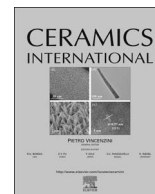




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Iridium, carbon and nitrogen multiple-doped TiO₂ Nanoparticles with enhanced photocatalytic activity

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ABSTRACT

The aim of this research is to enhance the photocatalytic activity of TiO₂ nanoparticles for the UV–visible light by multiple-doping with Iridium, carbon and nitrogen. The tridoped TiO₂ photocatalyst were prepared by wet chemical method, and characterized by X-ray diffraction, Raman spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, ultraviolet–visible light diffuse reflection spectroscopy and room temperature photoluminescence spectroscopy. Besides, the photocatalytic H₂ evolution performance of Ir-C-N tridoped TiO₂ under UV–visible light irradiation was evaluated. It was found that Ir existed as Ir⁴⁺ by substituting Ti in the lattice of TiO₂; meanwhile, C and N were also incorporated into the surface of TiO₂ nanoparticles in interstitial mode. Meanwhile, Ir-C-N tridoping extended the absorption of TiO₂ into the visible light region and narrowed its band gap to ~3.0 eV, resulting in enhanced photocatalytic H₂ evolution under UV–visible light irradiation. This could be attributed to narrow band gap and proper electronic structure of TiO₂ after Ir-C-N tridoping.

1. Introduction

TiO₂ as a cost-effective photocatalyst, has been thoroughly studied for several decades. It has a wide bandgap of 3.2 eV and can only be activated by ultraviolet radiation ($\lambda < 387$ nm) that constitutes only a small fraction (3%–5%) of the solar spectrum, which greatly restricts its practical application. To overcome its shortage, many researchers have made great efforts to modify the band structure of TiO₂ with metal cations (such as Fe³⁺, Cu²⁺ and W⁶⁺) and nonmetal anions (such as N, C and S) so as to expand its photoresponse to visible light. It has been recognized that such mono-doped TiO₂ systems usually contain partially occupied impurity bands that can act as recombination centers to counteract the doping efficiency [1,2], however, some reports had pointed out that codoping of TiO₂ with 3d transitional metals (such as Mo, W and Os) and nonmetals (such as C, N, F) can reduce the recombination centers which can effectively improve the charge carrier's migration efficiency and enhance the photocatalytic activity [3,4] as a result of a synergistic effect among such compensated donor-acceptor codopants [5].

Recently, nonmetal codoping, such as C-N, has gain intensive attention due to its ability to improve the photocatalytic activity of TiO₂ in visible light region [6–8] as a result of effectively hybridizing of C 2p and N 2p states with the O 2p states consisting of valence band of TiO₂ [9]. Unlike cation doping, anion doping could hardly affect the CB

band of TiO₂. However, it had been reported that C-N codoping in interstitial mode could form a continuum of impurity states close to the conduction band edge of TiO₂ which could facilitate charge transfer [10]. Furthermore, some researchers [11] demonstrated that TiO₂ nanotube array films multiple-doping with Ni, C and N can generate photocurrent under visible light irradiation ($\lambda > 420$ nm), and may find application in water splitting for H₂ generation.

In the near future, Kawasaki demonstrated that Ir⁴⁺-doped SrTiO₃ can be sensitive to visible-light [12]. The radius of iridium ion (0.625 Å) was similar with that of titanium ion (0.605 Å) and iridium ions could be incorporated into the lattice of TiO₂, extending the absorption of TiO₂ into visible light region [13,14]. However, the practical solar-to-hydrogen (STH) conversion efficiency of Ir mono-doped TiO₂ was very low due to the presence of localized Ir⁴⁺-related donor level in the forbidden gap, which would sharply decrease the photocarrier lifetime and mobility [15]. Tridoping of TiO₂ with Ir, C and N, may solve the above problem, eventually improving the photocatalytic activity of TiO₂ under UV–visible light irradiation.

In this paper, we demonstrated a noteworthy result that Ir-C-N tridoped TiO₂ powder, functioning efficiently as an H₂ evolution photocatalyst from water splitting under UV–visible light irradiation. Ir was incorporated into the lattice of TiO₂ in substitution mode, while C and N were also incorporated into the surface of TiO₂ nanoparticles in interstitial mode. Moreover, Ir-C-N tridoping could narrow its band

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gap of TiO₂ to ~3.0 eV, and effectively enhanced photocatalytic H₂ evolution performance. The reason for the high activity was discussed on the basis of photocatalytic reaction results.

2. Experimental

2.1. Sample synthesis

All reagents were used without further purification. Titanium tetrachloride (99.9%), Iridium trichloride (IrCl₃·3H₂O) and glucose (C₆H₁₂O₆) (99%) were used as the titania precursor and the chemical modifiers, respectively. Pure TiO₂, N doped TiO₂, C-N codoped TiO₂ and Ir-C-N tridoped TiO₂ nanoparticles were prepared as follows.

2.1.1. Preparation of TiO₂

5.5 mL (0.05 mol) TiCl₄ was added dropwise into the mixture of 50 mL ice water with stirring to form titanium oxychloride. This solution was converted to hydrated titanium dioxide by adjusting the pH to 7 using NaOH. The precipitate obtained was then repeatedly washed with deionised.

Water to free Cl⁻ and Na⁺, the resultant precipitate was calcined at 400 °C for 1 h, in this way pure TiO₂ nanoparticle was obtained.

2.1.2. Preparation of N doped TiO₂

The preparation of N doped TiO₂ was similar with that of pure TiO₂, except using 15 mL concentrated ammonium hydroxide in place of NaOH as precipitant. The product calcined was denoted as NT.

2.1.3. Preparation of Ir-C-N tridoped TiO₂

To further complete the surface-modification with Iridium and carbon, a desired amount of Iridium trichloride (1–5 wt%) and glucose (0.5–2 wt%) were added to the above prepared hydrated titanium dioxide (2.1.1), and then 100 mL of deionised water was added. This solution was dried in.

an air oven at 100 °C for 4 h. The precipitant obtained was then calcined at 400 °C for 1 h to obtain.

Ir-C-N tridoped TiO₂ (denoted as IrCNT).

2.1.4. Preparation of C-N codoped TiO₂

For comparison, C-N codoped TiO₂ (denoted as CNT) was also synthesized from the same procedure (2.1.3) without addition of IrCl₃·3H₂O.

2.1.5. Preparation of Pt-loaded photocatalysts

Platinum-loaded catalysts were prepared by a direct photodeposition method. Typically, an aqueous methanol (20 vol%) solution containing the catalysts and hexachloroplatinic acid (0.5% H₂PtCl₆·6H₂O) was irradiated by 1 h of irradiation (a 250 W high-pressure Xe lamp), followed by filtering and dried for 12 h. Their photocatalytic activity was evaluated by evolving H₂ under the irradiation of a 250 W high-pressure Xe lamp.

2.2. Sample characterization

For the morphology characterization of Ir-C-N tridoped TiO₂ surfaces, transmission electron microscopy (TEM, JEOL-1620, operated at 200 kV) was employed. The phase of the doped TiO₂ nanoparticles was identified by X-ray diffraction (Rigaku D/MAX-3; CuK_α=0.154 nm). In order to determine the surface composition and bonding state of the nanoparticles, X-ray photoelectron spectroscopy (ESCALab220i-XL) was utilized. The binding energy scale was calibrated to 284.6 eV for main C1s peak. To investigate the light absorption properties of doped TiO₂, analysis of reflectance absorption spectrum was performed using a UV-vis spectrophotometer (Lambda 850) equipped with an integrating sphere attachment. The photocatalytic H₂ evolution efficiencies of the Ir-C-N tridoped TiO₂ were

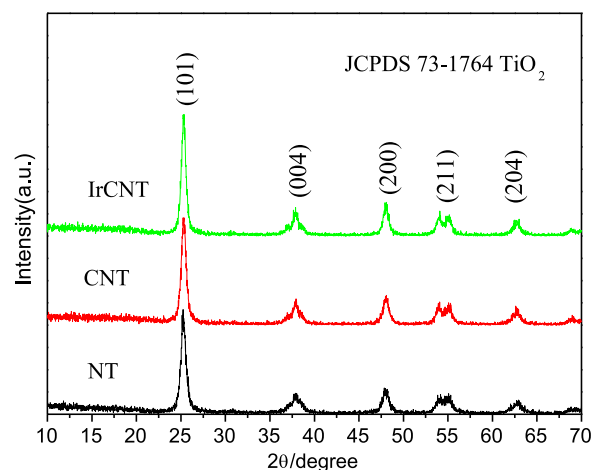


Fig. 1. Powder X-ray patterns of NT, CNT and IrCNT sample.

evaluated with 0.1 g of catalyst introduced into 100 mL 20 vol% menthol solution in Pyrex glass, irradiating 250W Xe lamp as the light source. The reaction temperature was maintained at 25°C with the help of an external water circulation jacket. The reactant solutions were evacuated several times to completely remove any air prior to irradiation. The average light intensity on the surface of the reactant solution was measured to be 400 mW/cm². The reaction was carried out for 4 h and the amount of hydrogen evolved was analyzed at every 1 h by gas chromatograph (GC-7900; Molecular sieve 5A, TCD detector, Ar carrier gas).

3. Results and discussion

3.1. Crystal structure and microstructure

The crystal structure of titanium dioxide greatly affects photocatalytic activity. Generally, the anatase phase is reported with high photocatalytic activity. Therefore, the phase characterization of NT, CNT and IrCNT sample was investigated by XRD, and the obtained patterns were shown in Fig. 1. A series of characteristic peaks, corresponding to the (101), (004), (200), (211) and (204) planes, were observed, and can be indexed to anatase TiO₂ (JCPDS NO. 73–1764). And the average crystallite size of the NT, CNT and IrCNT sample was about 15 nm equally, calculated from the full width at half-maximum of the (101) peak based on the Scherrer's formula ($d=0.9\lambda/(\beta\cos\theta)$), where λ is the characteristic X-ray wavelength applied (0.15418 nm), β is the half width of the peak at the 2θ value and 0.9 is the apparatus constant [16]. And the TEM image of IrCNT sample was displayed in Fig. 2, the particles possess approximately spherical or elliptic morphology with a size of about 10–20 nm, which is strongly consistent with the results of XRD.

3.2. Surface structure analysis

3.2.1. FT-IR and Raman spectroscopy analysis

Fig. S(1) showed the FTIR spectra of the three doped TiO₂. No functional groups corresponding to nitrogen species and glucose were observed, even though N peak was detected in the XPS below. In addition, the peaks at 3400 cm⁻¹ and 1640 cm⁻¹ corresponded to surface-adsorbed water and hydroxyl groups while the IR absorption in the spectral range of 500–800 cm⁻¹ can be assigned to the surface vibrations of the Ti-O-Ti bonds [17]. The Raman spectra (Fig. 3) indicated that all the samples calcined at 400 °C were present in pure anatase phase corresponding to the characteristic peaks around 144 cm⁻¹, 394 cm⁻¹, 514 cm⁻¹, and 638 cm⁻¹ [18]. No effect of impurity doping was observed on the position of peaks in Raman spectra, and the intrinsic anatase structure was integrally retained after

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