Photocatalytic Decomposition of Organic Compounds on WC/WO_3 Heterogeneous Hybrid with Vis-NIR Light

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ABSTRACT

In this work, we report a hierarchical WC/WO_3 hybrid in-situ synthesized by one-step solvothermal reactions. The hybrid as photocatalyst exhibited distinctive photocurrent responses and enhanced degradation of Rhodamine B molecules with visible and near-infrared light (λ=400 − 800 nm). The specific interfacial interaction between WC and two-dimensional WO_3 layers creates Schottky barrier, leading to interfacial charge transfer from conduction band of WO_3 to WC. This finding provides a cost-effective approach to capture low-energy photons in environmental remediation applications.

INTRODUCTION

Photocatalysis has a great potential in the applications of clean energy and environmental sustainability. Developing semiconductor catalysts that respond to low-energy photons is the most effective route to utilize solar energy. For example, titania (TiO_2) as one of the important semiconductor photocatalysts had been extensively studied to obtain a reduced bandgap energy for solar light harvesting, such as impurity doping.[1-3] Alternative semiconductors with intrinsic narrow bandgaps are also being explored.[3-4]

Tungsten trioxide (WO_3) semiconductor with a bandgap energy of 2.6 – 2.8 eV is capable of absorbing blue light (~ 12% solar light).[5-8] Thus, WO_3-based catalysts have been employed for water oxidation and water purification with visible light.[7, 9-10] Nevertheless, the efficiency of photocatalytic performance over the pristine WO_3 is still challenging due to its intrinsic property associated with band electronic density of states.[9] In particular, WO_3 material is an inactive photocatalyst for oxidative decomposition of organic compounds because of the inappropriate conduction band position for the reduction of O_2 via a single-electron processe.[1, 11] Introducing co-catalysts and forming a Z-scheme band structure, such as loading platinum (Pt) (Pt/WO_3)[12] and WO_2 material (WO_2/WO_3)[7] has been reported with their high photocatalytic activities for the decomposition or oxidation of organic compounds.[12-13] In this case, multi-electron reduction of O_2 by photoexcited electrons in WO_3 can be significantly accelerated the oxidation of organic compounds by holes in the valence band. For example, the Pt/WO_3 was reported to be an active photocatalyst for phenol decomposition.[1, 12] However, the employment of noble metals, especially Pt, may not be a cost-effective strategy for environmental remediation. Based on the electrons density of states of Pt, developing highly active alternatives to noble metals is highly desired.[14]

Binderless tugnsten carbide (WC) possesses the d-band similar to that of platinum,[14-16] leading to Particularly, an comparable electronic density of states near the Fermi level.[1, 15, 17-18] Furthermore, its appropriate work function of 5.0 eV, outstanding stability, and strong resistance against catalytic poisoning with specific oxygen adsorption make WC material a promising substitue for noble-metal co-catalysts.[1, 19] For example, WC exhibits enhanced photocatalytic activities of both hydrogen evolution and hydrogen oxidation reactions.[16, 20] Thereby, we seek to harness the synergistic effects of low-energy photons response of WO_3 and platinum-like bahavior of WC to promote the photocatalytic efficiency of oxidative decomposition of organic compunds.[21]

Here, we prepared the WC/WO_3 heterogeneous hybrid via a single-step solvothermal method. The hybrid has a hierarchical structure with a flower-like morphology comprising of two-dimensional WO_3 multilayers. More importantly, in the absence of noble metals, the WC/WO_3 hybrid photocatalyst exhibits remarkable photocurrent responses and excellent oxidative decomposition of organic dye pollutant (Rhodamine B) with visible and near-infrared light (λ=400 – 800 nm), Which can be attributed to its band structure and interfacial charge transfer.

RESULTS AND DISCUSSION

Synthetic approach of WC/WO_3 hybrid material is inspired by the roles of oleylamine and the reduction of isopropanol.[58, 59] The oleylamine molecules can electrostatically coordinate to organic W^{6+} and then self-assemble to form lamellar micelles.[60] This is due to the weakly cationic amphiphile and nitrogen terminus of oleylamine allowing for binding to organic W^{6+} precursor. The hydrolysis of W^{6+} can therefore occur on the micelles and consequently form two-dimensional WO_3 layers. The surface carbon in the form of chemically bonded W-C is the substitute for lattice oxygen of WO_3 surfaces, resulting in the formation of WC/WO_3 hybrid.

The SEM images (Figures 1a and b) of the as-prepared sample show a flower-like morphology. Figure 1c presents the characteristic diffraction peaks, which can be indexed to the hexagonal WO_3 (JCPDS No. 85-2460). Interestingly, we also found two weak diffraction peaks positioned at 31.5° and 48.2°, which correspond to the hexagonal WC (JCPDS No. 73-0471). In addition, we noticed that the W, O, and C elements were homogeneously distributed in the whole sample from EDS mapping, as shown in Figure 2a.

Interestingly, the flower-like structure of WC/WO_3 is consisting of two-dimensional (2-D) layers, as shown in TEM images (Figures 2a and b). Furthermore, the AFM image and height profiles in Figures 2c and d indicate a stacking thickness of around 3.0 nm , probably compromising of WC and WO_3 layers. The crystalline structure with hexagonal oriented patterns can be clearly indicated in HR-TEM images (Figure 2e and f). These observations establish that the synthesized WC/WO_3 material has a hierarchical 3-D flower-like structure obtained by self-assembling ultrathin 2-D layers.

To further investigate the structure of WC/WO_3, we performed scanning TEM (STEM) imaging using an annular dark-field detector (ADF). We can clearly see the hexagonal lattice of W atoms (Figure 3a), which closely matches WC atomic structure (see the overlaid atomic structure). This further confirms that 2-D WC layer was *in-situ* formed on the surface of WO_3 layers. However, there are also regions where the W atoms are linked together to form bright lines, with individual W columns unresolved, because of the overlap of layers of WC and WO_3 materials. As the W sublattices in WC and WO_3 are different, the W atoms in the two layers will not be aligned at every point (see Figure 3b). In the circled regions, the W atoms form hexagonal lattice patterns, while in some other regions the projected W atoms are close to their nearest neighbors and thus form line lattice patterns instead of well-resolved atoms. This phenomenon is consistent with the arrangement of W atoms in the experimental STEM image (Figure 3a).

X-ray photoelectron spectroscopy (XPS) study was carried out to provide chemical information of the WC/WO_3 hybrid. The survey XPS spectrum (Figure 4a) indicates that both pure WO_3 and WC/WO_3 materials contain the W, O, and C elements. However, the WC/WO_3 hybrid gives rise to a relatively stronger intensity of C element, indicating more C in WC/WO_3 hybrid. Figure 4b shows additional new peaks in W 4f spectra of WC/WO_3 hybrid, different from pure WO_3 materials. As shown in Figure 4c, both the WO_3 and WC/WO_3 samples have the set of peaks located at 35.8 eV (W $4f_{7/2}$) and 37.9 eV (W $4f_{5/2}$) corresponding to the lattice W-O bonds in WO_3.[7, 26] In addition, another set of intensities centered at 31.8 eV (W $4f_{7/2}$) and 33.9 (W $4f_{5/2}$) for WC/WO_3 can be resolved and assigned to the W-C chemical bonds based on the reported W $4f_{7/2}$ value (31.5 – 31.8 eV) of WC.[27-30] We also found the reduced tungsten (W^{5+}) with the binding energies at 34.3 eV (W $4f_{7/2}$) and 36.4 eV (W $4f_{5/2}$).[7, 31] The reduced tungsten atoms induce oxygen vacancies in the surface of WO_3 as a result of the formation of W-C bond.[32] Furthermore, the C 1s peak of WC/WO_3 hybrid (Figure 4d) can be fitted to two distinct peaks with binding energies at 284.6 and 283.4 eV which are assigned to the C-O oxygen-containing carbonaceous band and C-W chemical bond, respectively.[27-29] In other words, WC was generated on the surface of WO_3 layers.

The valence band maximum (VBM) positions of WC/WO_3 hybrid and pure WO_3 materials are also studied and displayed in Figure 5. The Fermi energy level is set at 0.0 eV.[17] For WO_3, the conduction band (CB) is largely composed of W 5d orbitals, while the valance band (VB) derives mainly from O 2p orbitals.[38] Furthermore, the orbital electrons $5d^4\,6s^2$ of W atom become $5d^0\,6s^0$ for WO_3 (W-O) and $5d^2\,6s^0$ for WC (W-C). Figure 5a shows that two VBMs for WC/WO_3 are detectable at approximately 0.7 eV (VBM-1) and 3.0 eV (VBM-2). The VBM-1 (0.7 eV) close to Fermi energy level originates from the orbital electrons $5d^2\,6s^0$ of W atom in WC. In contrast, the absence of VBM-1 for pure WO_3 indicates no photoelectron emission occurring close to the Fermi level as a result of the W^{6+} with empty 5d and 6s orbitals, bearing the atomic configuration of [Xe] $4f^{14}5d^06s^0$.[39] Moreover, the ESR result over WC/WO_3 (Figure 5b) displays a signal of single electrons (g = 1.95) originating from the single electron orbitals $5d^1$ of W^{5+},[7] which cannot be found for pure WO_3 material.

On the other hand, the WC/WO_3 hybrid also exhibits strong absorption in the UV-Vis-NIR region (Figure 5c). The VB photoemission spectrum of WC/WO_3 hybrid in Figure 5a shows that a higher intensity is close to the Fermi level, indicating more electron density of states attributable to the two orbital electrons $5d^2\,6s^0$ of W atom (WC).

The photocatalytic measurements including photocurrent density and oxidative decomposition of organic dye compounds, were performed on the WC/WO_3 hybrid catalyst with Vis-NIR light. Figure 5d shows distinct photocurrent signal under light irradiation (λ=400 – 800 nm), where the current response was measured as photocurrent density (I). The optical spectra of various filters fixed on the lamp for generation of single wavelength light (400, 500, 600, 700, and 800 nm). It is to be noted that photocurrent density depends on the photon power density of incident light. The WC/WO_3 hybrid displays a decreasing trend of photocurrent density with increasing wavelengths: $I_{400} > I_{500} > I_{600} > I_{700} > I_{800}$. For oxidative decomposition of organic compounds, we used the organic dye Rhodamine B (RhB) as a probe. The WO_3 material loaded with Pt (Pt/WO_3) (see SEM and TEM images in Figure S3) was prepared by photo-reduction method for comparison. The WC/WO_3 hybrid gave rise to the degradation rate of 89%, which is higher than 78% for Pt/WO_3 and 40% for WO_3 samples under visible light irradiation (400 nm), as indicated in Figure 5e. Further, we also evaluated the decomposition of RhB on WC/WO_3 hybrid with low-energy photons (Vis-NIR light, λ=400 – 800 nm) and compared its degradation rates with Pt/WO_3 and WO_3 samples. As displayed in Figure 5f, the WC/WO_3 hybrid exhibits enhanced photocatalytic degradation of RhB, well consisting with the trend of photocurrent responses (Figure 5c).

We comment on the roles of specific interfacial interactions between WC and WO_3 for improved photocatalytic activities. Figure 6 schematically illustrates the band structure of WO_3 (band gap = 2.6 eV), oxygen vacancies (OVs), Fermi level of WC (0.5 eV *vs* NHE), and three oxygen reduction potentials of -0.046 eV (one electron), 0.695 eV (two electrons), and 1.23 eV (four electrons).[1, 12] The Fermi level of WC is situated between the reduction potential of two-electron (0.695 eV) and conduction band minimum (0.1 eV) of WO_3.[1, 7] The intermediate band states caused by OVs enhance the absorption to the low-energy photons for WC/WO_3 hybrid photocatalyst. In addition, the WC material performs platinum-like behavior, forming a Schottky barrier and accelerating charge transfer and separation of WO_3.[14, 40] Thereby, the photo-induced electrons transfer following the routes: VB → OVs → CB →WC, as indicated by Figure 6. Finally, the electrons on WC preferentially undergo two-electron oxidation process and produce H_2O_2, reducing the recombination rate of excited electrons and holes. As a result, the holes cause the oxidative decomposition of organic dye RhB molecules.[1, 12] Although there are other factors to be taken into account, such as two-dimensional layered and hierarchical structure, the WC material with platinum-like properties is a potential noble metal substitute for photocatalytic applications. The Schottky barrier formed between WC and WO_3 plays an important role in improving photocatalytic degradation of organic RhB molecules.

CONCLUSION

The hierarchical tungsten carbide/tungsten trioxide (WC/WO_3) hybrid has been in-situ fabricated by a facile one-step solvothermal method. The WC as a potential substitute for noble metals accelerates charge transfer and separation of two-dimensional WO_3 layers. The hybrid exhibited excellent photocurrent responses and photocatalytic oxidative decomposition of organic dye compound with low-energy photons (visible and near-infrared radiation). Although there are other factors to take into account, such as two-dimensional and hierarchical structure, the specific interfacial interaction plays an essential role in improving charge transfer and separation. This work provides a cost-effective way to utilize solar energy for environmental remediation.

EXPERIMENTAL SECTION

Characterizations. Field-emission scanning electron microscopic (FE-SEM) images were measured on the JEOL JSM-6701F. Transmission electron microscopy (TEM),high-resolution TEM (HR-TEM), and scanning TEM (STEM) observations were carried out by using JEOL JEM-2100F TEM/STEM operated at 200 kV. X-ray Diffraction (XRD) patterns were recorded on Bruker D8 High-Resolution XRD featuring a four-bounce Ge(022) incident beam monochromator and highly monochromatic X-rays with Cu radiation (Cu Kα = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) measurement was conducted using a UHV vacuum generators ESCALAB Mk2 system with a monochromatic Mg-Kα source. All the binding energy positions were referenced to the C 1s peak of the surface adventitious carbon (at 284.6 eV). Thermogravimetric analysis (TGA) was measured on the instrument TA 2960 (DTA-TGA). Electron spin resonance (ESR) experiments were performed on JEOL FA200 (X-band) spectrometer at room temperature, centered at 331.756 mT with sweep width of 50 mT.

Synthesis of the WC/WO_3 hybrid. We first prepared the transparent solution by mixing tungsten chloride (WCl_6, 50 mg) and oleylamine (2 mL) after stirring around one hour. 1 mL of isopropanol was dropped into the above solution under stirring at room temperature. After stirring of around 30 min, this precursor solution was transferred to a Teflon autoclave with capacity of 50 mL for solvothermal reaction at 200 °C, 24 hour. Upon completion, the autoclave was cooled to room temperature and the black powder precipitate (WC/WO_3) was collected after washing with ethanol and ice drying in vacuum chamber for overnight.

Photocurrent responses test. A three-electrode system was used to measure the photocurrent. The working electrode is the WC/WO_3 sample coated on ITO (1 × 0.5 cm). Platinum gauze and Ag/AgCl serve as the counter and reference electrodes respectively. The 0.5 M H_2SO_4 aqueous solution was employed as the electrolyte in a quartz reactive cell. A 500 W xenon lamp provides the simulated sunlight. The chronoamperometry measurement of WC/WO_3 hybrid was obtained at 0.0 V while the simulator was switched on and off every 10 seconds manually using a shutter to record the change of photocurrent.

Detection of photocatalytic degradation of Rhodamine B (RhB). The WC/WO_3 hybrid of 20 mg was added into RhB aqueous solution (20 ml, 15 mg/L) followed by the ultrasonication for around 10 min. To ensure saturated adsorption of MB, this solution was kept in the dark for 4 hours at room temperature under constant magnetic stirring. A 500 W xenon lamp fixed with one filter was used as light source. After light irradiation for four hours, 5 mL of the reactive solution was sampled. The supernatant solution with remaining RhB molecules was obtained by centrifuging and removing the WC/WO_3 catalyst precipitate. The concentration of the remaining RhB was tested by UV-vis absorption spectrophotometer. Based on this procedure, we conducted the degradation of RhB with different light energies by fixing certain filters (400, 500, 600, 700, and 800 nm). For comparison, we also tested the degradation of RhB over the Pt/WO_3 and pure WO_3 materials with visible light (400 nm).

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests.

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