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H₂ Spillover Enhanced Hydrogenation Capability of TiO₂ Used for Photocatalytic Splitting of Water: A Traditional Phenomenon for New Application

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Black TiO₂ was usually obtained via hydrogenation at high pressure and high temperature. Herein, we reported a facile hydrogenation of TiO₂ in the presence of a small amount of Pt at relatively low temperature and atmospheric pressure. The hydrogen spillover from Pt to TiO₂ accounts well for the greatly enhanced hydrogenation capability. The as-synthesized Pt/TiO₂ exhibits remarkably improved photocatalytic activity for water splitting.

As an excellent photocatalyst for hydrogen generation and water treating, titanium dioxide (TiO₂) has drawn extensive attention. However, the wide-band-gap of TiO₂ makes it only respond to ultraviolet light. To improve the solar energy utilization efficiency, many strategies on band structure modification such as doping nonmetal or metal elements have been proposed to reduce the band gap of TiO₂. Recently, black TiO₂ has attracted enormous attention for its high absorptivity to visible/infrared light and high photocatalytic activity. By now, the synthesis of "disorder-engineered" black TiO₂ has become a research hotspot. Nevertheless, the reported hydrogenation methods have many disadvantages such as the requirements of high pressure and high temperature, and the ineffectiveness to crystalline TiO₂. Meanwhile, it is shown that the hydrogenation on amorphous titania precursors cannot ensure good photocatalytic activity. Hence, new strategies on TiO₂ hydrogenation should be developed.

Hydrogen spillover from noble metal nanoparticles (Pt, Pd, Ru or Rh) to supports is an often-observed phenomenon in many traditional catalytic reactions. Generally, the H₂ molecules are first chemically adsorbed and dissociated into atomic species by metallic nanoparticles; then they migrate to supports, providing active species for catalytic reactions. If the supports are reducible oxides, hydrogen spillover can greatly enhance their reducibility. So, it is reasonable to imagine that the combination of noble metals and TiO₂ would improve the reducibility of TiO₂. However, the reported hydrogenation of TiO₂ to TiO₂@TiO₂-x was always performed in the absence of noble metals (e.g., Pt), which were later loaded on the after-hydrogenated TiO₂@TiO₂-x. As the function of hydrogen spillover is ignored, the reaction condition is often rigorous. To demonstrate the effectiveness of hydrogen spillover and make the reaction condition milder, we designed a facile hydrogenation route on crystalline TiO₂, in which Pt was preloaded on TiO₂; then hydrogenation was carried out on the precursor at atmospheric pressure and relatively low-temperature. The whole process is described in the route 2 of Scheme 1. For comparison, another sample Pt/TiO₂(H₂) was also prepared in a way similar to the widely reported route (route 1 of Scheme 1), using the hydrogenated TiO₂@TiO₂-x as support for the subsequent Pt loading. Herein, we surprisingly found that the as-designed hydrogenation route at the condition of atmospheric pressure and relatively low-temperature is feasible and highly efficient for the synthesis of Pt promoted TiO₂/TiO₂-x catalysts. Compared with the sample prepared via route 1, the catalyst obtained through route 2 is much more active for water splitting to produce H₂.

**Scheme 1.** Strategies for the hydrogenation of Pt promoted TiO₂ to obtain the TiO₂@TiO₂-x. Route 1: hydrogenation of TiO₂ followed by the loading of Pt. Route 2: hydrogen spillover involved simultaneous hydrogenation of Pt/TiO₂.

The precursor of the supported catalyst 1wt% Pt/P25 was first prepared via conventional impregnation, then it was reduced by sodium borohydride to get metallic Pt. The Pt nanoparticles possessing an average diameter < 3 nm are highly dispersed on P25 as seen in Fig.1a. H₂ temperature-programmed reduction (TPR) is a well-developed technology for the characterization on the reducibility of oxygen species. So, the H₂-TPR was employed to evaluate the reducibility of...
P25 & Pt/P25 before hydrogenation in order to select proper hydrogenation temperature, the results of which are shown in Fig. 1b. As expected, P25 can hardly react with H₂, showing very weak signal and no reduction peaks; while after preloading of metallic Pt, the reduction signal is greatly enhanced from 160 °C, forming four obvious peaks at 400, 500, 700 and 750 °C. On the basis of the H₂-TPR results, Pt/P25 was annealed in 8% H₂/N₂ atmosphere at several different temperatures (200, 400, 500 or 700 °C) for 4 h, respectively. The hydrogenated samples are denoted as Pt/P25-x; x stands for the treatment temperature.

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(1) H₂ is firstly dissociated into H atoms by Pt (Eq. 1), then the adsorbed O₂ on the surface of TiO₂ is reduced to H₂O (Eq. 2) below 240 °C.

\[
\text{Pt} + \frac{1}{2} \text{O}_2 \rightarrow \text{PtO} \tag{1}
\]

\[
2\text{H} \rightarrow \text{H}_2 \quad (2)
\]

---

(2) Above 240 °C, the bond between surface lattice oxygen and Ti is interrupted by H atom, forming a hydroxyl group and an oxygen vacancy (Eq. 3)\(^{22}\).

\[
\text{Pt} + \text{O}_2 \rightarrow \text{Pt} \cdot \text{OH} \quad (3)
\]

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(3) As the temperature is further increased to 540 °C or higher, atomic H species would diffuse from surface into bulk, generating localized Ti-O(H)-Ti species\(^ {22}\), after dehydration, a reduced form (Ti₃O₅) of titanium dioxide (Eq. 4) is produced.

\[
\text{Pt} + \frac{3}{2} \text{O}_2 \rightarrow \text{Pt}_3\text{O}_5 \quad (4)
\]
former H₂–TPR analysis and the description in Eq. 3. The decrease of the binding energy for both Ti 2p and O 1s also suggests that the increase of surface electron density after hydrogenation. This deduction is supported by the EPR results in which electron-rich species namely oxygen vacancy combined with one electron (\(\text{Vo}^-\)) have been clearly detected.

The photoluminescence (PL) emission spectra of P25, Pt/P25 and Pt/P25-400 were also recorded (Fig. S5). The shapes of the PL spectra are very similar to each other, but the intensity of Pt/P25-400 is much lower as compared with those of P25 and Pt/P25, which indicates that the recombination of photoinduced electron-hole pairs is greatly suppressed. This phenomenon may be caused by the formation of bond tail states. The enhanced charge separation is believed to be the major reason for the improvement of photocatalytic activity.

The hydrogenated sample Pt/P25-400 was also characterized by HRTEM. From the image shown in Fig. 3a a disordered shell coating on both anatase and rutile crystalline cores could be observed, as marked by the blue dash line. Generally, the disordered shell is a typical morphology change of TiO₂ after hydrogenation. To obtain more information of the disordered shell, we selected an area in Fig. 3a (red box) to perform the Fast Fourier Transform (FFT) and Inverse Fast Fourier Transformation of image (b) performed on the red arrow pointed spots.

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In a summary, for the first time, we successfully synthesized the Pt–promoted TiO₂@TiO₂-x photocatalyst (Pt/TiO₂-x) via a facile H₂ spillover enhanced one-step hydrogenation with metallic Pt nanoparticles preloaded on TiO₂. Compared with the Pt/TiO₂ without treated by H₂ and the Pt/TiO₂-x with the TiO₂ hydrogenated first, the catalysts Pt/TiO₂-x exhibit much better catalytic activity for water splitting. The optimal hydrogenation temperature is 400 °C. The as-proposed hydrogen spillover involved hydrogenation strategy is a feasible and highly efficient hydrogenation route. The generation of oxygen vacancy and the formation of band tail states during hydrogenation are responsible for its high catalytic activity due to the suppression of electron-hole recombination.

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Notes and References

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Figure 3. (a) HRTEM image of Pt/P25-400; (b) the FFT image of the area marked with red dash line box in (a); (c) Inverse Fast Fourier Transformation of image (b) performed on the red arrow pointed spots.