Photocatalytic water oxidation using $SrTiO_3$ modified with Co_3O_4 under visible light: Effects of $SrTiO_3$ support

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Abstract: Photocatalytic activity of $Co_3O_4/SrTiO_3$ for visible-light water oxidation was investigated with respect to the size (i.e., crystallinity in other words) of the $SrTiO_3$ support. Co_3O_4 nanoparticles (2.0 wt% as Co), which act as visible light absorption and water oxidation center, were loaded by an impregnation method. Decreasing the $SrTiO_3$ particle size (improving the crystallinity) enhanced the photocatalytic activity by promoting the formation of Co_3O_4 nanoparticles that provided optimal light absorption and catalytic sites. However, Co_3O_4 aggregation occurred on larger $SrTiO_3$ particles, thereby decreasing activity.

Keywords: water oxidation, photocatalyst, cobalt oxide.

1. Introduction

$SrTiO_3$ is known as a good photocatalyst for water splitting reaction. However, $SrTiO_3$ has a wide band-gap so that it can absorb only UV light. Recently, our group reported a new water photooxidation system using a wide-gap semiconductor (e.g., TiO_2) in conjunction with cobalt hydroxide or oxide.[1, 2] In this system, electron transfer from cobalt species to the conduction band of support, as confirmed by photoelectrochemical measurements,[1] is believed to initiate the catalytic water oxidation under a wide range of visible light (up to 850 nm). Therefore, it is expected that feature size (or crystallinity) of support may affect the photocatalytic activity when cobalt oxide particles are loaded by the same procedure.

In this work, we synthesized $SrTiO_3$ by the polymerized complex (PC) method, followed by heating in air at different temperatures to obtain $SrTiO_3$ having different sizes. Co_3O_4 were loaded on the as-synthesized $SrTiO_3$ by an impregnation method, and the photocatalytic activities for water oxidation were investigated, in order to clarify the effect of support in this system.[3]

2. Experimental

$SrTiO_3$ was prepared by the PC method. Titanium tetra-isopropoxide, $SrCO_3$, ethylene glycol (EG), and citric acid (CA) were mixed in 100 mL of methanol at a Ti/Sr/EG/CA was 1/1/40/10 (by mole). The mixture was heated at 573–673 K to yield a gray powder, followed by calcined at 823 K for 5 h in air. The product was again calcined for 2 h in air at different temperatures (973–1373 K).

Co_3O_4 nanocluster were loaded onto the as-synthesized $SrTiO_3$ by an impregnation method. 1 mL of pure water containing a certain amount of $Co(NO_3)_2\cdot 6H_2O$ and 0.25 g of $SrTiO_3$ were placed in an evaporation dish put onto a steam bath. The suspension was stirred till the water was evaporated completely, followed by heating in air at 423 K for 1 h. The amount of Co loading was 2.0 wt%, as a metallic Co content of the samples.

3. Results and discussion

TEM images of $SrTiO_3$ calcined at different temperatures, further modified with Co_3O_4, are shown in **Figure 1**. It was confirmed that $SrTiO_3$ has larger particle size with increases calcination temperature.

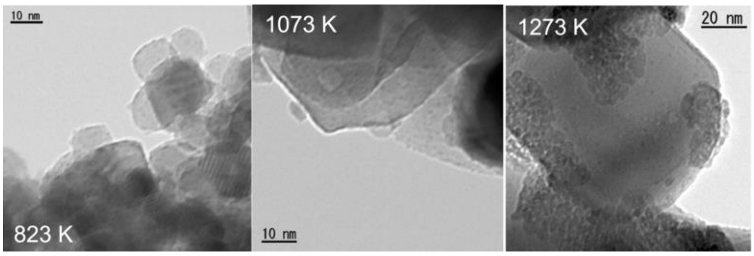

Figure 1. TEM images of $SrTiO_3$ calcined at different temperatures and further deposited with 2.0 wt% Co_3O_4.

However, Co_3O_4 nanoparticles became larger to form aggregates, even though the loading condition was the same. When $SrTiO_3$ calcined at 823 K was used as a support, the deposited Co_3O_4 was less than 1 nm in size without any aggregation. On the other hand, as can be seen in the 1273 K sample, Co_3O_4 became 30-50 nm in size in addition to smaller nanoparticles. Therefore, it was found that Co_3O_4 sizes are also influenced by the size of $SrTiO_3$ support.

UV-Vis-NIR DRS for 2.0 wt% $Co_3O_4/SrTiO_3$ are shown in **Figure 2**. All samples absorb almost entire range of visible light, while unmodified $SrTiO_3$ did not regardless of the preparation conditions. However, the visible light absorption became more pronounced with increases calcination temperature of $SrTiO_3$.

Figure 3 shows the photocatalytic activities for water oxidation reaction from aqueous $AgNO_3$ solution under visible light (λ > 480 nm). As a result, photocatalytic activity was improved with increasing the calcination temperature of $SrTiO_3$ from 823 to 1073 K. However, in case of 1173–1373 K, evolution rate of O_2 was lower than 1073 K. The decrease in activities at higher calcination temperatures (1173–1373 K) were presumably due to the formation of Co_3O_4 agglomerates that are usually less efficient in catalysis, as confirmed in **Figure 1**. On the other hand, lower activities were also observed when the visible light absorption is relatively weak (e.g., in the cases of 823 and 973 K, as shown in **Figure 2**). Therefore, this result demonstrated that both the morphology of Co_3O_4 nanoparticles and the visible light absorption capability are important for this system, and can be controlled by choice of an appropriate support.

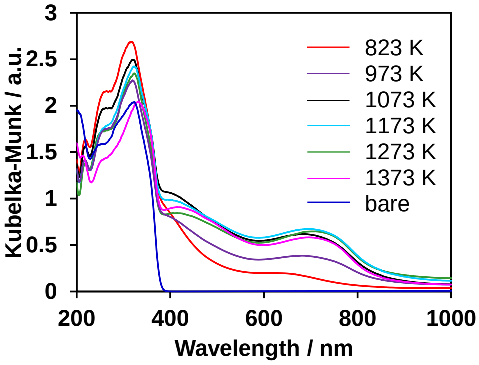

Figure 2. UV-Vis-NIR DRS of bare $SrTiO_3$ and $SrTiO_3$ calcined at different temperatures and further deposited with 2.0 wt% of Co_3O_4.

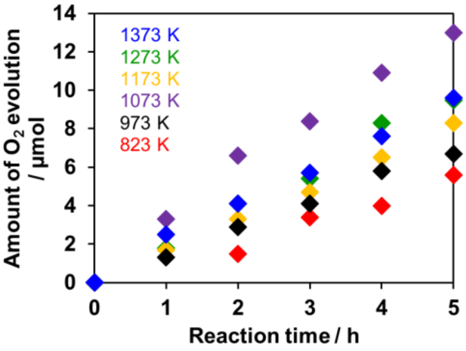

Figure 3. O_2 evolution over $SrTiO_3$ calcined at varying temperatures and further deposited with 2.0 wt% Co_3O_4 under visible light (λ > 480 nm). Reaction conditions: Catalyst, 100 mg with 200 mg of La_2O_3; reactant solution, $AgNO_3$ aq.(10 mM, 140 mL); light source, a 300 W xenon lamp fitted with CM-1 mirror and cutoff filters of L-42 and Y-48.

4. Conclusions

The photocatalytic activity of $Co_3O_4/SrTiO_3$ for water oxidation under visible light was investigated, focusing on the effects of the $SrTiO_3$ support. The size of deposited Co_3O_4 completely depends on the size of $SrTiO_3$ support, even though the modification was undergone by the same conditions. That is, larger sized- $SrTiO_3$ causes the aggregated Co_3O_4 particles, while highly dispersed Co_3O_4 was confirmed onto smaller $SrTiO_3$. The size growth of Co_3O_4 could enhance the visible light absorption capability so that photocatalytic activity was also increased. However, aggregated Co_3O_4 could decrease the reaction center, which causes less effective for water oxidation. Therefore, it was indicated that both the morphology of Co_3O_4 and the resulting visible light absorption capability could be controlled by an appropriate choice of support material.[3]

References

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