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CuO LOADED $SrTiO_3$ NANOPARTICLES: AN EFFICIENT Pt-FREE PHOTOCATALYST FOR H_2 EVOLUTION FROM WATER

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The photocatalytic H_2 evolution from water over CuO loaded $SrTiO_3$ nanoparticles has been investigated using CH_3OH as a sacrificial reagent. The results show that the CuO loaded $SrTiO_3$ nanoparticles are an efficient photocatalyst with a H_2 evolution rate of 5.81 mmol $h^{-1}g^{-1}$ under UV irradiation. Moreover, the photocatalyst is confirmed to be stable and can keep high activity for a long time.

1. Introduction

The photocatalytic H_2 production over $SrTiO_3$ has received much attention due to its excellent stability and current-voltage properties [1]. The results indicate that $SrTiO_3$ is a promising candidate when noble metals, such as Pt, are used as co-catalysts. However, Pt is expensive and rare, which is unfavorable to the large scale application of $SrTiO_3$. Therefore, the development of Pt-free and low cost co-catalysts is desired. Recently, it is reported that CuO can act as an efficient co-catalyst, and CuO loaded TiO_2 exhibits a high photocatalytic activity for the photocatalytic H_2 production [2]. Following this idea, it can be expected that CuO could be an efficient co-catalyst for $SrTiO_3$. However, there are few reports on the photocatalytic activity of CuO loaded $SrTiO_3$. In the present paper, we describe the preparation of CuO loaded $SrTiO_3$ nanoparticles and their photocatalytic activity for the H_2 production from the methanol aqueous solution.

2. Experimental

$SrTiO_3$ nanoparticles were prepared in a sol-gel process [1]. CuO loaded $SrTiO_3$ nanoparticles (CuO/$SrTiO_3$) were synthesized by the simple impregnation described previously [2]. Therein, $SrTiO_3$ nanoparticles loaded with 1.5 wt.% CuO were denoted as 1.5 % CuO/$SrTiO_3$. Pt-loaded $SrTiO_3$ nanoparticles were fabricated by the *in situ* photo-deposition [3]. The photocatalysts were characterized with Rigaku D/Max2550 VB/PC X-ray diffractometer (Japan), JEOL JEM-200CX transmission electron microscope (Japan), PHI 5000 Versaprobe spectrometer (Japan), and Micromeritics ASAP-2020 nitrogen adsorption apparatus (USA). The photocatalytic reaction was carried out in a gas-closed system with a quartz reactor. A 300 W high-pressure Hg lamp was used as light source. The amounts of H_2 evolution were analyzed with an on-line gas chromatograph (GC-112A, China, N_2 carrier).

3. Results and discussion

Fig. 1 shows the XRD patterns of 1.5 % CuO/$SrTiO_3$ and pure $SrTiO_3$. It can be observed that there exist six peaks at 32.42°, 39.98°, 46.48°, 57.79°, 67.80° and 77.17° in two patterns, corresponding to the (110), (111), (200), (211), (220) and (310) planes of cubic $SrTiO_3$ (JCPDS card No. 35-0734) [4], respectively. However, the diffraction peak of CuO is not observed in Fig. 1a. One possible explanation is that the CuO particles are too small to give well-defined diffraction peaks.

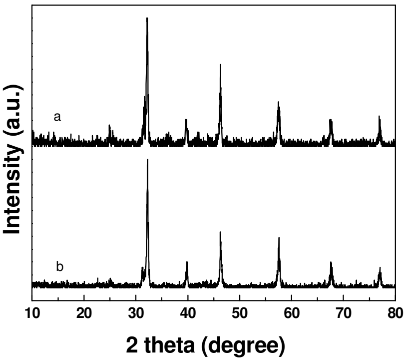

Figure 1. XRD patterns of 1.5 % CuO/$SrTiO_3$ (a) and pure $SrTiO_3$ (b).

XPS analysis (not shown here) displays that there exist two peaks at 933.6 eV and 953.4 eV corresponding to Cu-$2p_{3/2}$ and Cu-$2p_{1/2}$ of CuO, respectively [2]. These results show that the as-synthesized sample is made of $SrTiO_3$ and CuO.

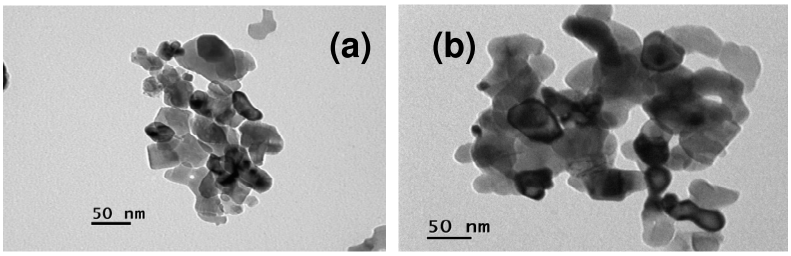

Figure 2. TEM images of pure $SrTiO_3$ (a) and 1.5 % CuO/$SrTiO_3$ (b).

The TEM images of pure $SrTiO_3$ and 1.5 % $CuO/SrTiO_3$ are shown in Fig. 2. It can be observed that there exists some aggregation in the $SrTiO_3$ loaded with CuO. Moreover, the CuO particles cannot be observed on the surface of $SrTiO_3$ nanoparticles. In combination with the XRD and XPS analyses, it can be deduced that CuO is homogeneously spread on the surface of $SrTiO_3$ nanoparticles.

Fig. 3 shows the irradiation time courses of H_2 production catalyzed by pure $SrTiO_3$, 1.5 % $CuO/SrTiO_3$ and $SrTiO_3$ loaded with 2 % Pt, respectively. It is seen that 1.5 % $CuO/SrTiO_3$ is a highly active photocatalyst with the highest rate of H_2 evolution of 5.81 mmol $h^{-1}g^{-1}$ under UV irradiation, while the H_2 production can be hardly observed using pure $SrTiO_3$ as a photocatalyst.

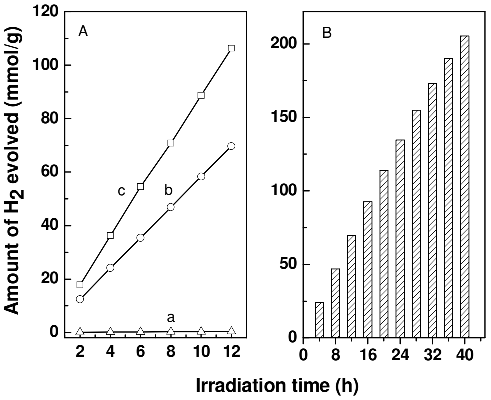

Figure 3. (A) Irradiation time dependence of the amount of H_2 evolved over pure $SrTiO_3$ (a), 1.5 % $CuO/SrTiO_3$ (b) and $SrTiO_3$ loaded with 2 % Pt (c); (B) time course of H_2 production catalyzed by 1.5 % $CuO/SrTiO_3$. 120 mg of catalysts and 60 mL of MeOH aqueous solution (60 %, v/v) at 45 °C.

The Brunauer-Emmett-Teller measurement indicates that the specific surface area of 1.5 % $CuO/SrTiO_3$ is 15.5 $m^2\cdot g^{-1}$, which is almost the same as that of pure $SrTiO_3$ (16.2 $m^2\cdot g^{-1}$). The TEM images show that the morphology of 1.5 % $CuO/SrTiO_3$ is similar to that of pure $SrTiO_3$. Therefore, the enhanced photocatalytic activity of $CuO/SrTiO_3$ ought to be ascribed to CuO. One possible explanation is that CuO acts as a charge transferring site and/or active site in the photocatalytic process. As a result, CuO provides an efficient separation of electrons and holes, thus enhancing the potential of hydrogen generation. Moreover, although the photocatalytic activity of 1.5 % $CuO/SrTiO_3$ is lower than that of $SrTiO_3$ loaded with 2 % Pt (8.83 mmol $h^{-1}g^{-1}$), its rate of H_2 evolution is more than 60 % of that of $SrTiO_3$ loaded with 2 % Pt. In addition, 1.5 % $CuO/SrTiO_3$ is a stable photocatalyst and can keep high activity over 40 h. Therefore, it can be concluded that CuO is an alternative to Pt as an effective co-catalyst for $SrTiO_3$.

In order to test the stability of 1.5 % $CuO/SrTiO_3$, the photocatalytic activity of 1.5 % $CuO/SrTiO_3$ was repeatedly examined many times. The results of two cycles are shown in Fig. 4 demonstrating that $CuO/SrTiO_3$ is stable enough to be recycled.

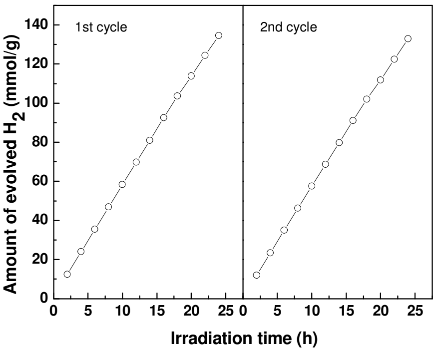

Figure 4. Hydrogen evolution in two cycles over 1.5 % $CuO/SrTiO_3$.

4. Conclusion

The $CuO/SrTiO_3$ is concluded to be a highly active photocatalyst for the photocatalytic H_2 production from water. The results provide us with new possibility for designing an alternative to Pt as a co-catalyst for $SrTiO_3$. Further efforts are currently undertaken.

Acknowledgements

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