A Bi$_{7.38}$Cr$_{0.62}$O$_{12+x}$ crystal as a novel visible-light-active photocatalyst up to $\sim$650 nm†

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The relatively wide band gap (>2.0 eV) and limited light absorption ranges (only up to 600 nm) of photocatalysts severely restrict the exploitation of solar energy. Herein, we developed a Bi$_{7.38}$Cr$_{0.62}$O$_{12+x}$ crystal photocatalyst with a narrow band gap of 1.98 eV and a broad light absorption range of $\sim$650 nm. Unlike other broad light absorption range photocatalysts (up to $\sim$650 nm) such as red phosphorus, Fe$_2$O$_5$, and CdSe, which are either unstable or show low photocatalytic performances, the as-synthesized Bi$_{7.38}$Cr$_{0.62}$O$_{12+x}$ crystal photocatalyst exhibits a steady photocatalytic activity for the decomposition of methylene blue, methyl blue, and phenol, and production of O$_2$.

2. Experimental

2.1 Chemicals and materials

Bi(NO$_3$)$_3$·5H$_2$O (AR, 99.0%), Cr(NO$_3$)$_3$·9H$_2$O (AR, 99.0%), AgNO$_3$ (AR, 99.0%), methylene blue (AR), and methyl blue (AR) were purchased from Aladdin Reagent Company. Acetic acid (AR, 99.8%) and methanol (AR, 99.5%) were purchased from Beijing Chemical Reagent Company. All the chemicals were used as purchased without any further purification. Commercial P25 TiO$_2$ was purchased from Degussa AG, Germany.

2.2 Synthesis of the Bi$_{7.38}$Cr$_{0.62}$O$_{12+x}$ crystal

In the typical synthesis of the Bi$_{7.38}$Cr$_{0.62}$O$_{12+x}$ crystal, 6 mmol of Bi(NO$_3$)$_3$·5H$_2$O and 0.5 mmol of Cr(NO$_3$)$_3$·9H$_2$O were dissolved in 50 mL of acetic acid and vigorously stirred at 250 °C to volatilize acetic acid. The mixture was heated to 600 °C at a rate of 5 °C min$^{-1}$ in a muffle furnace and maintained at this temperature for 5 h. Then, the Bi$_{7.38}$Cr$_{0.62}$O$_{12+x}$ crystal was obtained after cooling down the mixture to room temperature.

2.3 Synthesis of N-doped P25

N-doped P25 was prepared by treating the P25 samples in a tubular furnace under an NH$_3$ flow (purity 99.99%) at a high temperature of 500 °C for 4 h. The NH$_3$ flow was applied for
30 min before the heat treatment to remove the air and maintain until the products were cooled down to room temperature.

2.4 Characterizations

Scanning electron microscopy (SEM) images were obtained using JEOL JSM 4800F. Transmission electron microscopy (TEM) images were obtained using an FEI Tecnai G2 200 kV. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed using an unfiltered He I (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 eV. The crystalline structure was investigated via an X-ray diffractometer (XRD) (Bruker AXS D8 Focus) using Cu Kα radiation (λ = 1.54056 Å). The Brunauer–Emmett–Teller (BET) specific surface area was measured using a Micromeritics Gemini V surface area and pore size analyzer. UV-vis absorption spectra were obtained using a UV-3600 UV-vis-NIR scanning spectrophotometer (Shimadzu). X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALABMKII spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source.

2.5 Photocatalytic decomposition of methylene blue

The visible light photocatalytic activity of the Bi7.38Cr0.62O12+x crystal was evaluated by monitoring the decomposition of methylene blue and methyl blue in an aqueous solution under visible light irradiation from a 300 W Xe lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd, China) and a UVCUT-420 nm filter (Newport). A pyrex glass vessel was used as the photoreactor. The Bi7.38Cr0.62O12+x crystal (200 mg) was mixed with a methylene blue solution (50 mL, 10 ppm). After stirring for 60 min in dark to reach the adsorption equilibrium, the solution was illuminated under visible light irradiations. The concentration of the aqueous solution of methylene blue was determined using a UV-vis spectrophotometer via measuring the peak intensity at 664 nm.

2.6 Photocatalytic decomposition of methyl blue

The Bi7.38Cr0.62O12+x crystal (200 mg) was mixed with a methyl blue solution (50 mL, 30 ppm). After stirring for 60 min in dark to reach the adsorption equilibrium, the solution was illuminated under visible light irradiations. The concentration of the aqueous solution of methyl blue was determined using a UV-vis spectrophotometer via measuring the peak intensity at 659 nm.

2.7 Photocatalytic decomposition of phenol

The Bi7.38Cr0.62O12+x crystal (200 mg) was mixed with a phenol solution (50 mL, 200 µmol L⁻¹). After stirring for 60 min in dark to reach the adsorption equilibrium, the solution was illuminated under visible light irradiations. The concentration of the aqueous solution of phenol was determined using a UV-vis spectrophotometer via measuring the peak intensity at 270 nm.

2.8 Photocatalytic O₂ production measurements

The Bi7.38Cr0.62O12+x crystal (50 mg) was added to a AgNO₃ solution (100 mL, 0.1 M) within a closed gas circulation system (Perfect Light Company Labsolar-III (AG)). This mixture was exposed to UV-vis and visible light irradiation from a 300 W Xe lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd, China) and with an UVCUT-420 nm filter (Newport). The evolved gases were detected in situ using an online gas chromatograph (GC-2014C, Shimadzu) equipped with a thermal conductivity detector (TCD).

2.9 Surface photovoltage measurements

The surface photovoltage (SPV) measurement system consisted of a source of monochromatic light, a lock-in amplifier (SR 830-DSP) with a light chopper (SR 540), and a sample chamber. The monochromatic light is provided by a 300 W Xe lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd, China) and a monochromator (SBP500, Zolix). All measurements were performed at room temperature and under ambient pressure, and samples were not pretreated prior to the SPV measurements.

2.10 Detection of the hydroxyl radicals

The ESR signal of the radicals spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was measured via a Bruker ESP 300A spectrometer. The irradiation source was a 300 W xenon lamp with a cut-off filter (λ > 420 nm). The settings for the ESR spectrometer were as follows: center field, 3510.00 G; microwave frequency, 9.79 GHz; and power, 5.05 mW.

3. Results and discussion

The synthesis of the Bi7.38Cr0.62O12+x crystal consisted a solid phase reaction in which Bi(NO₃)₃ and Cr(NO₃)₃ acted as the precursors. As shown in Fig. 1A, in the XRD patterns of the as-synthesized Bi7.38Cr0.62O12+x crystal, the diffraction peaks at 27.72, 32.61, 45.71, 53.35, and 55.26 degrees, ascribed to the (2 0 1), (2 2 0), (2 2 2), (2 0 3), and (4 2 1) planes of Bi7.38Cr0.62O12+x, were indexed to the tetragonal phase (JCPDS no. 50-0373). The EDAX spectrum (Fig. 1B) indicated that the mole ratio of Bi, Cr, and O was close to the stoichiometric ratio of 12 : 1 : 19. Diffused reflective UV-vis spectroscopy spectrum is presented in Fig. 1C. The oranger powders display a strong absorption band in the visible light region. The bandgap E_g of Bi7.38Cr0.62O12+x was calculated to be 1.98 eV from the Tauc plot (Fig. S1†). Surface photovoltage spectroscopy (SPS) is a powerful tool to characterize charge separation at the nanoscale. As shown in Fig. 1D, the SPS spectrum presents an active negative surface photovoltage (SPV) response, indicating that Bi7.38Cr0.62O12+x is a p-type semiconductor. The SPV response reaches 647.4 nm, which is in agreement with the absorption spectrum (Fig. 1C). Furthermore, the strong SPV response indicates that the generated carriers can be efficiently separated, and therefore, Bi7.38Cr0.62O12+x may have a good photocatalytic activity.
Fig. 1 X-ray diffraction patterns (A), EDAX spectrum (B), diffusion reflection UV-vis spectrum (C), and surface photovoltage spectroscopy spectrum (SPS) (D) of the Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ crystal. The inset of C is an image of the Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ crystal.

The FE-SEM images (Fig. S2†) show that the Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ crystal is composed of blocks of several microns. The lattice fringe space of 0.322 nm, as observed in the HRTEM image (Fig. 2B), is characteristic of the (2 0 1) plane of the tetragonal phase of Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$. The Brunauer–Emmett–Teller (BET) surface area and pore size of the sample were calculated from a macroporous structure, and the BET surface area was determined to be 1.89 m$^2$ g$^{-1}$.

XPS (X-ray photoelectron spectroscopy) is a powerful technique to investigate the chemical states of a material. The Bi 4f and Cr 2p high-resolution XPS spectra of the Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ crystal are shown in Fig. 3. The Bi 4f spectra was resolved into two Gaussian peaks, located at around 158.6 eV and 163.8 eV. The Cr 2p XPS spectrum can be deconvoluted into two Gaussian peaks at 576.3 eV and 579.8 eV.

The visible-light photocatalytic activity of the Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ crystal was estimated based on the photocatalytic decomposition of methylene blue, methyl blue, and phenol in an aqueous solution under visible light irradiation from a 300 W Xe lamp (PLS-SXE 300, Beijing Trustech Co. Ltd, China) with a UVCUT-420 nm filter (Newport). As shown in Fig. 4 and S4–S6,† methylene blue, methyl blue, and phenol presented a negligible self-degradation. Photodegradation was completed after 80 minutes for methylene blue and methyl blue, and after 150 minutes for phenol. By contrast, N-doped P25 showed a relatively lower photocatalytic activity, with only about 30–40% of photodegradation. Furthermore, the photocatalytic degradation at $\lambda > 420$ nm was measured for several successive cycles, and the results are shown in Fig. 5. After five cycles, no loss in the photocatalytic activity was observed. Fig. 6 shows the O$_2$ production from the Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ crystal under UV-vis light and visible light irradiation. The O$_2$ production rate was 9.69 $\mu$mol h$^{-1}$ under UV-vis and 3.99 $\mu$mol h$^{-1}$ at $\lambda > 420$ nm for 50 mg of Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ in 100 mL of 0.1 M AgNO$_3$ solution as an electron scavenger. These photocatalytic experiments demonstrated that the Bi$_{7.38}$Cr$_{0.62}$O$_{12-x}$ crystal is a stable and efficient visible light-active photocatalyst.

To determine the probable active species involved in the photocatalytic decomposition, 100 mg of AgNO$_3$ (electron scavenger) and 5 mL of methanol (hole scavenger) were added. As shown in Fig. S7,† when 100 mg of AgNO$_3$ was added, the photodegradation was clearly accelerated and completed after 60 minutes, with the rate constant showing a one-time improvement. As an electron scavenger, AgNO$_3$ can rapidly deactivate the electron, and as a hole scavenger, methanol can facilitate the photodegradation process.
capture the generated electrons, leading to a higher separation efficiency of the photogenerated carriers and a longer lifetime of the photogenerated holes.\textsuperscript{43,44} The photodegradation is obviously suppressed by the addition of methanol (hole scavenger).\textsuperscript{45,46} These results verify that holes and hydroxyl radicals are the main active species oxidizing the adsorbed organic pollutants.\textsuperscript{47,48} These species are also reported to be the dominant active species in TiO\textsubscript{2}.\textsuperscript{49} To further verify the generation of hydroxyl radicals in the photodegradation reaction, we measured the ESR signal of the radicals spin-trapped by DMPO, as shown in Fig. 7. Under visible light irradiation, four characteristic peaks with a standard intensity ratio of 1 : 2 : 2 : 1 were clearly observed,\textsuperscript{50,51} which could be ascribed to \textsuperscript{1}O\textsubscript{2}−/DMPO−OH. By contrast, no ESR signal was detected under the dark condition.

To elucidate the origin of the band gap in Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+x}, we examined the electronic structure of Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+x} by density functional theory, as shown in Fig. S8.\textsuperscript{†} The density of states (DOS) calculations indicated that the valence band maximum (VBM) originated from the O 2p state, whereas the conduction band minimum (CBM) was mainly contributed by the Cr 3d and Bi 6p states. The UPS spectra (Fig. 8A) was utilized to confirm the valence band energy (E\textsubscript{v}) of the Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+x} crystal, which was computed to be 6.72 eV (versus vacuum level) by subtracting the width of the He I UPS spectra from the excitation energy (21.22 eV).\textsuperscript{52,53} According to the reference standard, for which 0 V versus RHE (reversible hydrogen electrode) equals −4.44 eV versus the vacuum level,\textsuperscript{54,55} E\textsubscript{v} was finally estimated to be 2.28 eV versus RHE. The conduction band energy (E\textsubscript{c}) was thus calculated to be 0.30 eV versus RHE from E\textsubscript{v} = E\textsubscript{c}. The possible photocatalytic mechanism of the Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+x} crystal is shown in Fig. 8B. The valence band energy (E\textsubscript{v}) is 0.58 eV higher than that of OH/\textsuperscript{1}OH (1.70 V), and 1.05 eV higher than that of O\textsubscript{2}/H\textsubscript{2}O (1.23 V). Thus, on the one hand, the generated holes have enough oxidizing power to oxidize adsorbed methylene blue, methyl blue, phenol, and water. On the other hand, the generated holes also have enough oxidizing power to react with OH to produce active hydroxyl radicals that can in turn oxidize the adsorbed methylene blue, methyl blue, and phenol.\textsuperscript{47}

4. Conclusions

In summary, we prepared a new type of Bi-based visible light-active photocatalyst, Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+3x} by a solid phase reaction with Bi(NO\textsubscript{3})\textsubscript{3} and Cr(NO\textsubscript{3})\textsubscript{3} as the precursors. The XRD and EDAX results confirmed that Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+x} was synthesized. The SEM and TEM images show that the crystal is composed of blocks of several microns. The UV-vis DRS spectrum presents a strong visible light absorption band. The XPS results confirmed that Cr(VI) is the main valence state in the Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+x} crystal. The photocatalytic decomposition of methylene blue and methyl blue, as well as the photocatalytic production of O\textsubscript{2} indicate that the Bi\textsubscript{7.38}Cr\textsubscript{0.62}O\textsubscript{12+x} crystal is a stable visible light-active photocatalyst. The holes and hydroxyl radicals are the main active species that can oxidize the adsorbed organic pollutants.

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