

One-pot solvothermal synthesis of S doped BiOCl for solar water oxidation

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Experimental Section

Materials

2-methoxyethanol, thiourea, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AgNO_3 , ethyl alcohol and 1-hexadecyl-3-methylimidazolium chloride ($[\text{C}_{16}\text{Mim}]\text{Cl}$) were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and were used without further purification. Deionized water (18 M Ω , Molecular) was used for all instrument and samples washes.

Preparation of S doped BiOCl

Firstly, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2-4mmol) was placed into 30-40 mL of 2-methoxyethanol solution with stirring. In addition, 1-hexadecyl-3-methylimidazolium chloride ($[\text{C}_{16}\text{Mim}]\text{Cl}$) (3-6mmol) was also dissolved in 30-40 mL of 2-methoxyethanol. After 20 min, both solutions were mixed together. Afterwards, 0.078g thiourea was added into the mixed solution and steadily stirred 20min. The

mixture was transferred into a 100 mL autoclave, which was maintained at 160 °C for 1 h and cooled down to room temperature. Finally, the as-prepared S-BiOCl sample was washed 3 times with deionized water and 2 times with ethyl alcohol, then dried in oven at 60 °C for 6 h. The undoped BiOCl are fabricated with the same procedure described above without the use of thiourea.¹

Characterization

The morphologies of the as-prepared products were obtained via the Hitachi S-4800 microscope with an accelerating voltage of 7.0 kV. The chemical element mapping was characterized through an energy dispersive X-ray spectrometer equipped in the SEM machine. Powder X-ray diffraction (XRD) spectra measurements were carried out on a Bruker AXS D8 advance powder diffractometer with Cu K α X-ray radiation. Raman spectra were performed using Horiba LabRAM HR system, and laser radiation (λ = 1064 nm) served as excitation source. UV-Vis diffuse reflection spectra (DRS) were measured using a Shimadzu UV 2550 recording spectrophotometer equipped with an integrating sphere. The photoluminescence (PL) properties of the samples were characterized by Spectrofluorometer with an excitation wavelength at 310 nm.

Computational Method

The first principles calculations were based on density functional theory within the Perdew–Burke–Emzerhof (PBE) exchange-correlation functional, the projector-augmented plane wave (PAW) approach were employed for the calculation of interactions between the valence electrons and the ionic cores. The structure of S

doped BiOCl with S at an O site or an Cl site was constructed on the basis of the 108-atom $3 \times 3 \times 2$ supercell, which corresponding the 0.93% atomic concentration. The Brillouin zone was sampled with a $2 \times 2 \times 2$ Monkhorst–Pack k-point grid. The convergence threshold for self-consistent iteration is set at 10^{-6} eV, and the atomic coordinates and cell parameters are fully optimized until the values of all the residual force components are less than 0.01 eV \AA^{-1} . The density of states (DOS) for each optimized S doped BiOCl structure was calculated by using the tetrahedron method with Blöchl corrections. All the calculations were performed using the Vienna ab-initio simulation package (VASP). To determine the energy required for substituting S for either O or Cl in BiOCl, the defect formation energies have been calculated by

$$E^f(\text{defect}) = E(\text{defect}) - E(\text{total}) + \mu_R - \mu_S$$

Where $E(\text{defect})$ is defined as the total energy of a supercell containing the defect, $E(\text{total})$ is the total energy of a BiOCl perfect crystal in the same supercell, μ_S is the chemical potential of S and μ_R is the chemical potential of the atom replaced by S (i.e., O or Cl).

Photocatalytic water oxidation activity measurement

The photocatalytic water oxidation activity of S doped BiOCl powder sample was performed in 100 mL of aqueous AgNO_3 solution (0.015M) including 100 mg of the photocatalyst, which was kept at 20-25°C in a quartz reactor. The reactor was sealed and vacuumized for 30 min in order to drive away the residual oxygen and switched on the 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.). Finally, the gas chromatography with a thermal conductivity detector was applied to analysing the quantities of O_2 production. For comparison, the photocatalytic activity of pure BiOCl

was also carried out under same conditions.

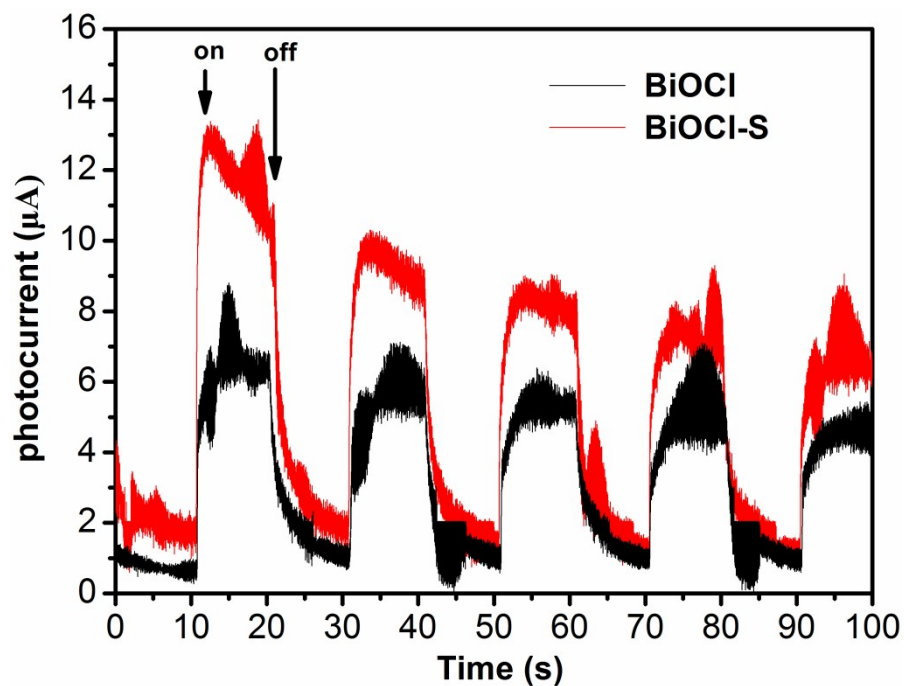


Fig. S1. Transient photocurrent responses of BiOCl and BiOCl-S under a bias of 0.4V.

The reference electrode was Ag/AgCl, and the electrolyte was 0.2 M Na₂SO₄

Transient photocurrent responses of the BiOCl and BiOCl-S were presented in Fig. S1. As can be seen, the photocurrent of BiOCl-S is higher than that of BiOCl, indicating more free electrons can be generated over BiOCl-S. Consequently, it can be concluded that the photogenerated electrons and holes in the BiOCl-S are separated more efficiently than those in the BiOCl.

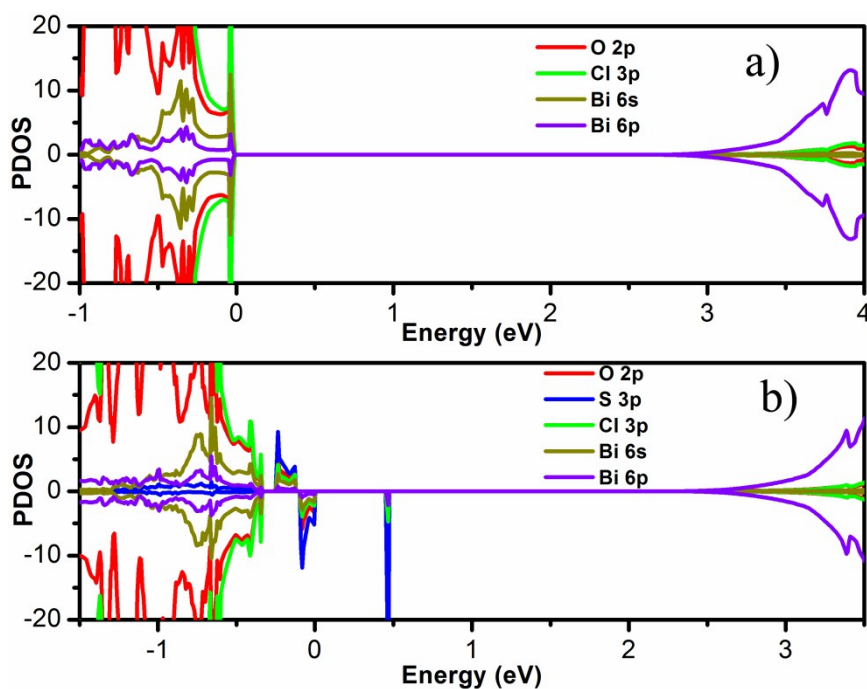


Fig. S2. Density of states (DOS) pattern of pure (a) and BiOCl-S (b)

We have calculated the density of states (DOS) of pure and S doped BiOCl. As shown in Fig S2, it is noted that the impurity states of BiOCl-S are mainly derived from the S 3p and O 2p orbitals, in addition, the Cl 3p and Bi 6s orbitals also make considerable contribution to these states. The strong hybrid between these orbitals is advantageous for the transfer of photo-generated carriers, which can further render the improvement of photocatalytic activity.

REFERENCES

- 1 H. F. Cheng, B. B. Huang, Z. Y. Wang, X. Y. Qin, X. Y. Zhang, Y. Dai, *Chem. Eur. J.* 2011, **17**, 8039.