Development of a facet-selective loading method for ultra-fine Rh cocatalysts and high activation of water splitting photocatalysts

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Abstract

The development of water-splitting photocatalysts capable of generating green hydrogen (H_2) from water and sunlight is crucial for achieving carbon neutrality. Photocatalysts with specific exposed crystal facets can facilitate efficient charge separation of electrons/holes, thereby achieving high activity for water splitting. However, there have been no reports of ultrafine (~ 1 nm) cocatalysts being loaded onto specific crystal facets of photocatalysts, despite cocatalysts being the actual reaction sites for water splitting. This study establishes a novel method for achieving facet-selective loading of ultrafine H_2-evolution cocatalysts onto the {100} facets, which are the H_2-evolution facets, of a strontium titanate photocatalyst. The resulting photocatalyst exhibits the highest apparent quantum yield achieved to date for strontium titanate. This research holds the potential to further improve various types of advanced photocatalysts and is expected to accelerate the transition to carbon neutrality.

1. Introduction

Water splitting photocatalysts have attracted attention in recent years because they can produce green H_2 from water and sunlight. Metal nanoparticles called cocatalysts are essential for the high activity of water splitting photocatalysts. Although the photodeposition (PD) method[1] is widely used for the preparation of these cocatalysts, it is difficult to precisely control their "size" and "electronic structure". Our laboratory has established the nanocluster deposition (NCD) method[2], in which nanoclusters can be loaded as cocatalyst precursors with controlled particle size. In addition, photocatalyst supports with controlled exposed crystal facets allow space-charge separation of excited electrons and holes, thereby realizing relatively efficient water splitting. In this study, we established a method to selectively load a 1.2 nm-$Rh_{2-x}Cr_xO_3$ H_2-evolution cocatalyst onto the {100} facets of strontium titanate ($SrTiO_3$), which is a H_2-evolution facet, to further improve water splitting activity.

2. Experiment

18-facet $SrTiO_3$[3] (18-STO) with exposed {100} and {110} facets were used as the photocatalyst support and glutathione-protected Rh complex (Rh:SG) as the cocatalyst precursor. First, a chromium oxide layer was formed on 18-STO, and then Rh:SG was adsorbed. In this process, the following two strategies were tried to selectively support the Rh cocatalyst on the {100} facets: 1) adding ethylene glycol to prevent the adsorption of Rh:SG on the oxygen (O_2)-evolution facets ({110} facets), and 2) photo irradiation under basic conditions. The ligand was then removed by calcination treatment, and the objective photocatalyst was obtained by photoirradiation (F-NCD; this method). Photocatalysts

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prepared by the NCD method and the PD method were used for comparison.

3. Results and discussion

3.1 Particle size and {100} facets selectivity

The particle size of the Rh cocatalyst particle and the crystal facets loaded on the photocatalyst prepared in this way were investigated using transmission electron microscopy (TEM) (Fig. 1). The results showed that for the NCD method (Fig. 1b), the selective loading rate on the {100} facets (number of facets with {100} facets/total number of facets) was 59%. On the other hand, the PD method (Fig. 1c) and the F-NCD method (Fig. 1a) loaded the catalysts on the {100} facets with high crystal facet selectivities (97% and 88%).

3.2 Water splitting activity evaluation

The water splitting photocatalytic activity of the obtained photocatalysts was evaluated. The results showed that the photocatalysts prepared by F-NCD method exhibited 1.5- and 2.6-times higher water splitting activity than those prepared by previous methods (NCD method and PD method; Fig. 2).

4. Conclusions

In this study, we have succeeded in establishing a crystal facet-selective loading method of ultra-fine Rh cocatalysts onto the H_2-evolution facets of 18-STO by using two strategies. As a result, the photocatalytic activity for water splitting was improved by 1.5 times and 2.6 times compared to the conventional methods of NCD and PD, respectively. These results suggest that the Rh cocatalyst particles loaded by F-NCD method were loaded finely and selectively on the H_2-evolution facets, which resulted in efficient charge separation and improved water splitting activity [4].

Acknowledgment

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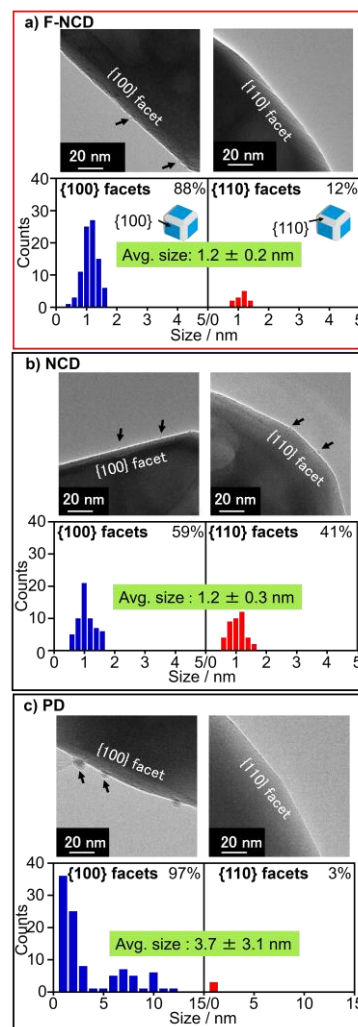
Fig.1 TEM images of cocatalysts of 18-STO prepared by (a) F-NCD method, (b) NCD method, and (c) PD method, and histograms of the obtained cocatalyst particle size and the loading ratio on each facet.
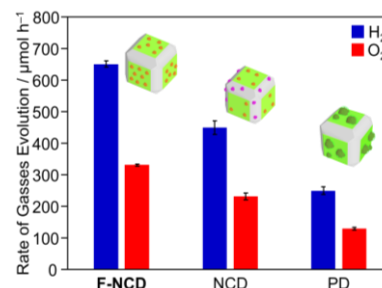

Fig.2 Comparison of the overall water-splitting activity of photocatalysts prepared by each method.