Pt-enhanced mesoporous Ti^{3+}/TiO_2 with rapid bulk to surface electron transfer for photocatalytic hydrogen evolution

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Abstract: Pt-doped mesoporous Ti^{3+} self-doped TiO_2 (Pt-Ti^{3+}/TiO_2) is in-situ synthesized via an ionothermal route, by treating metallic Ti in an ionic liquid containing LiOAc, HOAc and a H_2PtCl_6 aqueous solution under mild ionothermal conditions. Such Ti^{3+}-enriched environment, as well as oxygen vacancies, is proven to be effective for allowing the in-situ reduction of Pt^{4+} ions uniformly located in the framework of the TiO_2 bulk. The as-formed Pt^{n+}-O bonds could act as the bridges for facilitating the photo-generated electron transfer from the bulk to the surface of TiO2 with a higher electron carrier density.

Keywords: Ti^{3+}, Pt doping, H_2

1. Introduction

Since the discovery of photoelectrochemical water splitting using TiO_2 and a Pt electrode by Fujishima and Honda in 1972,[1-3] various semiconductor materials and other elemental doped materials have been developed as photocatalysts for water splitting. To the case of H_2 evolution, co-catalysts, such as Pt, CoOx and NiOx, are required to facilitate H_2 production by enhancing charge separation or providing more active catalytic sites.[4] Loading metallic Pt on the surface of TiO_2 using a photoredox deposition method has often been employed as a co-catalyst. In this case, the Pt/TiO_2 heterojunction may affect the charge transfer process forming a Schottky barrier between these components to separate the photoinduced electrons and holes, and the loaded Pt, which acts as an active site, could easily trap excited electrons and protons, which can catalyze H_2 evolution. Recently, different valence states of Pt modified TiO_2 have attracted much attention because of their excellent ability to inhibit the hydrogen oxidation reaction in proton exchange membrane for fuel cells and H_2 evolution process. Nevertheless, it is difficult to introduce the Pt species with various valence into the bulk framework of TiO_2 owing to the difficulty in replacing Ti with Pt. Actually, such Pt species embedded in the framework of TiO_2 could be very significant for accelerating the photogenerated electrons in the bulk to transfer to surface states, with a greatly enhanced quantum efficiency. Therefore, it is of great interest to explore a route for embedding Pt with various valence states in the framework of TiO_2, towards the objective of achieving high quantum efficiency for photocatalytic reaction. In the present work, platinum species, with various valence states, were doped in the framework of TiO_2 through an in-situ ionothermal method. Herein, the defect sites, including Ti^{3+}-dopants and oxygen vacancies, in the TiO_2 allow the Pt^{n+} to enter into the framework of mesoporous TiO_2 via substituting Ti. The doped Pt ions embedded in the TiO_2 lattice may facilitate the photogenerated electron transfer to metallic platinum on the surface of TiO_2 for efficient H_2 production via the Pt^{n+}-O bonds. In addition, a mesoporous structure for the Pt-Ti^{3+}/TiO_2 microspheres was also constructed by such a metal-induced self-assembly assisted by an in-situ ionothermal method.

2. Experimental (or Theoretical)

In a typical synthesis, 0.6 g of LiAc.$2H_2O$, 12 mL of DMF, 18 mL of glacial HOAc and different amounts of an H_2PtCl_6 (1.0 g/100 mL) aqueous solution were mixed in a 100 mL Pyrex beaker and magnetically stirred for 15 min to obtain a clear solution. Then, the mixture was transferred to an autoclave (50 mL). Meanwhile, a piece of Ti foil (99.5 %, 20 mm * 33 mm * 0.3 mm) was ultrasonically cleaned in a solution that consisted of deionized water, acetone, and ethanol at a volume ratio of 1:1:1, followed by adding into the autoclave along with 2 mL of an ionic liquid (1-methyl-imidazolium tetrafluoroborate). The mixture was maintained at 200 °C for 24 h, and the products were then washed with water and ethanol three times, followed by drying at 80 °C for 12 h. Finally, the as-obtained samples are represented by X wt% in-situ Pt-Ti^{3+}/TiO_2, where X represents the mass percentage ratio of Pt:Ti detected by ICP analysis. A black Ti^{3+}/TiO_2 sample was synthesized in the same manner without the H2PtCl6 aqueous solution according to our previously reported protocol.

3. Results and discussion

The morphologies of Ti^{3+}/TiO_2 and different amount of Pt loaded Ti^{3+}/TiO_2 samples were characterized by field emission scanning electron microscopy (FESEM). Figure 1a shows that the pure Ti^{3+}/TiO_2 was composed of stacked regular particles with an average size of about 25 μm. It is interesting that the flower-like TiO_2 consisting of nanorods could be produced by introducing the H_2PtCl_6 aqueous solution, as shown in Figure 1b-f. Herein, the introduced H_2PtCl_6 solution may have induced the self-assembly process, resulting in the formation of flower-like TiO_2 spheres. As known, the acidity plays an important role in shaping the morphology of the metal oxide catalysts. In the present work, equal amounts of the reagents (i.e., H_2O or HCl) were chosen to replace the H_2PtCl_6 solution for the fabrication of the catalysts.The morphology of the TiO_2 prepared in the presence of added H_2O or HCl was nearly same as that of the ionothermal Ti^{3+}/TiO_2 that was prepared without H_2PtCl_6. This is because the acidity of the reaction solution for Ti^{3+}/TiO_2 was effectively the same in the presence of a small amount of H_2O or HCl, owing to the presence of excess glacial HOAc (18 mL). Thus, we conclude that the flower-like TiO_2 morphology obtained in the presence of H_2PtCl_6 is because of the Pt doping.

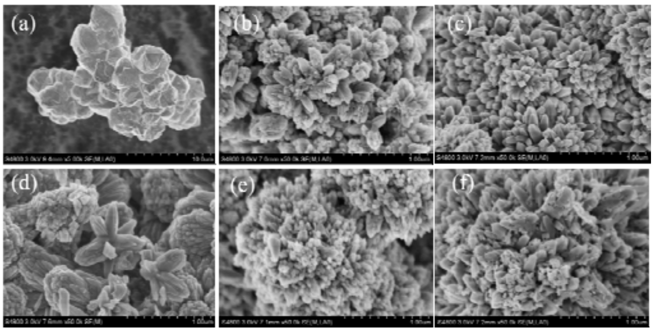

Figure 1. FESEM of Ti^{3+}/TiO_2 (a) and in-situ Pt-Ti^{3+}/TiO_2 with different Pt/Ti weight ratios (wt % Pt): (b) 0.18, (c) 0.19, (d) 0.20, (e) 0.21, and (f) 0.26.

4. Conclusions

In summary, uniform and ultrafine Pt with various valence states was in-situ doped into the Ti^{3+}/TiO_2 framework providing materials that exhibit excellent performance for H_2 evolution, much higher than those obtained by the traditional photoreduction method of metallic Pt loading within Ti^{3+}/TiO_2 and commercial P25. Such enhanced activity arises because the noble Pt metal-induced self-assembly resulted in the formation of flower-rod-like microspheres with mesoporous structure, leading to strong light absorption capability. High Ti^{3+} concentration as well as oxygen vacancies allow to dope various Pt valence states into the TiO_2 lattice with the formation of well dispersed Pt^{n+}-O species, possibly providing pathways for electron transfer, facilitating photogenerated charge transfer from the bulk to TiO_2 to surface with a high electron carrier density of 3.11×10^{20} cm^{-3}.

References

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