Photocatalytic Reduction of Cr(VI) on a 3.0% Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ Photocatalyst

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ABSTRACT: Herein, a 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was prepared for the photocatalytic reduction of the Cr$_2$O$_7^{2-}$ ion. The photocatalyst was characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, and ultraviolet–visible diffuse reflectance spectra. The Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample presented a photocatalytic reduction activity that is better than those of the Ce-doped sample and the intrinsic sample. Thereafter, different metal elements, Cu, Ag, Au, and Pt, were used as cocatalysts, which were loaded on the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample. The 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ photocatalyst showed optimal photocatalytic reduction activity in a 8 vol % methanol solution (pH = 7) under visible light irradiation. The kinetic constant of the optimal one is 0.0039 min$^{-1}$, which is 1.86 times that of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample. The photocatalyst is stable enough after a 24 h photocatalytic experiment.

1. INTRODUCTION

With industrial development, the toxic and harmful heavy metal ions can easily be found in surface and groundwater. Especially, the Cr(VI) ion usually exists in Cr$_2$O$_7^{2-}$, CrO$_4^{2-}$, and HCrO$_4^{-}$ forms, which have the features of toxicity, persistence, bioaccumulation, and mutagenicity that can cause serious diseases to humans. The World Health Organization has set a standard limit of 0.05 mg/L for chromium in drinking water. Hence, it is of great significance to remove chromium from an aquatic environment. Several strategies, including chemical precipitation, membrane filtration, physical absorption, and photocatalytic reduction of Cr(VI) to Cr(III), are used to decrease the concentration of chromium in aqueous solutions.

Among these methods, the photocatalytic reduction method is an efficient and low-cost greenway. For instance, photocatalytic reduction of Cr(VI) to Cr(III) over ZnO and TiO$_2$ samples is efficient under ultraviolet illumination. But the ultraviolet light only occupies 4% of the solar spectrum, which impedes the application of photocatalytic technology. The Bi$_2$WO$_6$/Bi$_2$V$_2$O$_7$ and Co$_3$O$_4$/Ag/Bi$_2$WO$_6$ heterojunction samples were fabricated for Cr(VI) reduction under visible light. Compared to the complex heterojunction, doping a metal ion into an ultraviolet-light-responsive photocatalyst to absorb visible light is simpler. The In-doped Zn(O,S) nanoparticles and La-/C-codoped TiO$_2$ nanomaterials present a high photocatalytic performance for the reduction of Cr(VI) compared to the undoped samples. Besides, a cocatalyst is beneficial for the enhancement of photocatalytic reduction performance, for example, Cr$_2$O$_3$ for titanate nanosheets and Cu$_2$O for Bi$_5$O$_7$I nanorods.

Tungstates are widely utilized in photocatalytic applications. However, the majority of the tungstates only act in the ultraviolet zone. To improve the photocatalytic activities of the famous g-C$_3$N$_4$ and titanate photocatalysts, the common way is to dope elements into their crystal structures. Herein, we introduced a visible-light-responsive Ce-doped SrWO$_4$ sample as a photocatalyst for the application of Cr(VI) reduction. In this paper, a photocatalytic reduction of a Cr$_2$O$_7^{2-}$ (10 ppm) aqueous solution was carried out in the...
presence of a methanol solution (8 vol %) under simulated sunlight. No acid and base was used during the photocatalytic reaction, keeping the pH value of the reaction system as 7. The photocatalytic performance was highly improved by the assistance of various cocatalysts, such as Cu, Ag, Au, and Pt. The kinetic constant was used to evaluate the photocatalytic reduction activity.

2. RESULTS AND DISCUSSION

The crystal structure of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was identified by X-ray diffraction (XRD) analysis. Figure 1 displays that the XRD pattern of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample is highly similar to the simulated SrWO$_4$ XRD pattern (ICSD-155793). This revealed that the as-prepared sample was a pure sample without impurity. Furthermore, the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ and 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ samples were analyzed by X-ray photoelectron spectroscopy (XPS) analysis. Figure 2a shows that they are composed of Sr, Ce, W, and O; however, because the Au content was too low, Au was not determined in the survey spectrum. The chemical valence of Au, Sr$^{2+}$, Ce$^{3+}$, W$^{6+}$, and O$^{2-}$ was identified by high-resolution XPS (See Figure 2). In our previous study, Au nanoparticles were loaded on the Sr$_{0.75}$Ce$_{0.15}$WO$_4$ sample by a similar photodeposition method. Hence, Au nanoparticles were deposited on Sr$_{0.70}$Ce$_{0.20}$WO$_4$. The O 1s band profile can usually be identified as surface lattice oxygen and chemisorbed oxygen species at ∼529.7 and ∼533.4 eV, respectively. The O 1s band profile is at ∼530.8 eV, which means it has a mixed composition of surface lattice oxygen and chemisorbed oxygen species. On comparing the high-resolution XPS images of Sr, Ce, W, and O with and without the Au cocatalyst, only the O 1s spectra became wider by the influence of the Au cocatalyst. This revealed that Au and O have a strong interaction.

The 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was observed by scanning electron microscopy (SEM). In a large-scale view, the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample seemed to have uneven size particles, which were in the range of 2–8 μm; however, the Au

Figure 1. XRD patterns of Sr$_{0.70}$Ce$_{0.20}$WO$_4$ and simulated SrWO$_4$.

Figure 2. (a–f) XPS analyses of the survey spectrum and high-resolution Au 4f, Sr 3d, Ce 3d, W 4f, and O 1s on Sr$_{0.70}$Ce$_{0.20}$WO$_4$ and 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$. 

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nanoparticles were observed on the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample in a small-scale view (see Figure S1). After that, the mapping images of the sample showed that Au, Sr, Ce, W, and O were evenly distributed in the 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample (see Figure 3). Besides, energy-dispersive spectroscopy (EDS) analysis provided an average atomic ratio of Au/Sr/Ce/W/O = 0.036:0.74:0.19:1:4.72 (see Figure S2). As shown in Figure 3f, the higher oxygen content can be attributed to the conductive adhesive background.

Figure 3. Mapping images of the 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample: (a) mapping region; (b) Au; (c) Sr; (d) Ce; (e) W; and (f) O.

Figure 4 exhibits the diffuse reflectance spectrum (DRS) image of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ photocatalyst, which shows that an absorption edge of this semiconducting material is about 390 nm. Thereafter, this figure was transformed into an inset figure, which is based on the Kubelka–Munk function. Because this material has an indirect band gap, the inset image is a plot of $(a/\alpha)^{1/2}$ against $hv$. The band gap of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample is 3.08 eV, which means that it is probably a visible-light-responsive material in the photocatalytic reaction. In our previous study, hydrogen was successfully generated over the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample under simulated sunlight, which implied that the conduction band potential of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample is less than 0 V. Additionally, the light absorption ability of 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ was obviously enhanced in comparison with Sr$_{0.70}$Ce$_{0.20}$WO$_4$ in the zone of 450–600 nm. A similar phenomenon appeared on the Ag/TiO$_2$ nanoflower material, which can be explained as the surface plasmon resonance effect.

Generally, the photocatalytic reaction of Cr(VI) reduction is performed in an acidic or alkaline solution. The photocatalytic reduction efficiency is decreased against the increase of the pH value, which is adjusted by HNO$_3$ and NaOH. In this work, the pH influence (1, 4, and 7) on the Cr(VI) reduction reaction was tested as well, which confirmed that the photocatalytic reduction activity increased with the decreasing pH value (see Figure S3). To avoid using an external acid or alkali, the Cr(VI) reduction reaction was carried out in a neutral solution under simulated sunlight. The Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was designed as the photocatalyst because it was better than Ce-doped SrWO$_4$ (see Figure 5). As we know, the metal ion was doped into the crystal structure of the semiconductor, which could adjust the band gap energy and the reduction/oxidation potential of the semiconductor. Usually, there is an optimal sample that has the best dosage of the doping amount for photocatalytic application. However, the optimal samples of Ce-doped SrWO$_4$ for water decomposition and Cr(VI) reduction reactions are Sr$_{0.76}$Ce$_{0.16}$WO$_4$ and Sr$_{0.70}$Ce$_{0.20}$WO$_4$, respectively, which can be explained by the fact that the necessary reduction potentials of these reduction reactions are different. The kinetic constant value of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample is 0.0021(0.5) min$^{-1}$. Afterward, various cocatalysts were used to promote the photocatalytic activity of this sample.

In Ding’s study, Cr$_2$O$_3$ was used to enhance the photocatalytic reduction activity of titanate nanosheets, which utilized the retarding the photogenerated charge recombination by the Cr$_2$O$_3$ cocatalyst. Hence, the photocatalysis activity of 0.5% Cr$_2$O$_3$-loaded titanate was 4.1-fold that of intrinsic titanate. In our work, Cu, Ag, Au, and Pt were utilized as cocatalysts. Figure 6a shows the reduction process of Cr(VI) against time, which reveals that both of these cocatalysts played...
Cr(VI) reduction activity than the Au/TiO₂ sample.36,37 Reference. Our photocatalysts have a better photocatalytic activity in the initial solution, the irradiation time, and the responding conditions: 100 mg of photocatalyst, 250 mL of solution, 10 ppm Cr₂O₇²⁻, pH = 7, and a 300 W long arc xenon lamp.

Table 1. Summary of Various Au Cocatalyst Materials for Cr(VI) Reduction under Simulated Sunlight

| photocatalyst | cocatalyst | C[Cr₂O₇²⁻] (ppm) | k (min⁻¹) | Cr(VI) removal (%) | pH | time (min) | refs |
|---------------|------------|-------------------|-----------|--------------------|----|------------|------|
| 1 TiO₂        | Au         | 5                 | 0.030     | 20                 | 2.5| 120        | 36   |
| 2 TiO₂        | Au         | 0.85              | 0.030     | 3                  | 3.7| 120        | 37   |
| 3 N-doped TiO₂| Au         | 5                 | 0.024     | 90                 | 5–6| 90         | 38   |
| 4 Bi₂WO₆      | Au         | 10                | 0.003     | 88                 | 1  | 80         | this paper |
| 5 BiVO₄       | Au         | 5                 | 0.003     | 88                 | 7  | 80         | this paper |

Figure 6. (a) Photocatalytic reduction activities of Sr₀.₇ₐCe₀.₂₀WO₄ with 3 wt % different cocatalysts against time; (b) first-order kinetic constants of photocatalytic Cr(VI) reduction over Sr₀.₇ₐCe₀.₂₀WO₄ with different 3 wt % cocatalysts under simulated sunlight irradiation. Photocatalytic conditions: 100 mg of photocatalyst, 250 mL of solution, 10 ppm Cr₂O₇²⁻, pH = 7, and a 300 W long arc xenon lamp.

Table 1 shows a summary of various Au cocatalyst materials for Cr(VI) reduction under simulated sunlight. The table lists the photocatalyst, the cocatalyst, the concentration of Cr₂O₇²⁻, the kinetic constant k, the Cr(VI) removal, the pH value of the initial solution, the irradiation time, and the responding reference. Our photocatalysts have a better photocatalytic Cr(VI) reduction activity than the Au/TiO₂ sample.36,37 However, the N-doped TiO₂, Bi₂WO₆, and BiVO₄ samples, which are famous narrow band gap semiconductors, have higher photocatalytic activity compared with the 3.0%-Au/Sr₀.₇ₐCe₀.₂₀WO₄ sample. In our opinion, the photocatalytic activity of Cr(VI) reduction is mainly dependent on the pH value and the band gap of the photocatalyst.

The stability of the photocatalyst is very important for photocatalytic application. Generally, a long-time reaction or cycle reaction is performed on the obtained optimal sample. In the photocatalytic H₂ production experiment, the cycle reaction was carried out by adding an external fresh sacrificial agent.41,42 In the photodegradation reaction, the photocatalyst needs to be recycled during the cycle reaction, which leads to a loss of the photocatalytic material.43,44 However, a Cr-based compound was formed in the photocatalytic reaction, which necessitated a photocatalyst regeneration for the cycle reaction.18 Figure 7 presents the results of a cyclic experiment over the 3.0%-Au/Sr₀.₇ₐCe₀.₂₀WO₄ sample. The first cycle showed that the absorbance of the 3.0%-Au/Sr₀.₇ₐCe₀.₂₀WO₄ sample shows a monotonic decline over time. The photocatalytic reduction efficiency reached 30% in the first 3 h. The photocatalytic reduction efficiency was decreased in the last 5 h, which may be due to the formation of a Cr-based compound on the photocatalyst, leading to a decrease in light absorption ability. Before the second cycle and third cycle experiments, the prephotocatalyst was washed 5 times with distilled water. However, the photocatalytic reduction activity was reduced because of inevitable photocatalyst loss. In general, the photocatalyst is stable enough after 24 h irradiation, which is supplied by the XRD analysis (see Figure S5).

Additionally, the used photocatalyst was characterized by SEM and XPS measurements to understand the photocatalytic mechanism of the Cr(VI) reduction reaction. The color of the intrinsic Sr₀.₇ₐCe₀.₂₀WO₄ sample was white. After the 3.0 wt %

Figure 7. Photocatalytic reduction efficiency of 3.0%-Au/Sr₀.₇ₐCe₀.₂₀WO₄ against time in a total of three cycles. Photocatalytic conditions: 100 mg of photocatalyst, 250 mL of solution, 10 ppm Cr₂O₇²⁻, pH = 7, and a 300 W long arc xenon lamp.
Au cocatalyst was loaded on the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample, its color became purple. However, the color of the used photocatalyst was dark green. The change in color from white to purple implied that the Au nanoparticle was formed, which can be indirectly supplied by the DRS and XPS images. The final dark green sample implied that a Cr-based compound was formed on the surface of the 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample. In the XRD pattern analysis of the used photocatalyst, all of the XRD peaks belonged to the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample, which means that the Cr-based compound is rare and amorphous (see Figure S5). Figure 8 shows the main difference between the 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample before and after photocatalysis is in that the undetected Au element and the formed Cr-based compound. Figure 8a indicates that Cr$_2$O$_3$ was formed after photocatalysis, which was supplied by the O 1s spectra (see Figure 8f). In the literature, composites that contain a noble metal and Cr$_2$O$_3$ are widely utilized as cocatalysts to improve the photocatalytic performance. Therefore, we reasonably speculate that Cr$_2$O$_3$ was covered with the Au cocatalyst, which led to the undetected Au element. Then, the SEM image of the used photocatalyst shows a different surface structure in comparison with the unused photocatalyst (see Figure S6). An adsorption performance of Cr(VI) for Sr$_{0.70}$Ce$_{0.20}$WO$_4$ and 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ samples was analyzed in the dark to demonstrate the adsorption–desorption equilibrium (see Figure S7). The adsorption performance slightly decreased after the Au cocatalyst was loaded on the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample. Both of them achieved the maximum adsorption value at 50 min and then began to desorb in solution.

In brief, the photocatalytic mechanism is illustrated in Figure 9. The photocatalytic process of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ semiconductor is the absorption of a photo by the band gap (3.08 eV), which generates electron–hole pairs in the semiconductor particle. The excitation of an electron from the valence band to the conduction band is initiated by light absorption with energy equal to or greater than 3.08 eV. A photogenerated hole is left on the valence band, which oxidizes methanol to H$_2$O and CO$_2$. However, the photogenerated electron is collected...
on the Au cocatalyst at first, and then the Cr(VI) reduction reaction occurs on the Au cocatalyst.

3. CONCLUSIONS

The Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was prepared for photocatalytic Cr(VI) reduction under simulated sunlight. Through selecting the optimal cocatalyst, a 3.0% Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was obtained. XRD, SEM, EDS, and XPS analyses revealed that the composite sample was successfully synthesized. The photocatalytic Cr(VI) reduction reaction was carried out in a neutral solution. The kinetic constant of the optimal 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample is 0.0039 min$^{-1}$, which is 1.86 times that of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample. The photocatalytic reduction activity of the sample is stable after a 24 h cycle experiment. To develop a novel efficient photocatalyst, it needs to have a narrow band gap to absorb visible light.

4. EXPERIMENTAL SECTION

4.1. Materials. In the following experiments, K$_2$Cr$_2$O$_7$ (AR), AgNO$_3$ (AR), and HCl (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.; CeO$_2$ (99.9%) purchased from Aladdin; WO$_3$ (99.8%), Cu(CH$_3$COO)$_2$ (AR), AgNO$_3$ (AR), AuCl$_3$·xH$_2$O (AR), and H$_2$PtCl$_6$·6H$_2$O (AR) were purchased from Macklin; and SrCO$_3$ (AR), C$_2$H$_5$H$_2$N$_2$O (AR), CH$_3$COCH$_3$ (AR), and CH$_3$OH (AR) were purchased from Chengdu Kelong Chemical Reagent Co., Ltd.

4.2. Photocatalysts. The Ce-doped SrWO$_4$ samples were synthesized by the solid-state reaction as reported in our previous literature. For instance, the Sr$_{0.70}$Ce$_{0.30}$WO$_4$ sample was obtained at 1000 °C in air. The 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was obtained by loading the 3 wt % Au cocatalyst on the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample. The cocatalyst was loaded by the photodeposition method. Taking the 3.0% Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample for example, 100 mg of Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample, 6 mL of AuCl$_3$·xH$_2$O (0.5 mg/mL), 3 mL of distilled water, and 1 mL of methanol solution were put in a 300 mL reactor in ultrasound for 10 min. A 300 W Hg lamp supplied the light illumination during the 1 h photodeposition process. The necessary stirring and cooling devices were used during the photodeposition process. Finally, the reactor that contained the photocatalyst was dried in a drying oven at 70 °C for 6 h.

4.3. Characterizations. The crystal structure of the Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was analyzed on an X-ray diffraction (XRD) diffractometer using Cu Kα irradiation. The morphology and size of the 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample were tested on a scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS) analysis. The elemental composition of the 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample was measured on an X-ray photoelectron spectrometer (XPS) using an Al Kα X-ray source. The light absorption capacity of the as-prepared sample was measured by an ultraviolet–visible diffuse reflectance spectrum (DRS), using a U-4100 spectrometer equipped with an integrating sphere attachment. The absorbancy of the chromogenic Cr(VI) was monitored on a U-4100 spectrophotometer.

4.4. Photocatalytic Experiments. Photocatalytic Cr(VI) reduction experiments were tested on a setup that was composed of a quartz cold trap and a 300 mL Pyrex glass vessel. In a run, 0.100 g of photocatalyst was added to the vessel; 250 mL of mixture solution that contained 10 ppm Cr$_2$O$_7^{2-}$ ion and 8 vol % methanol was added to the vessel as well. Thereafter, the vessel was put in ultrasound equipment to evenly disperse the photocatalyst in the aqueous solution (20 min). After another 10 min dark operation, a 300 W long arc xenon lamp was inserted in the cold trap to supply modulated sunlight to the photocatalytic experiments. Four milliliters of solution was collected at regular 20 min intervals. Besides, a circulating cooling water system was used to maintain the reaction temperature at 25 ± 5 °C. These collected solution samples were colorized by diphenylcarbazide and H$_2$SO$_4$ to measure the absorbancy of Cr(VI) by the colorimetric method. To quantitatively assess the photocatalytic reduction performance of the as-prepared samples, the reaction kinetic constants of these reactions were calculated by the first-order model of ln($C_0/C$) versus time.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03743.

SEM and EDS images of the 3.0%-Au/Sr$_{0.70}$Ce$_{0.20}$WO$_4$ sample and the plots of photocatalytic reduction activities over various photocatalysts (PDF)

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**Notes**

The authors declare no competing financial interest.

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