

# Photodecomposition of H<sub>2</sub>S to Produce H<sub>2</sub> over CdS/Carbon-doped TiO<sub>2</sub> Composite Catalyst

Bai Xue-feng\* and Fan Hui-juan

Institute of Petochemistry, Heilongjiang Academy of Sciences, Harbin, Heilongjiang  
150040(China)

\*bxuefeng@163.net

## Introduction

H<sub>2</sub>S is a type of by-product obtained from oil refinery, natural gas processing and other chemicals production. Till now, the well-established Claus process has been applied to deal with H<sub>2</sub>S. It involves partial oxidation of H<sub>2</sub>S to sulfur and water where hydrogen is wasted. If hydrogen can be recycled from H<sub>2</sub>S instead of being directly oxidized into water, an immense amount of H<sub>2</sub> would be regenerated. The photocatalytic decomposition H<sub>2</sub>S to H<sub>2</sub> over semiconductor photocatalysts is considered as a process to convert solar energy into fuels and the process requires less energy than the photodecomposition of water<sup>[1]</sup>. CdS is suitable for the visible light and used widely to catalyze photochemical reaction. But CdS is very unstable against photocorrosion in aqueous solutions under irradiation. There are many attempts to overcome the photocorrosive nature of CdS. S<sup>2-</sup> ion as sacrificial agent can prevent oxidation of CdS by scavenging the photogenerated holes. Composite systems have been considered as a promising method to prevent electron-hole recombination and improve the photocatalysis efficiency and photostability of CdS, such as CdS/ZnS<sup>[2]</sup>, CdS/TiO<sub>2</sub><sup>[3]</sup>. Recently, Band-gap narrowing by the introduction of non-metal anions (N<sup>[4]</sup>, C<sup>[5]</sup> and S<sup>[6]</sup>) into TiO<sub>2</sub> was found to improve catalytic activity under visible light irradiation. In this paper, a CdS/carbon-doped TiO<sub>2</sub> composite catalyst (CdS/C-TiO<sub>2</sub>) had been prepared and used for photocatalytic decomposing H<sub>2</sub>S to H<sub>2</sub> to study the possibility in improving the photocatalysis efficiency.

## Materials and Methods

A CdS/C-TiO<sub>2</sub> was prepared by hydrothermal method at 240°C for 6 h at 1/2 molar ratio of CdS to C-TiO<sub>2</sub>. C-TiO<sub>2</sub> was prepared by immersion and calcination method using citric acid and TiO<sub>2</sub>-P<sub>25</sub> supplied by Degussa Corporation (Anatase 80%, rutile 20% and specific area 50 m<sup>2</sup>g<sup>-1</sup>) at 3/1 mass ratio of citric acid to TiO<sub>2</sub>

UV-Vis diffuse reflectance spectra (UV-Vis) was recorded on a scanning spectrophotometer (UV-2450, Shimadzu, Japan) equipped with an integrating sphere (ISR-240A). X-ray photoelectron spectroscopy (XPS) analysis was performed in a Thermo ESCALAB spectrometer using Al K $\alpha$  X-ray ( $h\nu = 1486.6$  eV). The binding energy was referenced to the C1s line at 284.6 eV for calibration.

The photocatalytic reaction of decomposing H<sub>2</sub>S to H<sub>2</sub> was performed in an inner-irradiation type reactor using a 175 W high-pressure lamp as the irradiation source and Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> aqueous solution as reaction media. For the experiment under visible light irradiation, an inner circulating system containing 1 mol/L NaNO<sub>2</sub> was used to remove UV light ( $\lambda < 400$  nm).

## Results and Discussion

From XPS survey spectra (Fig.1.a) of C-TiO<sub>2</sub>, it is observed that the sample contains Ti, O, and C, and binding energies for Ti2p<sub>3/2</sub>, O1s, and C1s are 458.8, 529.7 and 284.6 eV, respectively. To investigate the carbon states in CdS/C-TiO<sub>2</sub>, C1s core levels were measured by XPS as shown in Fig.1.b. Two peaks are observed at 284.6 and 288.6 eV. The feature at 284.6 eV can be assigned to the presence of adventitious elemental carbon for calibration, and

the peak (288.6 eV) indicates the presence of C–O bonds, and it is revealed that C may substitute for some of the lattice Ti atoms and form a Ti–O–C structure<sup>[7]</sup>.

From UV-Vis spectra (Fig.2) of pure TiO<sub>2</sub>, C-TiO<sub>2</sub> and CdS/C-TiO<sub>2</sub>, it is observed that a noticeable red shift appear (Fig.2a). This result reveals that the carbon dopants are incorporated into the lattice of TiO<sub>2</sub>, which alters its crystal structure and band gap energy, furthermore, expands its photo response range. From Fig.2b, it can be observed that the UV-Vis spectra of CdS/C-TiO<sub>2</sub> consist of two characteristic peaks of CdS and TiO<sub>2</sub>, this structure is beneficial to the separation and transmission of electron-hole pairs.

It was showed from the photocatalytic decomposition reaction that H<sub>2</sub> production rate of CdS/C-TiO<sub>2</sub> is 10291.7  $\mu$ mol/g·h which is 2.09 times than that of CdS/TiO<sub>2</sub> (4952.4  $\mu$ mol/g·h). The CdS/C-TiO<sub>2</sub> exhibits more efficient visible light activity than CdS/TiO<sub>2</sub>. It may be reason that the carbon substitute for some of the lattice Ti atoms results in the band gap narrowing of C-TiO<sub>2</sub>, which could absorb more visible light.

CdS/C-TiO<sub>2</sub> composite photocatalyst exhibited obvious improvement in optical absorption and photocatalytic activity. This result is ascribed to the presence of Ti–O–C structure which can narrow the band gap.

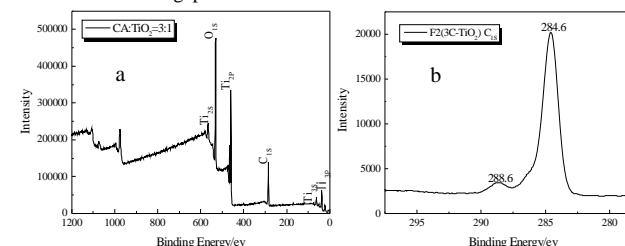


Fig.1 XPS spectra of (a) survey spectrum, (b) C1s

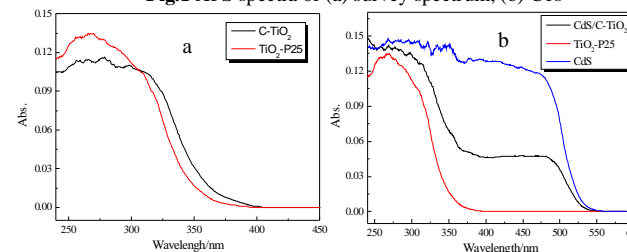


Fig.2 UV-Vis of (a) pure TiO<sub>2</sub> and C-TiO<sub>2</sub> and (b) CdS/C-TiO<sub>2</sub>

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