RuO_2-loaded Sr^{2+}-doped CeO_2 with d^0 Electronic Configuration as a New Photocatalyst for Overall Water Splitting

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Ruthenium oxide-loaded Sr^{2+}-doped CeO_2 with f^0d^0 electronic configuration was found to have photocatalytic activity for overall water splitting into H_2 and O_2 under UV irradiation, whereas neither undoped CeO_2 nor stoichiometric compounds such as $SrCeO_3$ and Sr_2CeO_4 was photocatalytically active.

In view of current interest of photon energy conversion, the development of photocatalysts for overall water splitting is among attractive issues. In the past three decades, many active metal oxide photocatalysts that have an ability of decomposing water into H_2 and O_2 have been reported. They are classified into two groups: one is a transition-metal oxide group involving Ti^{4+}, Zr^{4+}, Ta^{5+}, Nb^{5+}, and W^{6+} ions with d^0 electronic configuration.[1–6] The other is a typical metal oxide group consisting of Ga^{3+}, In^{3+}, Ge^{4+}, Sn^{4+}, and Sb^{5+} ions with d^{10} electronic configuration.[7–9] For the development of photocatalysts, the next candidate will be a lanthanide metal oxide group, and we pay attention to $Ce^{IV}O_2$ because of [Xe] $f^0d^0s^0$ electronic structure, which is a kind of d^0 electronic configuration. CeO_2 has been widely used as optical materials owing to its high UV-light absorbing property and its low toxicity. For water-decomposing photocatalyst, Arakawa et al. showed that CeO_2 has an ability of producing oxygen from a suspending solution of CeO_2 containing Ce^{4+} ions as an electron acceptor.[10] However, no photocatalytic ability for pure water splitting was reported, to our best knowledge. We have discovered that Sr^{2+}-doped CeO_2 makes an active photocatalyst when RuO_2 was loaded as a promoter. Here, we report the photocatalytic properties of RuO_2-loaded Sr^{2+}-doped CeO_2 as the first example of photocatalytically active lanthanide oxides for water splitting. The band structures of undoped and Sr^{2+}-doped CeO_2 were calculated by a DFT method.

For Sr^{2+}-doped CeO_2, four kinds of the mixtures of CeO_2(Nacalai Tesque, EP) and $SrCO_3$(Nacalai Tesque GR) with different molar ratios ($\alpha = Sr/(Sr + Ce) = 0.05, 0.10, 0.20$, and 0.50) were used as a starting material and calcined in air at 1273 K for 10 h. The obtained samples were referred to as α-Sr-doped CeO_2 where α represents the molar ratio of starting mixtures. Undoped CeO_2 was subjected to the same temperature conditions. The stoichiometric compounds of $SrCeO_3$ and Sr_2CeO_4 were prepared by calcination of equimolar mixtures of CeO_2 and $SrCO_3$ in air at 1473 K for 10 h. To deposit RuO_2 as a promoter, the prepared metal oxides were impregnated up to incipient wetness with $Ru_3(CO)_{12}$ in THF solution, dried at 357 K, and oxidized in air at 673 K for 4 h to convert the complex to RuO_2. The RuO_2 loading was 1 wt %. The overall water splitting reaction was carried out in a closed gas circulation reaction system with an inner irradiation-type quartz vessel. A photocatalyst (1.1 g) was dispersed in 700 mL of distilled water by stirring with a magnet rotator and irradiated by a 450-W high-pressure mercury lamp. The amounts of H_2 and O_2 evolved in the gas phase were analyzed by a gas chromatograph directly connected to the reaction system.

Figure 1 shows the XRD patterns of undoped CeO_2 and Sr^{2+}-doped CeO_2 with different molar ratios of Sr^{2+}. Undoped CeO_2 exhibited a single-phase X-ray diffraction peaks due to a fluorite structure, and Sr^{2+}-doping caused no significant peak shifts. The ionic sizes of Ce^{4+} and Sr^{2+} ions with eight-coordination are 111 and 140 pm, respectively. Little shift of the X-ray diffraction peaks upon Sr^{2+}-doping is explained in terms of similarity of the ionic size of Ce^{4+} and Sr^{2+}, although the latter is slightly larger. With increasing molar ratio of Sr^{2+}, however, new peaks appeared at around $2\theta = 29.5$, 42.2, 52.6, and 60.6° which were assigned to the peaks of two stoichiometric compounds of $SrCeO_3$ and Sr_2CeO_4.

RuO_2-loaded undoped CeO_2 exhibited negligible photocatalytic activity for water splitting under UV irradiation. Figure 2 shows the results of RuO_2-loaded $0.10Sr^{2+}$-doped CeO_2. Both H_2 and O_2 were evolved at the initial stage of reaction. In the repetition of reaction, a considerable activity decrease occurred in the second and third runs, but the photocatalytic activity was nearly the same after the fourth run. During the reaction, the ratio of H_2 to O_2 production was maintained at 2.0. These results indicate that water splitting on RuO_2-loaded Sr^{2+}-doped CeO_2 proceeds photocatalytically.

Figure 3 shows photocatalytic activity as a function of molar ratio of doped Sr^{2+}. With increasing molar ratio of Sr^{2+}, both the activities for H_2 and O_2 evolution increased markedly, passed through a maximum at $\alpha = 0.10$, above which the activity decreased monotonically. In contrast to Sr^{2+}-doped CeO_2, neither $SrCeO_3$ nor Sr_2CeO_4 exhibited photocatalytic activity in the presence of RuO_2.

We recently reported the photocatalytic activity of RuO_2-

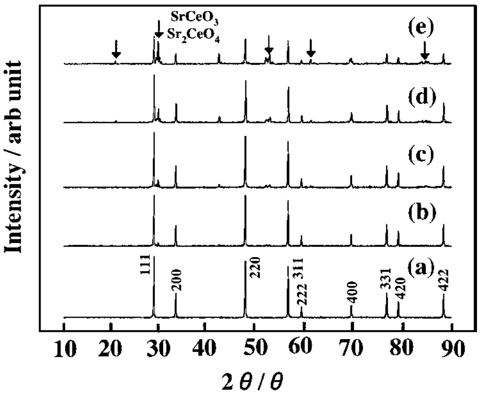

Figure 1. XRD patterns of undoped (a) and Sr^{2+}-doped CeO_2 with different molar ratios ($\alpha = 0.05$ (b), 0.10 (c), 0.20 (d), and 0.50 (e)).

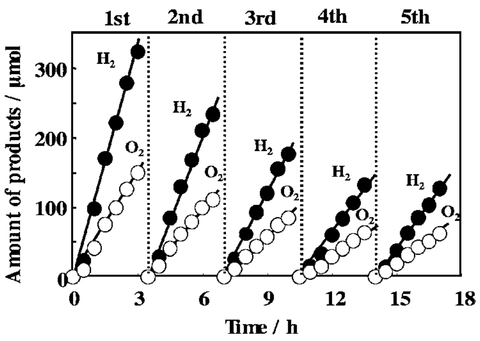

Figure 2. Photocatalytic overall water splitting on RuO_2-loaded 0.10Sr^{2+}-doped CeO_2 (●; H_2, ○; O_2).

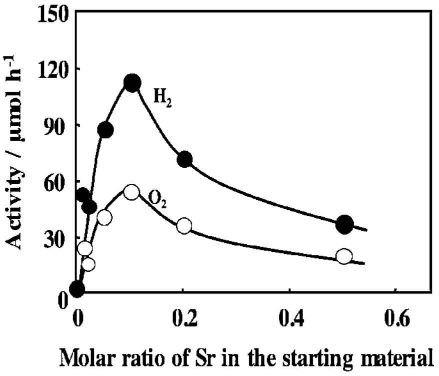

Figure 3. Photocatalytic activity as a function of molar ratio of doped Sr^{2+} (●; H_2, ○; O_2).

loaded GaN with d^{10} electronic configuration for water splitting.[11] Undoped GaN exhibited negligible activity, meanwhile divalent metal ion (Zn^{2+}, Mg^{2+}, and Be^{2+})-doped GaN showed a sufficient photocatalytic activity. The results demonstrate that a small amount of the dopant converts the photocatalytically inactive metal nitride to an efficient photocatalyst for water splitting. Such a marked dopant effect on the photocatalytic performance is hardly reported. It should be noted that Sr^{2+}-doped CeO_2 has the remarkable dopant effect on photocatalyst activation.

The DFT calculation showed that the valence band of CeO_2 is formed by O2p orbital, whereas the conduction band consists of Ce5d orbital. Unoccupied Ce4f orbital appeared between the valence and the conduction band. In Sr^{2+}-doped CeO_2, the Ce5d band was hybridized with Sr5s5p orbital. In UV–visible diffuse reflectance spectra, the absorption of undoped CeO_2 occurred at around 400 nm and leveled off at 350 nm. The adsorption characteristics of Sr^{2+}-doped CeO_2 was similar to that of undoped CeO_2. The threshold absorption at around 400 nm is assigned to electron transfer from O2p orbital (HOMO) to Ce4f orbital. When the photocatalytic reaction was carried out using a Pyrex glass cell (the wavelength of light available for reaction was >300 nm), no photocatalytic reaction proceeded at all. This indicates that the electrons excited to the Ce4f orbital have nothing to do with the photocatalytic reaction, whereas the electrons transferred from the O2p to the Ce5d orbital play an important role in the water splitting. A photocatalysis model is shown in Figure 4.

The stability of a crystal structure and metal ion valency in metal oxides is determined by an ionic size ratio of $r(M^{n+})/r(O^{2-})$ where $r(M^{n+})$ and $r(O^{2-})$ are the ion size of a metal ion and an oxygen anion, respectively. The ideal ionic size ratio of $r(M^{n+})/r(O^{2-})$ for a fluorite structure of a MO_8 eight-coordination is 0.732. In the case of the CeO_2, the ratio is calculated to be 0.703 which deviates considerably from the ideal value. This indicates that a part of Ce^{4+} is converted to Ce^{3+} ion to maintain the fluorite structure. Yabe et al. showed that the partial replacement of Ce^{4+} by larger and/or less positively charged cations permits to maintain the fluorite structure without the reduction of Ce^{4+} to Ce^{3+}.[12] Since Sr^{2+} is slightly larger in ionic size and less positively charged than Ce^{4+}, the Sr-doping leads to the formation of completely Ce^{3+}-free CeO_2. There is a possibility that Ce^{3+} works as a recombination center for photoexcited charges, and its removal is useful for the activation of photocatalyst. To confirm the validity of the view, the effects of dopants with different ion sizes and valency on the activity of CeO_2 is important, and a study is in progress.

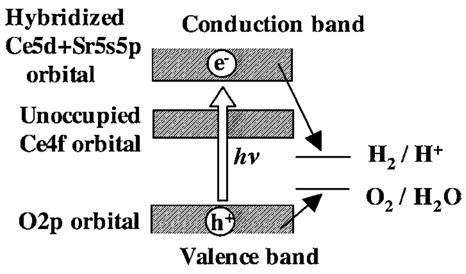

Figure 4. A photocatalysis model for Sr^{2+}-doepd CeO_2.

Sr^{2+}-doped CeO_2 is the first example of lanthanide metal oxides as a photocatalyst for overall water-splitting reaction. The discovery is encouraging for the development of a new photocatalyst.

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