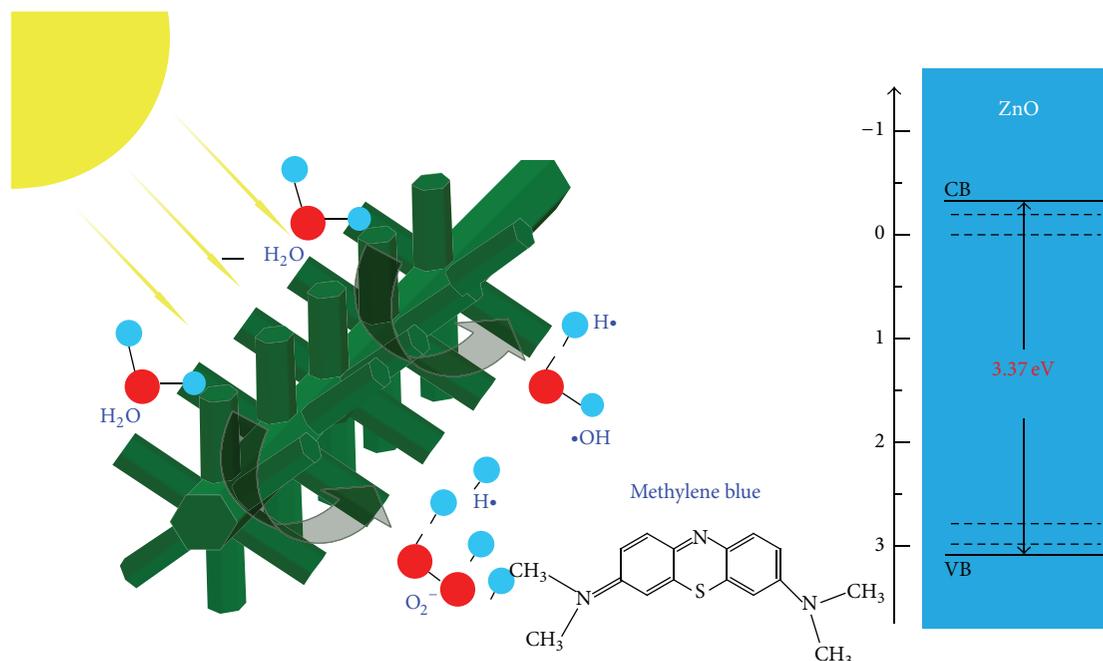


FIGURE 4: Schematic diagram of photocatalytic mechanism of ultralong Sn-doped ZnO nanostructures.

Conflict of Interests

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

Acknowledgments

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