Photocatalytic Activity for Water Decomposition of RuO_2-Loaded $SrIn_2O_4$ with d^{10} Configuration

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A p-block metal oxide of $SrIn_2O_4$ with d^{10} configuration was found to be a new photocatalyst for the overall splitting of water when combined with RuO_2.

Most of the metal oxide photocatalysts developed in a past decade for the decomposition of water to H_2 and O_2 have been NiO- or RuO_2-loaded titanates, niobates, zirconates and tantalates. The representative titanates were $A_2La_2Ti_3O_{10}$ (A = K, Rb, Cs),[1,2] $A_2Ti_6O_{13}$ (A = Na, K, Rb)[3,4] and $BaTi_4O_9$,[5,6] and the niobates were $A_4Nb_6O_{17}$ (A = K, Rb)[7,8] and $Sr_2Nb_2O_7$.[9] ZrO_2[10] was found to be active, and, recently, $ATaO_3$ (A = Na, K),[11,12] MTa_2O_6 (M = Mg, Ca, Sr ,Ba)[13,14] and $Sr_2Ta_2O_7$[9] were shown to have the ability for water decomposition. The feature of these metal oxide photocatalysts is to be composed of octahedrally coordinated d^0 transition metal ions such as Ti^{4+}, Zr^{4+}, Nb^{5+}, and Ta^{5+}. To our knowledge, no stable metal oxides other than d^0 transition metal oxides have been reported. In an attempt to establish a new kind of the photocatalysts, we have paid attention to p-block metal oxides with d^{10} configuration and found that $SrIn_2O_4$ has the capability of decomposing water when combined with RuO_2.

In the synthesis of $SrIn_2O_4$ powder, strontium nitrate (Wako Chemicals, 99.9% pure) and indium nitrate (Nacalai Tesque, Inc, EP Grade) in a 1:2 molar ratio were dissolved in water and then ethanol solutions, and oxalic acid ethanol solution was added to the solution. The coprecipitate thus prepared was aged at 353 K, dried at 393 K and calcined in air for 16 h at different temperatures between 1073 and 1473 K. The formation of $SrIn_2O_4$ was confirmed based on the X-ray diffraction peak patterns reported previously.[15] For RuO_2 loading, $SrIn_2O_4$ was impregnated up to incipient wetness with ruthenium carbonyl complex, $Ru_3(CO)_{12}$, in THF solution, dried at 357 K and calcined in air at 673 K. The photocatalytic reaction was carried out in a gas circulation apparatus equipped with a quartz reaction cell which was described elsewhere.[3–6] Briefly, about 250 mg of the photocatalyst was placed in ca. 20 mL distilled and ion-exchanged water and stirred by bubbling with Ar gas circulation. A dispersed photocatalyst in the reaction cell was irradiated by Xe lamplight at 400 W. The gas phase products were analyzed by an online gas chromatograph.

Figure 1 shows the production of H_2 and O_2 from water on a 1 wt% $RuO_2/SrIn_2O_4$ photocatalyst under UV irradiation. From the initial stage, both H_2 and O_2 increased nearly in proportion to irradiation time. The gas phase products were evacuated, and the reaction was repeated under the same conditions. In the second run, the evolution of H_2 and O_2 occurred in a manner similar to that in the first run, indicating little deterioration of photocatalytic activity. The photocatalytic activity of RuO_2-loaded $SrIn_2O_4$ was 1/2–1/8 that of the active RuO_2-loaded Ti-based photocatalysts such as $RuO_2/A_2Ti_6O_{13}$ (A= Na, K, Rb) and $RuO_2/BaTi_4O_9$ investigated in our previous studies.[5,16] The results clearly indicate that $SrIn_2O_4$ consisting of In^{3+} with d^{10} configuration makes a good photocatalyst for water decomposition when combined with RuO_2.

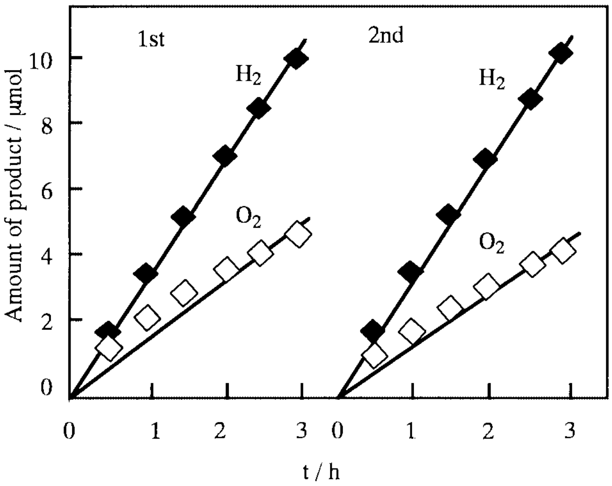

Figure 1. Evolution of H_2 and O_2 from water on 1 wt% RuO_2-loaded $SrIn_2O_4$ under UV irradiation. $SrIn_2O_4$ was prepared by calcination at 1273 K.

Figure 2 shows the UV diffuse reflectance spectra of $SrIn_2O_4$ prepared at different calcination temperatures. Light

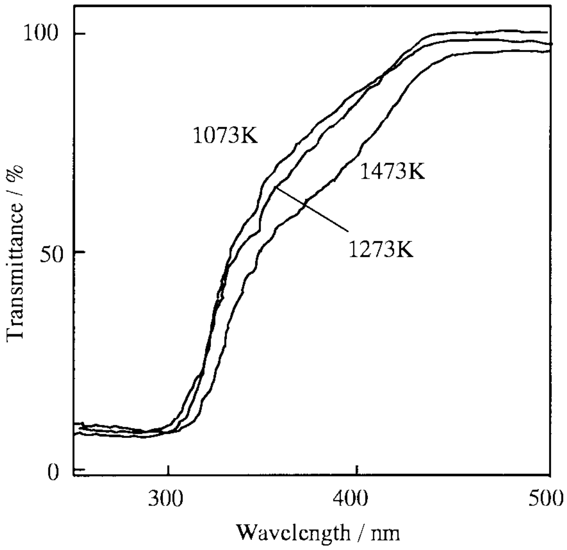

Figure 2. UV reflectance spectra of $SrIn_2O_4$ subjected to different calcination temperatures.

absorption occurred at around 450 nm, increased gradually and steeply at a wavelength shorter than 350 nm, and reached a maximum at around 300 nm. The absorption spectrum of a sample prepared at 1273 K was nearly the same as that at 1073 K, whereas the threshold wavelength shifted slightly toward longer wavelength when calcined at 1473 K.

The influence of calcination temperature of $SrIn_2O_4$ on the photocatalytic activity of $RuO_2/SrIn_2O_4$ is shown in Figure 3. The activity was low for $SrIn_2O_4$ calcined at 1073 K, increased with increasing calcination temperature, passed through a maximum at 1273 K, and decreased. In the X ray diffraction patterns, the main peaks of $2\theta = 31.4°$ and 32.8°, assigned respectively to the reflection from the (320) and (121) planes, became narrower and larger with increasing temperatures up to 1473 K. This indicates that the crystallization of $SrIn_2O_4$ progressed with increasing temperatures above 1173 K. The SEM observation showed that the average particle size was 0.21–0.37 μm for calcination below 1273 K and increased sharply to 1.0 μm for calcination between 1273 and 1373 K. Based on the results, an increase in the photocatalytic activity with calcination from 1073 to 1273 K is associated with increasing crystallinity of $SrIn_2O_4$, whereas a decrease in the photocatalytic activity above 1273 K appears to be related to a decrease in the surface area of $SrIn_2O_4$. Decreases in surface area cause not only reduction of the concentration of photocatalytic active sites but also changes in the dispersed states of RuO_2. A previous study of the effects of RuO_2 dispersion on the photocatalytic activity of RuO_2-loaded $M_2Ti_6O_{13}$(M=Na, K, Rb) showed that the growth of RuO_2 to large particles resulted in significant decreases in the photocatalytic activity.[16] The small surface area of $SrIn_2O_4$ facilitates the agglomeration and growth of RuO_2 particles, leading to lowering of the photocatalytic activity.

In the correlation between photocatalytic activity and the local structure of metal oxides, it is interesting to note a similarity between $SrIn_2O_4$ and a representative titanate of $BaTi_4O_9$ with d^0 configuration. $SrIn_2O_4$ belongs to an orthorhombic crystal structure with a unit cell of $a = 0.9809$, $b = 1.1449$ and $c = 0.3265$ nm[15]: the structural feature is the presence of a pentagonal-prism-like tunnel where there are two distorted InO_6 octahedra. In a highly active RuO_2-loaded $BaTi_4O_9$ photocatalyst, $BaTi_4O_9$ has two kinds of the distorted TiO_6 octahedra in the pentagonal prism tunnel structure,[17] and it is proposed that internal electric fields (dipole moments) caused by the distortion of the octahedra are responsible for high efficiency of photoexcited charge formation and hence for good performance in photocatalytic water decomposition.[18,19] Analogous to this, it appears that the presence of the pentagonal-prism tunnel structure of $SrIn_2O_4$ is associated with the photocatalytic activity of $RuO_2/SrIn_2O_4$.

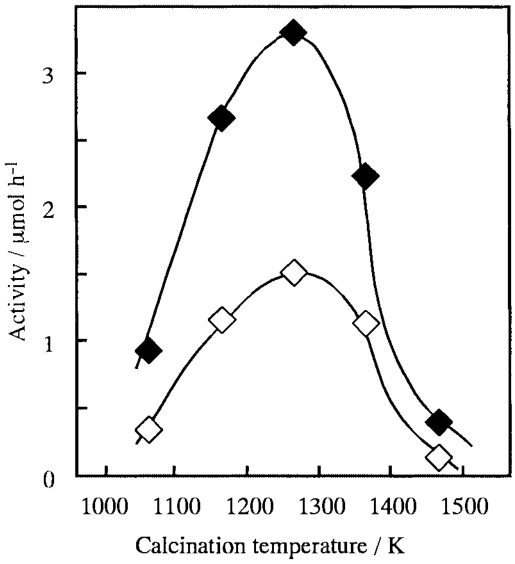

Figure 3. Changes in photocatalytic activity of 1 wt% RuO_2-loaded $SrIn_2O_4$ with calcination temperature of $SrIn_2O_4$. ◆:H_2 ; ◇:O_2.

In conclusion, the present findings predict that a p-block metal oxide with d^{10} configuration will be a new group of photocatalysts for the overall splitting of water.

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