



Improved photocatalytic activity of TiO₂ modified with unique O–Zn–Cl surface species



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ABSTRACT

TiO₂ modified with unique surface O–Zn–Cl species is prepared by a simple sol-gel method. The Zn modified TiO₂ samples exhibit improved photocatalytic activity on photo-reduction of CO₂ into CH₄, compared with pure TiO₂. The surface structure and photocatalytic properties are investigated by Raman, XRD, XPS, UV–vis absorption spectra, PL and time-resolved PL decay curves techniques. It is revealed that the existence of O–Zn–Cl species can extend the absorption into visible region, inhibit the recombination of charge carriers and prolong the lifetime of photogenerated electrons. Therefore the O–Zn–Cl modified TiO₂ samples represent an improved photocatalytic performance on photo-reduction of CO₂ into CH₄.

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1. Introduction

Titanium Dioxide is usually regarded as one of the most promising opti-electrical functional materials, which can be applied in many fields, such as photocatalysis and photosynthesis [1–5]. Huge efforts have been devoted to improve the photocatalytic performance of TiO₂, for example doping with metal or non-metal elements [6–11], composition with other semiconductors [12–15] and surface modification [16–21]. Among these proposes, the introduction of Zn species into TiO₂ system by doping, composition or modification has been investigated by many researchers. Wang and his co-workers develop a method to introduce Zn submitting for Ti in TiO₂ film with enhanced energy conversion efficiency in dye sensitized solar cells [22]. Xu et al. prepared Zn surface doped TiO₂ nanotubes with enhanced photocatalytic activity on photodegradation of methyl orange [23]. Li et al. investigate the ZnO composited with B doped TiO₂ with enhanced visible photocatalytic activity [24]. Recently, we found a new kind of species, O–Zn–Cl species, formed on the surface of TiO₂ when the calcination temperature is below 500 °C and the dopant content is below 5% [25]. However, the influence of the surface O–Zn–Cl species on the band structure, opti-electrical properties and the photocatalytic performance of TiO₂ is still unknown. Moreover, modifying TiO₂ with surface species is usually considered as an efficient tech-

nique to enhance the photocatalytic performance by creating a new surface energy level, extending response into visible region and suppressing the recombination of charge carriers [16–21]. Our previous work has demonstrated the unique O–Me–Cl_x (Me = In, Ni or Pd) surface species modified on the surface of TiO₂ can increase the absorption in visible region, promote the separation of charge carriers and enhance the photocatalytic activity. It is expected the TiO₂ modified with O–Zn–Cl species would act as the same role to improve the photocatalytic activity of the photocatalytic under visible irradiation.

Herein, the Zn modified TiO₂ is prepared by a simple sol-gel method and exhibits enhanced photocatalytic on photo-reduction of CO₂ with H₂O into CH₄. Owing to the surface energy level of O–Zn–Cl species, the visible response is enhanced and the photogenerated electrons and holes are separated effectively, improving the photocatalytic activity. The band structure, behaviors of the charge carriers as well as the photocatalytic mechanism are also studied in details.

2. Experimental details

2.1. Catalyst preparation

All chemicals used were of analytical grade and the water was deionized water (>18.2 MΩ cm). At room temperature, certain amount of Zn(NO₃)₂ were dissolved into 40 mL of ethanol. After mixing for half an hour, 1 mL HCl solution (12 mol/L) and 12 mL

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of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was added dropwise into the mixture under vigorous stirring. Then 1 mL of deionized water was added for further hydrolysis. The pH value of the mixture is evaluated to be 0.5. The mixture was stirred until the formation of TiO_2 gel. After aging for 24 h, the TiO_2 gels were dried at 100 °C for 10 h and annealed at 450 °C in a muffle for 150 min. The obtained sample was denoted as TiO_2 -Zn, where the molar ratio of Zn to Ti (Zn/Ti) is 5%. Pure TiO_2 is also synthesized, just without the addition of $\text{Zn}(\text{NO}_3)_2$.

2.2. Characterization

Raman spectra were taken on a Renishaw inVia Raman microscope by using the 785 nm line of a Renishaw HPNIR 785 semiconductor laser. X-ray diffraction (XRD) patterns were acquired on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu K α , $\lambda = 1.54056 \text{ \AA}$) at a scan rate of $0.02^\circ 2\theta \text{ s}^{-1}$. The average crystal size was calculated using the Scherrer equation ($D = k\lambda/B\cos\theta$). After degassing at 180 °C, the BET surface area was determined via the measurement of nitrogen adsorption-desorption isotherms at 77 K (Micromeritics Automatic Surface Area Analyzer Gemini 2360, Shimadzu). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCA Lab 220i-XL spectrometer by using an unmonochromated Al K α X-ray source (148.6 eV). All spectra were calibrated using the binding energy (BE) of the adventitious C1s peak at 284.6 eV. Diffuse reflectance UV-vis absorption spectra (UV-vis DRS) were collected with a UV-vis spectrometer (U-4100, Hitachi). Photoluminescence (PL) spectra were acquired by using the 325 nm line of a nano-second Nd:YAG laser (NL303G) as excitation source. The experimental setup consists of a spectrometer (Spex 1702), a photomultiplier tube (PMT, Hamamatsu R943), a lock-in amplifier, and a computer for data processing. All of the measurements were carried out at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$).

2.3. Evaluation of photo-reduction activity

The photo-reduction activity of the photocatalysts was evaluated by photo-reduction of CO_2 and H_2O into CH_4 . 150 mg of photocatalyst was uniformly dispersed on a glass sheet with an area of 9.4 cm^2 . A 500 W spherical Xenon arc lamp (Philips, Belgium, $35 \text{ mW}/\text{cm}^2$, 290–800 nm) was used as the light source of photocatalytic reaction. The glass sheet was placed at the bottom of a sealed Pyrex glass reaction vessel (410 mL) which is located 10 cm away from the light source and vertical to the light beam. Prior to the illumination, the high purity of CO_2 gas (99.99%), via a flow controller, was followed into the reaction setup for 45 min for reaching ambient pressure. Then the reaction vessel was sealed and 2 mL of deionized water was injected into the reaction system as reducer. During irradiation, about 0.4 mL of gas was continually taken from the reaction cell every 2 h for subsequent CH_4 and CO concentration analysis by using a gas chromatograph (Techcomp GC-7890F, equipped with a $1 \text{ m} \times \phi 3 \text{ mm}$ TDX-01 packed column and a flame ionization detector (FID)). N_2 was used as the carrier gas. Since FID cannot detect CO and CO_2 , an additional converter (Techcomp converter loaded with Ni catalyst) was attached to the GC system between the column and detector, which can reduce CO to methanol ($\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH}$) and CO_2 to methane ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$). Hence, CO and CO_2 could be analyzed simultaneously.

3. Results

To investigate the surface structure of the Zn modified TiO_2 samples, Raman spectra of TiO_2 and TiO_2 -Zn are plotted in Fig. 1. Both the TiO_2 and TiO_2 -Zn samples show the typical characteristic

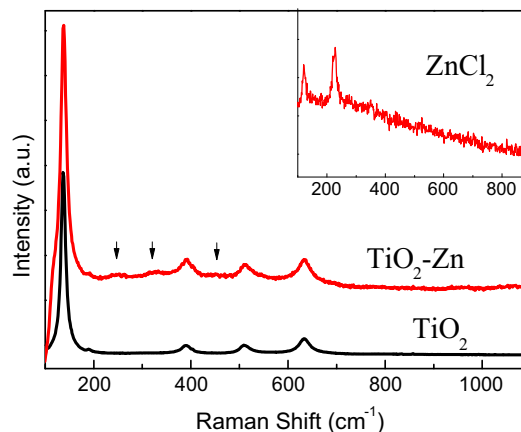


Fig. 1. Raman spectra of TiO_2 and TiO_2 -Zn. Inset shows the Raman spectrum of ZnCl_2 .

bands at about 142 cm^{-1} , 195 cm^{-1} , 395 cm^{-1} , 515 cm^{-1} and 637 cm^{-1} , attributed to the E_g , B_{1g} , A_{1g} , B_{2g} and E_g vibrational modes of anatase [7], respectively. In comparison with pure TiO_2 , some new weak Raman peaks at about 256 cm^{-1} , 333 cm^{-1} and 450 cm^{-1} are observed for TiO_2 -Zn sample. The Raman peaks at about 333 cm^{-1} and 450 cm^{-1} are ascribed to the E_2 mode of ZnO. The Raman peak at about 256 cm^{-1} is the same as that for ZnCl_2 (inset of Fig. 1). These Raman spectra demonstrate the existence of Zn–O bonds and Zn–Cl bonds, indicating the introduced Zn^{2+} ions link with O and Cl simultaneously to form O–Zn–Cl species. To further demonstrate the existence of O–Zn–Cl species, XRD and XPS are carried out in the following sections.

The XRD spectra of pure TiO_2 and TiO_2 -Zn are shown in Fig. 2. It is obvious that only the characteristic peaks of anatase TiO_2 are observable and no other phase such as rutile are detected, suggesting anatase is the only phase for TiO_2 and TiO_2 -Zn. It is known that the ionic radius of Zn^{2+} ions is larger than that for Ti^{4+} ions (Zn^{2+} : 74 pm, Ti^{4+} : 68 pm). An increase of lattice parameters and cell volume is expected if Zn^{2+} ions substitute the lattice Ti^{4+} ions. However, it is found from the inset of Fig. 2 that the peak position of (1 0 1) plane remain almost unchanged and the lattice parameters as well as the cell volume is almost the same (Table 1) [26], compared with TiO_2 . Hence it can be concluded that the introduced Zn^{2+} are not doped into TiO_2 lattice in substitutional mode, implying that the introduced Zn^{2+} ions exist as surface O–Zn–Cl species.

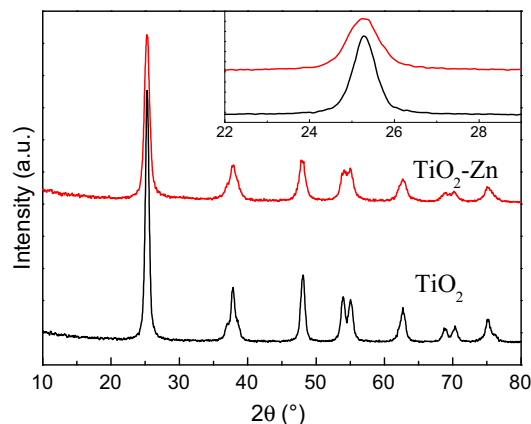


Fig. 2. XRD spectra of pure TiO_2 and TiO_2 -Zn. Inset shows the enlargement of (1 0 1) plane for anatase.

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