Strain effects of metal dispersion on crystal phase and photocatalytic activity of TiO_2

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Abstract: Effects of metal dispersion on the crystal phase of TiO_2 were studied and it was found that tensile strain was formed by dispersion of Au or Pt and Anatase phase of TiO_2 was stabilized by tensile strain. Water splitting activity of metal dispersed TiO_2 was also studied and it was found that hydrogen formation rate can be increased by metal dispersion. Therefore, it was found that tensile strain in TiO_2 is effective for increasing photocatalytic activity to water splitting.

Keywords: Metal dispersion, Water splitting, TiO_2, Tensile strain.

1. Introduction

Water splitting with photocatalyst is expecting as the most ideal and cost effective clean hydrogen-generation process which directly converts solar energy to hydrogen. In the conventional study, mechanism for water splitting on photocatalyst have not been studied in details, however, formation of H_2 on noble metal is easily occurred with reasonably low activation energy, however, formation of O_2 from OH^- coupling is slow and seems to be rate determining steps. Therefore, it seems that increase in coupling of surface oxygen which could be related with oxygen vacancy is important for increasing photocatalytic activity to water splitting. [1] The photocatalytic activity is also strongly dependent on the co-catalyst. Co-catalyst works as active site and promotes charge separation. Until now, many efforts have been focused on designing co-catalyst. However, designing photocatalyst from oxygen vacancy mobility have not been performed up to now. Recently, lattice strain are attracting much interest from increase in oxygen ion transport in oxide and we reported that metal dispersion in bulk of Pr_2NiO_4 oxide is effective for introduction of lattice strain resulting in increase in vacancy transport. [2] In this study, effects of metal dispersion in TiO_2 which is the typical photocatalyst are studied from lattice strain as shown in Fig.1 and the influence of photocatalytic activity by dispersion of metal were also studied.

2. Experimental

Metal particle dispersed TiO_2 (P-25) was prepared by metal precursor loading followed by sintering. P-25 TiO_2 (Ishihara Industry Co. Ltd) was used as a starting material. Noble metal chloride and oxalic acid were used without any purification. The colloidal solution was mixed in the TiO_2 suspension in ethanol and distilled water (1:1). The reaction system was being stirred at 80 °C in water bath for 1 h with reflux. This suspension was heated to evaporate solvent at 180 °C and calcined in air at 350 °C for 2 h. The calcined powder was sintered with Spark Plasma Sintering at various temperature and pressure using cylindrical graphite of 10 mm die. After sintering process, sample discs were heated at 350 °C for 2 h in air for removing carbon impurity. Annealed samples were grinded by hand grinding method for 5 min.

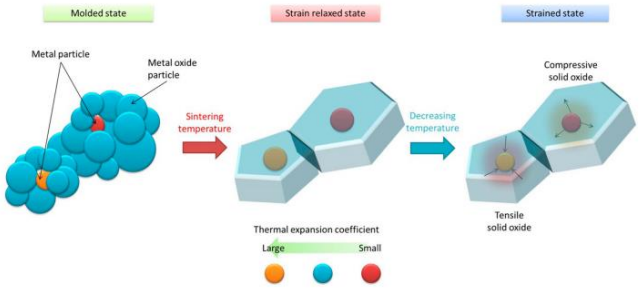

Figure 1. Schematic image of three-dimensional strain. Differing thermal expansion coefficients

For photocatalytic reactions, 30 mL of 10 vol % methanol solution as a sacrificial reagent (electron donor), 50 mg of prepared photocatalyst were mixed in the glass cell with magnetic stir bar. The reaction mixture was evacuated and filled with Ar. This was followed by irradiation using a Xenon lamp (300 W). The activity of the photocatalyst for hydrogen generation was measured over 5 h.

3. Results and discussion

Figure. 1 (a) shows XRD pattern of the powder sample obtained by SPS process. When no Au was dispersed, XRD shows that only rutile phase was observed after SPS sintering, however, with increasing Au amount dispersed in TiO_2, it was found that XRD peaks assigned to Anatase phase were observed and the peak intensity was increased with increasing the amount of Au dispersed. In addition, diffraction peaks of Rutile as well as Anatase phase was shifted to lower angle with increasing Au amount dispersed. Therefore, it was found that tensile strain was formed in TiO_2 lattice and also Anatase phase is stabilized under strain lattice. Figure. 1 (b) shows that H_2 formation amount on Au dispersed TiO_2 at 1.5 and 2.5 wt% Au dispersed. When no Au dispersed, Rutile TiO_2 shows almost no H_2 formation although methanol was added as sacrificial reagent. However, when Au was dispersed, H_2 formation was observed and obviously H_2 formation rate was increased with increasing Au amount. Therefore, this increase in H_2 formation rate can be explained by stabilizing Anatase phase by tensile strain and increase in oxygen vacancy diffusivity. It is also noted that H_2 formation rate on 2.5 wt% Au dispersed sample is larger than that of P-25 and so increased H_2 formation rate is not simply assigned to the Anatase phase but contribution of oxygen vacancy is also important. Although contribution of oxygen vacancy is not clearly pointed up to now, coupling of OH^- for generation of O_2 is essential and so I think oxygen vacancy may have large role for water splitting reaction on photocatalyst. On the other hand, as discussed, considerable attention has been paid to the "strain effect" on charge separation. Therefore, by using chemo-chemical strain effects, increase in photocatalytic activity is expected. Therefore, in this study, new concept for improving photocatalytic activity is successfully demonstrated.

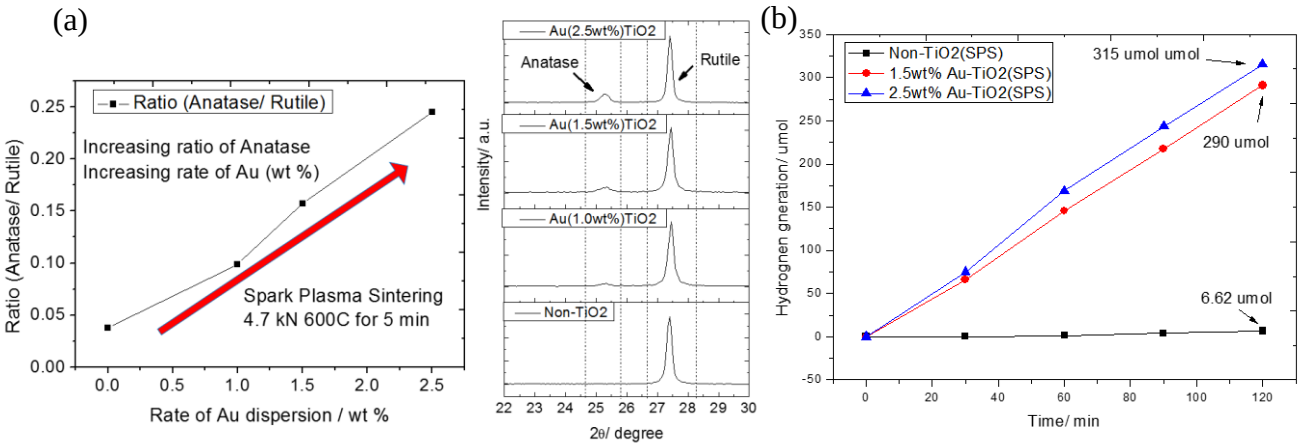

Figure 2. (a) Comparison of the XRD pattern of spark plasma sintered Au TiO_2 powders for different ratio (0, 1.0, 1.5, 2.5 wt%) (b) Time course of hydrogen evolution on Au-TiO_2 (SPS) according to amount of gold.

4. Conclusions

Au dispersion into TiO_2 forms three dimensional tensile strain which stabilized Anatase phase of TiO_2. It was found that tensile strain enhanced the photocatalytic activity and this enhancement was strongly related with increased diffusivity of oxygen vacancy. As the result, tensile strain in 3D is highly interesting from increasing photocatalytic activity.

References

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