



Porous carbon-doped TiO₂ on TiC nanostructures for enhanced photocatalytic hydrogen production under visible light



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ABSTRACT

Titanium dioxide (TiO₂) has been widely investigated as a photocatalyst material because of its stability and hypotoxicity. However, the photocatalytic activity of TiO₂ is suppressed by the large band gap and the high recombination rate of the charge carrier, which leads to confined application. Moreover, how to improve photocatalytic H₂ production without any co-catalyst remains a big challenge. Here, we report a conceptual strategy in a core-shell nanostructure of simultaneously reducing the band gap and the charge carrier recombination rate by introducing a carbon-doped porous TiO₂ layer onto a metallic TiC nanostructure using a facile in situ thermal growth method. TiC@C-TiO₂ core-shell nanostructure materials have higher photocatalytic activity in methanol aqueous solution than those of pure P25 and carbon-doped TiO₂, which results from enhanced visible light absorption, drastic charge transfer, and the large surface area. Notably, the novel core-shell nanostructures still exhibit excellent photocatalytic H₂ production without Pt co-catalyst. The results demonstrate that TiC is an ideal support for TiO₂ photocatalysts, and this novel core-shell nanostructure can significantly shift the position of the band edge of the obtained material. This study presents a design principle for photocatalytic materials as highly efficient visible light photocatalysts.

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1. Introduction

Semiconductor photocatalysts have gained tremendous attention recently due to their potential use in various fields, such as clean renewable energy [1–3] and environment remediation [4–8], aimed at coping with the energy crisis and environment issues nowadays, since Fujishima and Honda found semiconductors could be utilized for the photodecomposition of water in 1972 [9]. Especially, titanium dioxide (TiO₂) has been extensively investigated because of its superior quality of stabilization, hypotoxicity, and photosensitivity. However, the further application of TiO₂ is greatly impeded by its wide band gap (3.0 eV for rutile and 3.2 eV for anatase) and the short lifetimes of photoinduced electron–hole pairs. TiO₂ only absorbs UV light, about 4% of the solar spectrum, into photocatalytic reactions, which means low photoelectronic transition efficiency. In an effort to eliminate these drawbacks, attempts to increase photocatalytic activity have been made, including doping nonmetallic and metallic elements [10–17], optimizing morphology [18,19–21], hydrogenation

[22], surface sensitization [23,24], and combining with narrow-band-gap semiconductors [25–30]. Even though the absorption efficiency of TiO₂ is improved by narrowing the band gap, the recombination rate of photoinduced electron–hole pairs is augmented, because of massive impurities and defects introduced into TiO₂ that cause harm to the lattice and become recombination centers of photogenerated carriers. On the other hand, doping metal elements and coupling with other semiconductors for TiO₂ generate additional cost and undermine stabilization, which has a disadvantageous effect on the practical employment of TiO₂. Therefore, it is crucial that facile and efficient modification of TiO₂ should not only enhance photocatalytic activity, but also take into account cost and stabilization.

Novel core-shell structure morphology has been more and more popular in the world, which can realize rapid separation of photogenerated electron–hole pairs and enhanced light absorption as well as the greater specific surface area [31–35]. Efficient core-shell structure photocatalysts with high photocatalytic activity and stabilization may be attributed to a proper band gap of the components and a lattice match in the boundary for maintaining the stabilization at the photocatalytic process. Incorporating an appropriate component with TiO₂ to form these novel core-shell

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structures has been done with numerous highly active photocatalysts, such as carbon black@TiO₂ core-shell microspheres [36], CdS@TiO₂ core-shell nanocomposites [37], SiO₂@TiO₂ core-shell nanoparticles [38], and TCNQ@TiO₂ core-shell structures [39].

Early transition metal carbides (TMCs) such as earth-abundant ceramics are the ideal support for precious-metal shells [25,27,28,40,41]. Titanium carbide (TiC) as an early transition metal carbide possesses many admirable material properties, including superior stabilization under rigorous condition and high electrical conductivity [26,42]. TiC is well known to be an attractive electrode material for electroanalytical processes, and it shows fast electron transfer in the quinone system [43], and the good modification for the electronic structure of noble metals (e.g., Pt [27,44] and Ir [26]). Here we develop a carbon-doped porous TiO₂ layer on the TiC nanostructure for highly efficient visible-light-responsive photocatalytic hydrogen (H₂) production, which starts with TiC nanoparticles in situ thermal growth of a carbon-doped porous TiO₂ layer by carefully considering the balance of the layer thickness, the carbon content, and the porosity to achieve efficient electron transport and narrow bandgap. It is possible for photocatalysts to facilitate electron transfer and improve the conductivity by introducing TiC into the interior of TiO₂. Furthermore, TiC can absorb hydroxyl radicals on the surface [44], which is beneficial for the decomposition of water. The photocatalytic activity of TiC@C-TiO₂ material is intensively enhanced due to the high visible absorption efficiency and the poor recombination rate of photogenerated charge carriers.

2. Experimental

2.1. Materials and reagents

TiC nanoparticles, methanol, and chloroplatinic acid reagents in this experiment were all commercially available. The TiC nanoparticles (~40 nm) were purchased from the Hite Technology Co., Ltd., China. Methanol (analytical purity, AR) from Tianjin Kaitong Chemical Reagent Co., Ltd, China was used without further purification. Chloroplatinic acid (H₂PtCl₆·6H₂O, analytical purity, AR) as a co-catalyst material was obtained from Tianjin Damao Chemical Reagent Factory, China. Ultrapure water was produced by UPH-20L and utilized in the entire experiment.

2.2. Preparation of TiC@C-TiO₂ core-shell nanostructures

The TiC@C-TiO₂ was prepared by means of a commercially available TiC precursor oxidized in air. In brief, samples of 0.2 g of TiC precursor was oxidized in a tube furnace in air at 350 °C for 30, 60, 90, 120, and 180 min, labelled as TC1–TC5, respectively, at a moderate heating rate. Additional samples were prepared 300, 400, and 450 °C for 60 min, named TC6–TC8, respectively.

Pt nanoparticles were deposited on the surface of TiC@C-TiO₂ photocatalyst by a photodeposition method as follows: 0.2 g of TiC@C-TiO₂ was suspended in 60 ml aqueous solution containing 20 ml methanol by stirring simultaneously, and 6 ml of H₂PtCl₆ (1 mg/ml) was then added. The resulting solution was stored in a glass container and evacuated for 10 min in order to eliminate oxygen dissolved in the solution. Afterward, the solution was illuminated with UV light employing a Xe lamp for 2 h. Finally, the obtained precipitate was segregated by centrifugation, washed four times with ultrapure water, and then dried in an oven at 80 °C for 12 h. P25 purchased from Degussa was treated conformably as above for comparison with TiC@C-TiO₂.

2.3. Materials characterization

The phase composition of all samples was detected by X-ray diffraction (XRD) conducted on a Rigaku D/MAX-Rb operated at 40 kV and 100 mA with CuK α radiation, scanning at a step size of 0.02° from 20° to 80°. The surface morphology and the composition were studied by scanning electron microscopy (SEM, Hitachi, S4800) and energy-dispersive spectroscopy (EDS), respectively. Transmission electron microscopy (TEM) and EDS were also performed on a JEOL-ARM200F with an operating voltage of 120 kV to observe the morphologies and element mapping of samples. High-angle annular dark-field (HAADF) and bright-field (BF) images were achieved at acceptance angles of 90–370 and 0–23 mrad, respectively. Surface areas and pore distribution of samples were determined by ASAP 2020 HD88 using the Brunauer–Emmett–Teller (BET) method, which measured N₂ adsorption-desorption isotherms at 77.5 K.

X-ray photoelectron spectroscopy (XPS) was carried out on a PHI QUANTERA-II manufactured by Ulvac-PHI, Inc., operated at 15 kV and 25 W with monochromatic Al K α (1486.6 eV) radiation. The binding energies of all elements were rectified by the C1s line at 284.8 eV. The survey scans of surface compositions were obtained with a 1.00 eV step size and a 280.00 eV pass energy. The narrow scans for the high-resolution spectra of C1s, O1s, and Ti2p, discovering the chemical bond, were performed with a 0.025 eV step size and a 26.00 eV pass energy.

Ultraviolet-visible-near infrared (UV-vis-NIR) spectra of all the samples were recorded in the region 240–800 nm on a Hitachi U-4100 spectrophotometer equipped with an integrating sphere at room temperature. PL emission measurement was conducted on a JobinYvon Nanolog-3 spectrofluorometer with emission wavelength 240 nm. The electron spin resonance (ESR) spectrum was obtained from a Bruker A300 instrument with a 6.36 mW microwave powder and a 9.41 GHz modulation frequency. Typically, a sample of 6 mg was put into the bottom of a quartz tube, the temperature was lowered to 100 K, and the sample was analyzed in the dark.

The photoelectrochemical (PEC) performance was assessed on a typical three-electrode cell employing an electrochemical station (CHI 660E, Shanghai Chenhua Instruments). A saturated calomel electrode (Hg/Hg₂Cl₂, SCE) and Pt foil (1 × 1 cm²) were used as the reference electrode and counter electrode, respectively. An electrode of TC2 and P25 were used as the working electrode. In a simple prepared-electrode process, a sample of 20 mg was dispersed in a 20 ml ethanol solution via ultrasonic vibration for 30 min to obtain a uniform slurry. A certain amount of slurry was coated on ITO glass (4 × 1 cm), which was then dried in an oven at 80 °C. The sample area on ITO glass was 1 × 1 cm. NaOH aqueous solution (1.0 M) was used as an electrolyte. A 300 W Xe lamp was employed as a light source for simulating solar irradiation. Linear sweep voltammetry (LSV) at a 5 mV/s scan rate investigated the photocurrent density from –0.8 V to 0.6 V in the dark or under light. The transient photocurrent responses (TPR) of TC2 and P25 were obtained at 0.4 V vs SCE for 550 s. A Mott–Schottky plot was deduced from an impedance-potential test at a frequency of 9610 Hz and a potential amplitude of 5 mV at a potential range from –1.4 V to 0.6 V in the dark.

2.4. Photocatalytic H₂ evaluation measurements

The photocatalytically generated hydrogen reaction was performed in a quartz reactor linked with an enclosing gas circulation system, a vacuum pump, and a Model GC7900 gas chromatography system (TCD detector, 99.999% highly pure nitrogen as carrier gas) that monitored hydrogen gas. In a typical routine, 40 mg of photocatalyst was joined in 60 ml of methanol aqueous solution (metha-

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