Synthesis of a novel N–H–TiO₂ photocatalyst by annealing in NH₃ and H₂ for complete decomposition of high concentration benzene under visible light irradiation

Minghui Li, Wulin Song*, Lei Zeng, Dawen Zeng, Changsheng Xie

State Key Laboratory of Materials Processing and Die and Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China

1. Introduction

Benzene, as one of the confirmed carcinogenic substances, is difficult to degrade due to its conjugated π-bond [1]. Hence, there is absolutely a need to develop an effective approach to remove it. It is widely accepted that TiO₂ has many advantages, such as abundance, chemical stability and high activity under ultraviolet (UV) irradiation, providing an efficient way to solve the environment problems [2]. However, the wide band gap and rapid recombination of photogenerated electrons and holes hinder visible light absorption and photocatalytic activity of TiO₂ photocatalyst. Hence various approaches have been developed to engineer band structure and introduce defects, which will improve optical absorption and photocatalytic performance of TiO₂. Among the efforts to modify TiO₂, nitrogen doping and hydrogenation have been extensively investigated [3,4]. Unfortunately, the efficiency of current TiO₂ photocatalyst in decomposing pollutants under visible light remains low so far [5]. Furthermore methods for preparing highly active TiO₂ usually required complicated procedure or rigorous conditions, which definitely became the obstacles for practical application [6].

Here, we present a highly efficient N–H–TiO₂ photocatalyst prepared by a simple hydrothermal method. Surprisingly N–H–TiO₂ exhibits amazing photocatalytic activity in quickly and thoroughly degrading high concentration benzene under visible light irradiation, which is timesaving, economical and efficient with simple preparation technology for large-scale application in removing indoor pollutants.

2. Experiments

TiO₂ was synthesized by a hydrothermal method. Typically, 2 mL tetra-n-butyl titanate was added dropwise to 75 mL distilled water under vigorous magnetic stirring and then the hydrolysate transferred into a 100 mL Teflon-lined autoclave to react at 160 °C for 12 h. Afterwards, the obtained precipitate was separated by a centrifuge and washed several times, and then dried in an oven at 80 °C overnight to acquire TiO₂ nanoparticles. TiO₂ was further modified by annealing at 600 °C in H₂ for 2 h as well as in NH₃ and H₂ for 4 h, denoted as H–TiO₂ and N–H–TiO₂ respectively.

The structures and morphologies of samples were observed by X-ray diffraction (XRD, X’Pert PRO diffractometer with Cu Kα radiation) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30 field-emission TEM). Ultraviolet-visible diffuse reflectance spectra (UV–vis DRS) were obtained on a Shimadzu U-3010 spectrometer using BaSO₄ as a reference. Photoluminescence (PL) emission spectra were acquired under excitation at 325 nm using an Edinburgh Instruments PLSP920 spectrometer.

Photocatalytic activities of the samples were tested by degrading benzene under visible light irradiation for 3 h. A 300 W Xe-arc
lamp (CEL-HXF300) with a UV-cutoff filter ($\lambda < 400$ nm) was used as the light source. Generally, 100 mg TiO$_2$ was dispersed on the loading plate. Afterwards, 150 ppm (± 5 ppm) benzene was injected into the reaction chamber of a gas chromatograph (GC) to measure the concentration of benzene and CO$_2$. Then the samples H–TiO$_2$, N–H–TiO$_2$ and N–H–TiO$_2$-s (N–H–TiO$_2$ stored over 6 months) were tested successively. The degradation efficiency is calculated by the functions $C/C_0$ and $C/C_0$, where $C_0$ is initial concentration of benzene or CO$_2$, and $C$ is concentration during the photodegradation process. A blank control test without photocatalyst was conducted for reference.

3. Results and discussion

The visible light photocatalytic activity of TiO$_2$, H–TiO$_2$, N–H–TiO$_2$ and N–H–TiO$_2$-s samples was evaluated with a blank control test, as shown in Fig. 1. The result shows that N–H–TiO$_2$ and N–H–TiO$_2$-s exhibit the best photocatalytic activity, which indicates the unique performance and good stability of N–H–TiO$_2$. The conversion of benzene over N–H–TiO$_2$ under visible light irradiation is as high as 100% within 3 h. Meanwhile, the performance of H–TiO$_2$ is better than that of TiO$_2$ while the blank test gives almost no activity when decomposing benzene. Obviously, the fundamentally enhanced performance of N–H–TiO$_2$ can be attributed to the synergistic effect of N doping and hydrogenation.

Fig. 2 displays the crystalline structures of all the samples characterized by XRD. The diffraction peaks of all the samples can be indexed to anatase (JCPDS File no. 21-1272). Moreover, H–TiO$_2$ and N–H–TiO$_2$ have increased crystallinity after annealing. The average particle sizes of TiO$_2$, H–TiO$_2$ and N–H–TiO$_2$ are, respectively estimated to be 19.46, 36.72 and 33.55 nm by the Scherrer formula, consistent with TEM images presented in Fig. 3. Furthermore, surface amorphous structure introduced by hydrogenation can be clearly observed in H–TiO$_2$ depicted in the range 25–35° of XRD and the blurry edge of HRTEM image (e). This result is similar to those of previous investigations for TiO$_2$ nanoparticles annealed in reducing atmospheres, which show that the disordered phase separates fully crystalline inner part from disordered (amorphous) surface of a nanoparticle [7,8].

Fig. 4 shows the optical absorption properties examined by UV–vis DRS. The onset of optical absorption edge of N–H–TiO$_2$ has extended to 550 nm compared with TiO$_2$, which indicates the typical redshift of nitrogen doped TiO$_2$ [9]. This can be assigned to the significant cause for enhanced visible light absorption and band gap narrowing of N–H–TiO$_2$. Besides, a new absorption band up to infrared region emerging in H–TiO$_2$ means that band structure of TiO$_2$ has been modified by hydrogenation, which has been reported by previous studies [10,11].
Photoluminescence spectra of TiO$_2$, H–TiO$_2$ and N–H–TiO$_2$ are shown in Fig. 5. The PL emission of TiO$_2$ is intrinsic because of its inferior crystallinity. Nevertheless, after hydrogenation at high temperature, the crystallinity of H–TiO$_2$ increases along with numerous oxygen vacancies emerging in the bulk of H–TiO$_2$, which act as recombination centers resulting in sharp increase of PL intensity [12]. It is known that surface defects can serve as charge carrier traps and absorption sites to prevent e–h recombination, while bulk defects are only trap sites where e–h recombines [13]. Therefore, visible light activity of H–TiO$_2$ can be attributed to the disordered surface layer introduced by hydrogenation rather than bulk defects. On the other hand, PL intensity of N–H–TiO$_2$ is found to decrease dramatically due to surface oxygen vacancies introduced by nitrogen doping. Evidently, the results suggest that the presence of oxygen vacancies in surface or bulk plays distinct roles in different samples. Allowing for the photocatalytic activity of TiO$_2$, H–TiO$_2$ and N–H–TiO$_2$ the benefit of surface amorphous structure may be offset partially by bulk defects formed in hydrogenation, while N doping will relieve this situation by introducing surface oxygen vacancies.

4. Conclusion

We have demonstrated that N–H–TiO$_2$ shows highly efficient photocatalytic activity when decomposing benzene under visible light irradiation. Band gap modification and surface oxygen vacancies due to N doping and surface amorphous structure induced by
hydrogenation are responsible for the enhanced visible light absorption and superior performance of N–H–TiO₂ photocatalyst.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Nos. 51071073 and 50927201), and the National Basic Research Program of China (Grant nos. 2009CB939702 and 2009CB939705).

References