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COMMUNICATIONS

Self-Doped Ti^{3+} Enhanced Photocatalyst for Hydrogen Production under Visible Light

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Abstract: Through a facile one-step combustion method, partially reduced TiO_2 has been synthesized. Electron paramagnetic resonance (EPR) spectra confirm the presence of Ti^{3+} in the bulk of an as-prepared sample. The UV−vis spectra show that the Ti^{3+} here extends the photoresponse of TiO_2 from the UV to the visible light region, which leads to high visible-light photocatalytic activity for the generation of hydrogen gas from water. It is worth noting that the Ti^{3+} sites in the sample are highly stable in air or water under irradiation and the photocatalyst can be repeatedly used without degradation in the activity.

Driven by increasing energy needs, decreasing fossil fuel resources, and environmental concerns of nuclear energy, the search for clean and renewable energy is attracting massive research interest. Utilization of solar energy to produce hydrogen gas from water has long been considered the ultimate solution. Since the discovery in 1971 that TiO_2 could act as a photochemical water-splitting catalyst,[1] over 100 photocatalysts have been reported.[2] Because of its abundance, non-toxicity, and stability, TiO_2 has been extensively studied. However, for practical applications, pure TiO_2 is not a good candidate, because it is only active under ultraviolet (UV) irradiation in order to overcome the band gap of 3.2 eV for anatase phase. Therefore, band gap engineering is required if we want to use TiO_2 as a water-splitting catalyst under visible light irradiation. Initially, cations such as Al, Nd, Sb, Ag, Ru, V, Cr, Mn, and Fe were used as dopants to introduce states into the TiO_2 band gap.[3] However, problems such as thermal instability, increased carrier recombination centers, and the need for an expensive ion-implantation facility pose significant limitations for this strategy.[4] It was once proposed that doping nitrogen into TiO_2 is a better choice compared to doping with cations or other anions.[4] However, later studies both theoretically and experimentally have raised questions about this N-doping strategy and its suitability as the most efficient method.[5] Furthermore, the reported activity for the photoreduction of water to hydrogen is quite low.[6]

Reduced TiO_2 (TiO_{2-x}), which contains the Ti^{3+} or oxygen vacancy, has been demonstrated to exhibit visible light absorption.[7] It was believed that the introduced localized oxygen vacancy states with energies 0.75 to 1.18 eV below the conduction band minimum of TiO_2 are lower than the redox potential for hydrogen evolution, which, in combination with the low electron mobility in the bulk region due to this localization, makes the photocatalytic activity of the reduced TiO_2 negligible.[8] However, theoretical calculations show that a high vacancy concentration could induce a vacancy band of electronic states just below the conduction band.[3] The relevant experiments also prove the improved activity of reduced TiO_2 under visible light. Therefore, these results demonstrate that it is possible to fabricate visible-light responsive TiO_2 by introducing Ti^{3+}.

The reported methods to produce TiO_{2-x} include heating TiO_2 under vacuum or reducing conditions (e.g., H_2), chemical vapor deposition, and high energy particle (laser, electron, or Ar^+) bombardment.[5] For practical application, these strategies have a number of limitations such as multiple steps, harsh synthesis conditions, or expensive facilities. Furthermore, the surface oxygen defects are usually not stable enough in air as the Ti^{3+} is easily oxidized and is even susceptible to oxidation by dissolved oxygen in water.[9,10] Therefore, developing a simple and economic strategy to synthesize a stable reduced TiO_2 photocatalyst is still a great challenge, which may be one reason why very limited studies have been reported for TiO_{2-x} photocatalyic activity, especially photocatalytic water splitting.

Here we report a one-step method to synthesize reduced TiO_2, which exhibits extremely high stability and is active for photocatalytic hydrogen production from water.

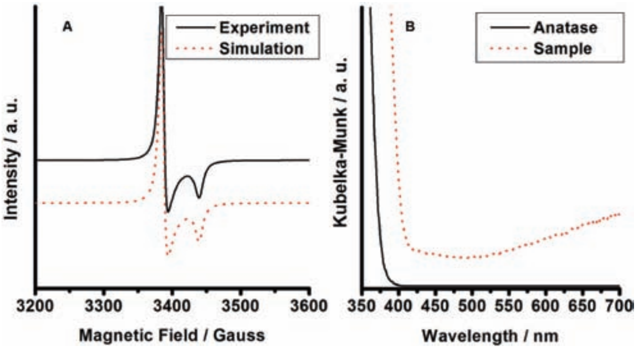

Figure 1. (A) Experimental (solid line, measured under 75 K) and simulated (dashed line) EPR spectra for sample. (B) UV−visible diffuse reflectance spectra for commercial anatase TiO_2 (solid line) and sample (dash line).

By combustion of an ethanol solution (10.0 g, 99.5% ethanol and 2.5 g, 37.1% hydrochloric acid) of titanium(IV) isopropoxide (2.00 g, 98+%) and 2-ethylimidazole (1.80 g, 98%) at 500 °C in air and annealing for 5 h, blue powders (sample) are obtained. During the combustion, the imidazole will react with oxygen and form CO, CO_2, NO, NO_2, etc. The Ti(IV) could be reduced to Ti(III) by the reducing gas (CO and NO).

The powder X-ray diffraction analysis (Figure S1) shows that the as-produced sample is a mixture of anatase phase and rutile phase TiO_2.

To test for the presence of Ti^{3+}, low temperature electron paramagnetic resonance (EPR) spectra were recorded (Figure 1A). The as-synthesized sample gave rise to a very strong EPR signal, while no signal was seen for the commercial Degussa P25 (a mixture of anatase and rutile TiO_2, Figure S2). Anisotropic powder pattern g-values of $g_x = g_y = 1.975$ and $g_z = 1.944$ were obtained from a simulation that yielded a near perfect fit to the data. The observed g-values are characteristics of a paramagnetic Ti^{3+} center in a distorted rhombic oxygen ligand field.[11] The EPR data also indicate that there is no Ti^{3+} present on the surface of the sample. It is believed that surface Ti^{3+} would tend to adsorb atmospheric O_2, which would be reduced to O_2^-

and shows an EPR signal at $g \approx 2.02$.[12] The absence of such a peak in Figure 1A would indicate that only the rhombic Ti^{3+} is present in the bulk, which is a key factor in the observed excellent stability of our sample. Furthermore, P25 shows no EPR signal, meaning neither pure anatase nor pure rutile can account for the EPR peaks observed in the sample. From this information we conclude that Ti^{3+} is present in the sample and that only rhombic Ti^{3+} exists in the bulk. Surface analysis of the sample using X-ray photoelectron spectroscopy (XPS) shows no Ti^{3+} peaks and further confirms the conclusion that Ti^{3+} exists in the bulk.

Figure 1B shows the UV−visible absorption spectra for the sample and the commercial anatase. The spectrum of the sample shifts to a longer wavelength revealing a decrease in the band gap. Meanwhile, the absorbance in the visible range is enhanced compared to the stoichiometric anatase. This phenomenon is consistent with the assumption that an electronic band is located just below the conduction band of pure TiO_2.

A theoretical simulation using PWscf package[13] was executed to support the existence of a Ti^{3+} induced electronic band and to further understand its likely influence on the band structure of oxygen-deficient TiO_2. The calculations, based on a plane-wave pseudopotential density functional theory (DFT) approach, were performed on $1 \times 1 \times 2$ and $2 \times 2 \times 1$ anatase supercell with one O atom removed from each system in order to simulate different concentrations of Ti^{3+}. The plane-wave basis set with an energy cutoff of 30 Ryd was satisfactory for an ultrasoft pseudopotential with PBE (Perdew−Burke−Ernzerhof) exchange correlations to capture the properties of anatase phase. Brillouin-zone integration was computed with k points in a Monkhorst-Pack (10, 10, 5) grid. We see a miniband rising up closely below the conducting band minimum (Figure S4). It is found that the width of the band is related to the concentration of the Ti^{3+} or oxygen vacancy, since the width increases as the concentration of oxygen vacancy increased from 1 per 32 to 1 per 16 oxygen atoms. Very similar results have also been reported by Figueras.[3] The above calculations proved that the Ti^{3+} inside the bulk TiO_2 is responsible for the band gap narrowing. Furthermore, the presence of the vacancy band has been reported as an extra benefit for light absorption. The high concentration of oxygen vacancy could break the selection rule for indirect transitions, resulting in an enhanced absorption for photon energy below the direct band gap,[3] which has been observed in our UV−visible spectra.

The photocatalytic activity of the sample for water reduction was studied using the system supplied from Trustteck Co., Inc. After loading 0.300 g of sample with 1% Pt (0.003 g), the photocatalyst was placed into a 120 mL 25% methanol (as a sacrificial agent) aqueous solution in a closed-gas circulation system. A Xe lamp (300 W) with a 400 nm cut-on filter was used to ensure that only visible light (>400 nm) illuminated the photocatalyst. Figure 2 shows a typical time course of H_2 evolution. This photocatalytic reaction exhibits a stable H_2 release rate of ∼15 μmol/h/0.300 g. Even after illumination for 200 h, the activity is still maintained with no noticeable decrease observed, demonstrating the excellent stability of the sample. To understand the solar energy conversion efficiency of the sample, the average external quantum efficiency (EQE) in the range of 400 nm −455 nm was measured and found to be 0.79%. We further measured the EQE with a 420 nm band-pass filter, which gave an EQE of 0.35%, consistent with the above result. The commercial anatase TiO_2 has also been studied for comparison. Although it exhibits high activity under UV light, no apparent H_2 peak appears under visible light (>400 nm) illumination for the anatase TiO_2, providing strong evidence for extending the photocatalytic activity to the visible light range through our strategy.

To exclude the possible influence of the nonmetal dopants such as nitrogen, we replace the 2-ethylimidazole with urea and keep other experimental parameters unchanged. The elemental analyses (Table S1) prove the presence of the N in the sample from urea. However, this sample shows almost no H_2 production activity under visible light illumination (<0.1 μmol/h/0.300 g). Also, the reported C-doped TiO_2 visible light water-splitting reaction requires a photoeletrochemical reaction system and voltage bias,[14] which are not necessary for our Ti^{3+} sample. Therefore, the visible-light photocatalytic activity of our sample is not due to C- or N-doping.

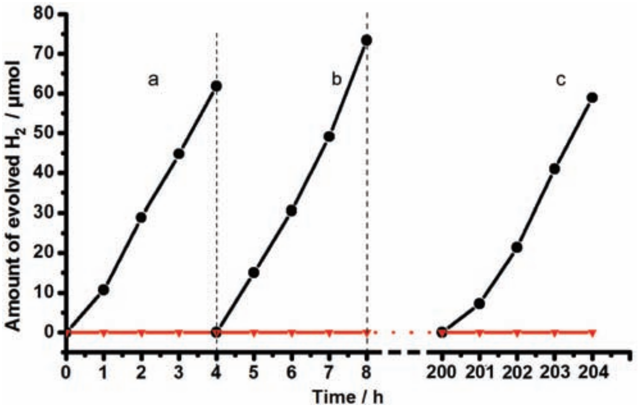

Figure 2. Time course of evolved H_2 under visible light (>400 nm) irradiation. (a) Reaction for 4 h; (b) evacuate and continue reaction for another 4 h; (c) illuminate for 200 h, evacuate system, and continue reaction for 4 h. (●) Sample; (▼) Anatase.

In conclusion, we have developed a simple one-step method to synthesize Ti^{3+}-doped TiO_2. The as-prepared reduced TiO_2 exhibits high stability in air and water with light irradiation. Experimental data show good conversion efficiency in the visible light region (>400 nm). Both theoretical calculations and experimental results support that it is the introduced Ti^{3+} that accounts for the extension of the photocatalytic activity from the UV to the visible light region. The present study demonstrates a simple and economical method for narrowing the band gap and for the development of a highly active photocatalyst under visible light irradiation.

Acknowledgment. We are grateful for support of this work by the NSF (DMR-0907175).

Supporting Information Available: The synthetic procedure, facilities information, XRD patterns, more EPR spectra, and elemental analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA103843D