Development of $La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$ photocatalysts for hydrogen evolution from water under visible light irradiation

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Abstract: $La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$ oxysulfoselenide solid solutions were synthesized in the whole composition range, and their physical properties and photocatalytic hydrogen evolution activities were studied. The absorption edge wavelength became longer from 650 to 820 nm with the increase of the Se content. $La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$ modified with NiS as a cocatalyst showed photocatalytic activity in hydrogen evolution from aqueous solution containing electron donors. The hydrogen evolution activity of $La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$ was improved significantly by controlling the particle size and coloading Pt and NiS cocatalysts. This study highlights the potential advantages of oxysulfoselenides over oxysulfides for longer-wavelength solar-powered hydrogen production.

Keywords: Oxysulfoselenide, Solid solution, Cocatalyst

1. Introduction

Photocatalytic water splitting has been studied extensively as a potential means of renewable solar hydrogen production on a large scale.[1] $La_5Ti_2CuS_5O_7$, originally synthesized by Meignen *et al.* in 2004,[2] functions as a photocatalyst evolving hydrogen and oxygen from aqueous solutions containing electron donors and acceptors, respectively,[3] and as both photocathode and photoanode depending on back contact materials.[4] Notably, $La_5Ti_2CuS_5O_7$ photocathodes generates photocurrent attributable to hydrogen evolution at a positive potential of +0.9 V vs. RHE stably.[5] These features render $La_5Ti_2CuS_5O_7$ an interesting and promising material for use in photocatalytic solar hydrogen production. However, the absorption edge wavelength of $La_5Ti_2CuS_5O_7$ is 650 nm. It is desirable to shift the absorption edge toward longer wavelengths to aim at high solar-to-hydrogen energy conversion efficiency.

Generally, the band gap energy of semiconducting sulfoselenide solid solution systems becomes narrower with increasing the Se content.[6] A similar tendency is expected for oxysulfoselenide solid solution systems. However, no earlier work was found on oxysulfoselenide solid solutions as photocatalysts for hydrogen evolution. In this study, $La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$ ($LTCS_{1-x}Se_xO$ hereafter) solid solutions were synthesized, and their physical properties and hydrogen evolution activities were investigated.[7,8]

2. Experimental

$LTCS_{1-x}Se_xO$ samples were prepared by a solid state reaction in sealed quartz tubes.[7,8] La_2O_3, La_2S_3, TiO_2, Cu_2S, S, La, Se, and Cu_2Se were mixed in a nitrogen-filled glove box. The precursor mixtures were sealed in evacuated quartz tubes and heated at 1273 K for 48 h. Hydrogen evolution reactions were conducted in a Pyrex reaction vessel connected to a closed gas circulation system. Aqueous solution (150 mL) containing 10 mM Na_2S and 10 mM Na_2SO_3 was used as a reaction solution. $LTCS_{1-x}Se_xO$ samples were modified with NiS and/or Pt cocatalysts. NiS was loaded by *in-situ* precipitation while Pt was loaded by photodeposition. When NiS and Pt cocatalysts were coloaded, $LTCS_{1-x}Se_xO$ samples were firstly modified with Pt, after which NiS was loaded onto the Pt-loaded $LTCS_{1-x}Se_xO$.[8] The photocatalyst suspension was irradiated with visible light using a Xe lamp equipped with a cut-off or band-pass filter.

3. Results and discussion

The $LTCS_{1-x}Se_xO$ ($0.2 \le x \le 1$) samples show X-ray diffraction patterns similar to those for LTCSO. Structural refinements revealed that the lattice constants and cell volumes of the $LTCS_{1-x}Se_xO$ series followed the Vegards' law. These results indicate successful formation of LTCS$_{1\text{-}x}$Se$_x$O solid solutions over the whole composition range. Figure 1A shows diffuse-reflectance spectra (DRS) of LTCS$_{1\text{-}x}$Se$_x$O. The absorption onset of the LTCS$_{1\text{-}x}$Se$_x$O solid solutions shifted toward longer wavelengths with increasing the Se content, from 650 nm for the LTCSO oxysulfide to 820 nm for the LTCSeO oxyselenide.

Figure 1B presents hydrogen evolution rates of the LTCS$_{1\text{-}x}$Se$_x$O solid solutions loaded with NiS under visible light irradiation (λ > 420 nm). The LTCS$_{1\text{-}x}$Se$_x$O solid solutions evolved hydrogen from aqueous solution containing the sacrificial reagents. Through the comparison of the action spectra, it was confirmed that the LTCS$_{1\text{-}x}$Se$_x$O oxysulfoselenide ($x \geq 0.2$) did utilize longer-wavelength visible light than the oxysulfide LTCSO, in accordance with the DRS data. Nevertheless, the hydrogen evolution rate became lower with increasing the Se contents. Scanning electron microscopy observation revealed that the LTCS$_{1\text{-}x}$Se$_x$O ($x \geq 0.2$) had significantly larger particle sizes (exceeding 10 μm) than the LTCSO. Accordingly, the lower activity of LTCS$_{1\text{-}x}$Se$_x$O ($x \geq 0.2$) was attributable in part to the excessive growth of particles. In fact, the hydrogen evolution activity of LTCS$_{1\text{-}x}$Se$_x$O ($x \geq 0.2$) was improved several-fold by reducing the particle size through optimization of the synthesis temperature at each composition. The activity was further enhanced by coloading Pt and NiS cocatalysts.

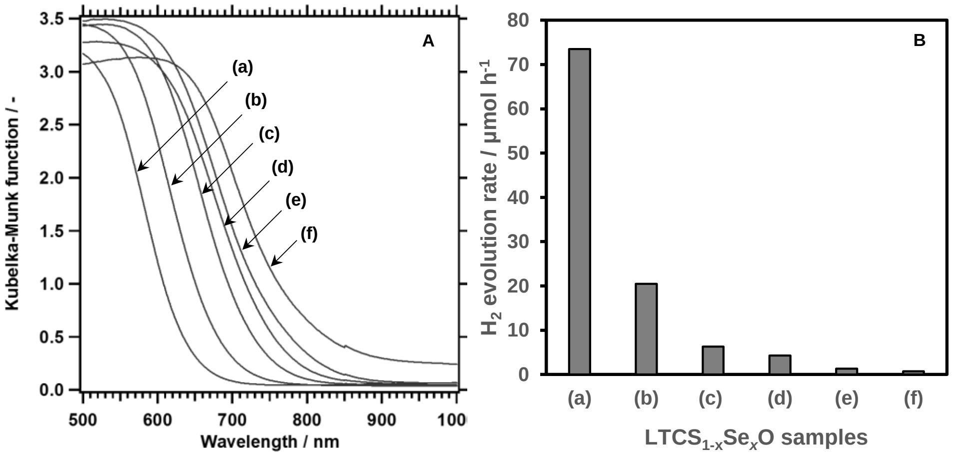

Figure 1. (A) DRS data and (B) H_2 evolution rates for LTCS$_{1\text{-}x}$Se$_x$O samples. The values of x were (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0, respectively. For the hydrogen evolution reaction, the samples were modified with the NiS cocatalyst and irradiated with visible light from a Xe lamp (λ > 420 nm).

4. Conclusions

The LTCS$_{1\text{-}x}$Se$_x$O oxysulfoselenide solid solutions utilized longer-wavelength photons for photocatalytic hydrogen evolution reactions than the LTCSO oxysulfide although their hydrogen evolution rates were lower because of the excessive particle growth. The photocatalytic activity was enhanced significantly by reducing the particle size and coloading Pt and NiS cocatalysts. This study demonstrates the potential advantages of oxysulfoselenides over oxysulfides in utilization of longer-wavelength visible light for hydrogen production.

References

1. T. Hisatomi, K. Domen, *Faraday Discuss.* 198 (2017) 11.
2. V. Meignen, L. Cario, A. Lafond, Y. Moëlo, C. Guillot-Deudon, A. Meerschaut, *J. Solid State Chem.* 177 (2004) 2810.
3. T. Suzuki, T. Hisatomi, K. Teramura, Y. Shimodaira, H. Kobayashi and K. Domen, *Phys. Chem. Chem. Phys.* 40 (2012) 15475.
4. G. Ma, Y. Suzuki, R. B. Singh, A. Iwanaga, Y. Moriya, T. Minegishi, J. Liu, T. Hisatomi, H. Nishiyama, M. Katayama, K. Seki, A. Furube, T. Yamada, K. Domen, *Chem. Sci.* 6 (2015) 4513.
5. J. Liu, T. Hisatomi, G. Ma, A. Iwanaga, T. Minegishi, Y. Moriya, M. Katayama, J. Kubota and K. Domen, *Energy Environ. Sci.* 7 (2014) 2239.
6. S. Chen, X. G. Gong, S. Wei, *Phys. Rev. B* 75 (2007) 205209.
7. S. Nandy, Y. Goto, T. Hisatomi, Y. Moriya, T. Minegishi, M. Katayama, K. Domen, *ChemPhotoChem* 1 (2017) 265.
8. S. Nandy, T. Hisatomi, Guijun Ma, T. Minegishi, M. Katayama, K. Domen. *J. Mater. Chem. A* 5 (2017) 6106.