



Passivation of defect states in anatase TiO₂ hollow spheres with Mg doping: Realizing efficient photocatalytic overall water splitting

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ABSTRACT

Since tremendous numbers of defect are distributed in anatase TiO₂ materials, the photocatalytic overall water splitting (POWS) can not be occurred on anatase TiO₂ nanostructures under normal sunlight. Meanwhile, it is still lacking of effective method to suppress the intrinsic defect states in anatase TiO₂. In the present work, it has been found that the defect induced light absorption in anatase TiO₂ hollow spheres could be reduced by Mg doping. In-depth detecting of the defect states evolution is investigated by the transient infrared absorption-excitation energy scanning spectroscopic measurement (TRIRA-EESS), indicating that the Mg doping could eliminate the intrinsic deep defect states and weaken the shallow defect states in TiO₂. The efficient and stable sunlight-driven POWS is firstly realized on anatase TiO₂ hollow spheres only after doping of Mg rather than Ni, Cr. The H₂ and O₂ evolution rates can be as high as 850 and 425 μmol g⁻¹ h⁻¹, respectively. First principle calculations reveal that the weakening of defect states in Mg doped anatase TiO₂ is mainly caused by the unique electronic structure of Mg dopant.

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1. Introduction

Photocatalytic overall water splitting (POWS) for hydrogen generation is one of the most promising ways for supplying clean and sustainable energy [1–3]. Titanium dioxide (TiO₂) is the benchmark semiconductor used in photocatalysis [4–6]. Among the three phases of TiO₂, anatase is the most active phase for photocatalytic H₂ generation [7,8]. In recent decades, many groups have tried variety of methods, such as nanotechnology, selective facets, cocatalysts, etc., to modify the anatase TiO₂ [9–11]. And there has been a great progress in photocatalytic half water splitting for H₂ production [12,13]. However, defects are inevitably distributed in anatase TiO₂ [14]. The defects could introduce tremendous numbers of defect states in the band gap, which always cause carriers' recombination [15,16]. More seriously, the defect states could weaken the photo-generated carriers' oxidation and reduction capacities in anatase TiO₂ [17]. Li and Weng et al. found that large numbers of defect states especially the deep trapping states are lying in the band gap of anatase TiO₂ [18], thereby impeding the POWS realization

on anatase TiO₂ [19]. Consequently, the POWS has never been taken place on anatase TiO₂ materials under normal sunlight, despite anatase TiO₂ has a suitable band structure both for photocatalytic water reduction and oxidation [20,21]. Therefore, suppression of the defect states in anatase TiO₂ is the key for further developing their applications in photocatalysis. Li et al. reported that a part of defect states in anatase TiO₂ could be suppressed by ultraserve ultraviolet irradiation [19]. However, the defect states were only temporary suppressed and could be recovered without the irradiation of the specific light source. Reviewing the previous results, it is still lacking of efficient and stable method to reduce the defect states in anatase TiO₂.

To date, various transition metal elements have doped into the TiO₂ lattice [22]. The electrons on d orbit have abundant energy levels, which could cause more interband states [23–25]. Thus, doping with transition metal elements in TiO₂ is always introducing more considerable trapping states, which are widely considered to be harmful the POWS realization [26,27]. However, Mg elements have not the complicated d orbit electrons and the ionic radius of Mg²⁺ (65 pm) is similar of Ti⁴⁺ (68 pm). For instance, Iwamoto and Hanaya have report that Mg doping could promote the energy position of conduction band minimum, which is very different from the transition metal doping [28,29]. Herein, through the experiments

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and first principle calculations, we found that the Mg doping could suppress rather than introduce trapping states in anatase TiO₂. Therefore, the efficient and stable POWS under normal sunlight is achieved on the Mg doped anatase TiO₂ ultrathin hollow spheres.

2. Experimental section

2.1. Materials synthesis

The carbon spheres were hydrothermally synthesized using the method reported by Sun et al. [30,31] To synthesize the 0.5% Mg doped TiO₂ (Mg-TiO₂) ultrathin hollow spheres, 50 mg of as-prepared carbon spheres was dispersed in 100 mL anhydrous ethanol by ultrasonication, followed by adding 3 mg of Mg(NO₃)₂·6H₂O and 1 g tetrabutyl titanate. The as-obtained mixture was stirred for 4 h. A rinsing process involving two cycles of centrifugation/washing/re-dispersion was performed with anhydrous ethanol. After dried in an oven in air at 80 °C for 6 h, the Mg-TiO₂ ultrathin hollow spheres were obtained by calcinating the products in air at 400 °C for 12 h. The continuously variable concentration of Mg ions in TiO₂ could be attempted by regulating the concentration of Mg(NO₃)₂·6H₂O in the solution. The as-prepared catalyst for H₂ production and POWS was modified with Pt as a cocatalyst for water splitting based on photo-deposition method reported elsewhere [32]. Briefly, a moderate amount of H₂PtCl₆ was mixed in the aqueous (90%)/methanol (10%) solution containing samples. Then the solution was put under a 300 W xenon lamp. The synthesis of Ni, Cr doped anatase TiO₂ hollow spheres is similar to that of Mg-TiO₂ hollow spheres preparation except of changing the Mg(NO₃)₂·6H₂O as Ni(NO₃)₂·6H₂O and Cr(NO₃)₂·9H₂O respectively. The rutile TiO₂ sample is obtained by calcination of the P25 at 1000 °C for 12 h.

2.2. Materials characterization

Inductive coupled plasma and atomic absorption spectroscopy (ICP-AAS) measurements were used to analyze the ratio of Mg and Ti in samples, after digesting the Mg-TiO₂ hollow spheres in hot sulfuric acid (4 M H₂SO₄ solution). The Mg in 1% doped concentration was detected precisely by ICP-AAS, whereas, the Mg doping concentration in 0.1 and 0.5 was the averaged value of five independent ICP-AAS measurements. The structure properties of Mg-TiO₂ hollow spheres were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (SEM) and high-resolution TEM (HR-TEM). The chemical states of samples were measured by X-ray photoelectron spectroscopy (XPS). The Raman spectroscopy of all the samples was recorded on a Dilor Labram-1B microspectrometer. UV-vis diffuse reflectance experiments were carried out on an ultraviolet-visible spectrophotometer. To further investigate the thermodynamics for different POWS performances on Mg-TiO₂ hollow sphere based photocatalysts, the midgap energy level of Mg-doped anatase TiO₂ were also characterized by transient infrared absorption-excitation energy scanning spectroscopy (TRIRA-EESS), which can identify deep trapped electron energy levels above the valence band (VB) but below the Fermi level of the trapped electrons. Briefly, a 355 nm laser pulses from a Nd:YAG laser (Quanta Ray, Spectra Physics) with a pulse duration of 10 ns and a repetition rate of 10 Hz were used to pump an optical parametric oscillator (GWU premiScan-ULD/240, Spectra Physics) which acted as a wavelength-scanning excitation source (output signal beam tunable from 410 to 709 nm, and idler beam from 710 to 2630 nm) to excite the mid-gap states. The principle of TIRA-ESS is to scan the excitation energy within the band gap of TiO₂ from the visible to near IR region, and use the transient mid-IR-difference spectra to probe the photo-excited electrons within the conduction band or

at the localized excited states below the CB. Both the CB electrons and the excited localized electrons can be detected by the mid-IR probe and distinguished by their remarkable difference in the corresponding absorption spectrum and the decay kinetics (slower decay for the former and faster decay for the latter). All the TIRA-ESS were probed at 2090 cm⁻¹ at a delay time of 250 ns after the excitation pulse in a chamber with a vacuum of 1.0 × 10⁻⁶ mbar. The excitation energy is 0.6 mJ/pulse with a beam size of 4 mm in diameter, and the IR absorbance has been scaled by the excitation intensity in terms of the number of photons (10¹² per pulse).

2.3. Computational details

The calculation model of TiO₂ is anatase phase. The calculated crystal structures are shown in Fig. S8. All the calculations were carried out using the density functional theory (DFT) based on the software package VASP. The exchange-correlation effects and core electrons were taken into account via the generalized gradient approximation (GGA-PBE). We considered Mg/Ni doping effects using 2 × 2 × 2 supercell. One Mg/Ni atom was filled in the interstitial position of TiO₂. The oxygen vacancy was next to the dopant. All the plane waves kinetic energy cut-off were set to 340 eV. The mechanical equilibrium was accomplished by conjugate gradient minimization of the forces to a tolerance of 5 × 10⁻² eV Å⁻¹, and the atomic positions to a tolerance of 2 × 10⁻³ Å, the total energy to a tolerance of 2 × 10⁻⁶ eV.

2.4. Photocatalytic reactions

Photocatalytic reactions were studied on Labsolar-III AG system. The samples were carried out in a Pyrex reaction vessel connected to a gas circulation system at room temperature. POWS was investigated in 100 mL of pure water containing 20 mg of samples. The light source was a 300-W xenon lamp (PLS-SXE300UV) and used the band filters to simulate it as AM 1.5 G sunlight. The reaction started without mechanical stirring and the solution was maintained at 5 °C by a water bath system. The evolved gases were analyzed by gas chromatography (TCD). Argon gas was used as the carrier gas.

2.5. Quantum efficiency (QE)

To obtain an accurate QE value, 100 mg sample was used in this measurement. And the experiment condition is similar to the POWS test. The quantum efficiency was calculated by the following equation: $\Phi (\%) = (2 \times R/I) \times 100$, where R and I represent the number of evolved H₂ molecules and the number of absorbed photons in 1 h, respectively. Here, Φ is the quantum efficiency. The light source was a 300-W xenon lamp attached with a band pass filter ($\lambda = 350 \pm 10, 375 \pm 5, 400 \pm 5$ nm). The intensity of the light irradiation was measured by a thermopile, which was located at the bottom of the reaction cell. For example, taking the measurement of QE for overall water splitting at 350 nm irradiation as a typical case, the irradiation intensity measured was 0.31 mW/cm². It is corresponded to a total absorbed light energy in one hour of 27.96 J. We further took the average energy of photons at 350 nm to be 3.54 eV. The number of the absorbed photons would be $4.92 \times 10^{19} \text{ h}^{-1}$, which was considered as the I value. For the best samples, the rate of H₂ evolution was 7.94 μmol h⁻¹. Therefore, the total number of evolved H₂ molecules in 1 h was 4.78×10^{18} (R), and the calculated Φ was 19.4% accordingly.

3. Results and discussions

In this work, the alkaline-earth metal Mg element was chosen to modify the property of anatase TiO₂ nanostructures. Since

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