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Enhancement of visible-light-driven photocatalytic activity for water-splitting reaction by loading size-controlled Pt Nanocluster as cocatalyst

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Abstract

Platinum nanoparticle (Pt NP) is well-known as a useful cocatalyst for hydrogen (H_2) evolution reaction (HER). However, it is difficult to load Pt NPs with their size and electronic state controlled precisely using conventional methods on a water-splitting photocatalyst (WSP). In our work, we synthesized ultrafine Pt nanocluster (NC) by polyol reduction and ligand exchange method, and established a new method to load them on g-C_3N_4 (gCN) as a cocatalyst while maintaining their size and electronic state. The HER activity of the obtained WSP was higher than those of the conventional method. It is suggested that the enhanced activity of obtained WSP using by our method was attributed to 1) the increase in the number of active sites due to the finer particle size of the Pt NC cocatalyst and 2) the suppressed carrier recombination by the metallic electronic state of Pt NC cocatalyst.

1. Introduction

It is essential for a "**carbon neutral**" to enhance photocatalytic activity of the WSP, which can generate H_2 from water and sunlight. In general, in order to improve the activity of the WSP, metal NPs as cocatalysts are loaded onto the WSP. However, it is difficult to load Pt NPs on the WSP with their size and electronic state controlled precisely using conventional methods. We have established a new method to synthesize size-controlled metal (Au, Rh *etc.*) NCs and load them onto WSPs, and have succeeded in increasing their activity(1,2,3). On the other hand, in order to implement such a WSP in society, it is essential to use visible-light-responsive photocatalyst. gCN is a visible-light-responsive photocatalyst composed entirely of organic materials, which has been actively studied in recent years not only because it is a sustainable material but also because it has several advantages. In this study, we established a new method for monodisperse loading of ultrafine Pt particles on gCN while maintaining its size and electronic state, to enhance their activity.

2. Experiment

g-C_3N_4 was synthesized by thermal polymerization of urea, and Pt NC was synthesized using the polyol reduction and ligand exchange methods, respectively. Pt_{NC}/gCN was prepared by adsorbing Pt NCs onto gCN while stirring them in toluene, and then calcinating them. For comparison with conventional preparation methods of cocatalyst, the WSPs loaded with Pt NPs were obtained by conventional photodeposition (Pt_{NP}PD/gCN) and impregnation (Pt_{NP}Imp/gCN) methods, respectively.

3. Results and discussion

3.1 Characterization & Activity

We measured the size of Pt particles from transmission electron microscopy (TEM) images. As a result, the size of Pt particles on Pt_{NC}/gCN was 1.2 ± 0.2 nm (Fig. 1, inset), which was finer size and narrower distribution than that of Pt_{NP}PD/gCN (2.1 ± 0.5 nm) and Pt_{NP}Imp/gCN (1.5 ± 0.6 nm). Also, the Pt L_3-edge X-ray absorption near surface structure (XANES) spectra showed that the Pt particles in Pt_{NC}/gCN were loaded in a more metallic electronic state than those in Pt_{NP}Imp/gCN (Fig. 2). The H_2 evolution activity of Pt_{NC}/gCN was 3.5 times and 13 times higher than that of Pt_{NP}PD/gCN and Pt_{NP}Imp/gCN, respectively (Fig. 1).

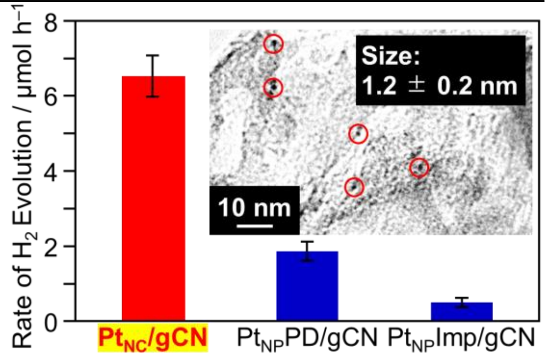

Fig. 1 Activities of each WSPs
(Inset: TEM image of WSP. A (Pt_{NC}/gCN))

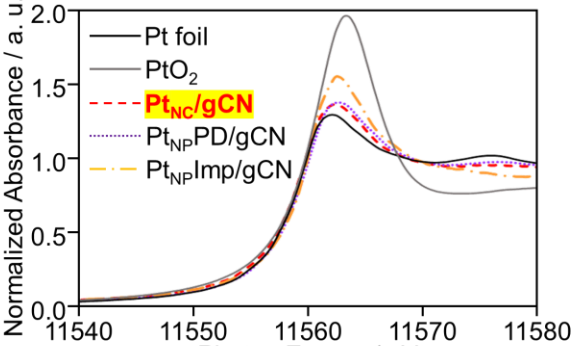

Fig. 2 Pt L_3-edge XANES spectra of standard samples (Pt foil, PtO_2) and each WPSs

3.2 Mechanism of the enhancement

The behavior of trapped electrons and holes was observed by transient absorption spectroscopy. In the decay curve at 667 nm (Fig. 3), where the behavior of holes is observed, no difference in decay speed was observed in our method, while the decay speed was faster in the one loaded with the conventional method. The Pt particles loaded by our method do not trap holes that may recombine with excited electrons inside them, and thus recombination was suppressed (Fig. 4).

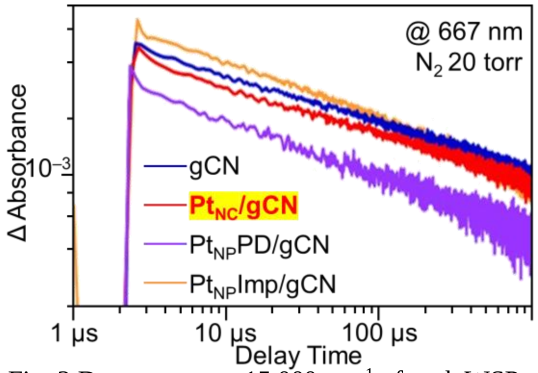

Fig. 3 Decay curve at 15,000 cm^{-1} of each WSPs

4. Conclusions

1) The Pt_{NC}/gCN which is prepared by our method showed 3.5- and 13-times higher HER activity than those which are prepared by conventional photodeposition and impregnation methods, respectively. 2) This increase in activity was induced by an increase in the number of active sites due to the finer size, and suppression of carrier recombination due to metallic electronic state of Pt cocatalyst. In the future, we are expected to apply the Pt nanocluster cocatalysts to a variety of other highly active photocatalysts.

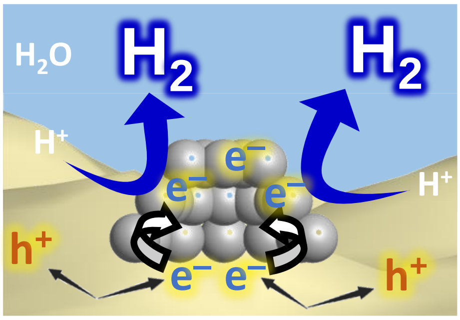

Fig. 4 Mechanism of the enhancement (Pt_{NC}/gCN)

References

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