Carbon and Nitrogen-codoped TiO_2 with High Visible Light Photocatalytic Activity

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Titanium dioxide codoped with carbon and nitrogen was synthesized by a microemulsion–hydrothermal process. There was a synergistic effect for the carbon and nitrogen-codoped TiO_2, which offset the deficiencies of carbon or nitrogen single doped TiO_2. The results showed that the photocatalytic activity of C and N-codoped TiO_2 was considerably improved because the band gap of TiO_2 was greatly narrowed by C and N-codoping.

Titanium dioxide has been extensively studied and applied because of its high efficiency, low cost, nontoxity, and photostability. However, the widespread usage of TiO_2 is prevented by its wide band gap (3.2 eV), which responds only under UV light irradiation accounting for only a small fraction (4–5%) of solar light. Therefore, considerable efforts have been invested to broaden the photoresponse of TiO_2 to the visible-light region so as to improve the photocatalytic efficiency.

Recently, it was found that doping or modification with nonmetals such as boron,[1] carbon,[2–4] nitrogen,[5–8] and sulfur[9] could shift the absorption edge of TiO_2 to lower energy. Asahi et al.[5] reported that films and powders of $TiO_{2-x}N_x$ revealed a dramatic improvement over pure titanium dioxide under visible light in their optical absorption and the level of photocatalytic activity. According to his theory, the substitution doping of N could contribute to the band-gap narrowing by mixing its 2p state with O2p states. Whereas the exotic states owing to the C impurity were too deep in the band gap of TiO_2 to overlap sufficiently with the intrinsic states of valence band of TiO_2, the photocatalytic activity of TiO_2 was not liable to be obviously improved by C-doping. On the basis of the above-mentioned theory, we speculated that the C and N-codoping should give rise to a synergistic effect. On the one hand, the exotic states of N-doping located between the C-doping states and the valence band of TiO_2, which could connect with the states of C-doping and available overlap with the band states of TiO_2; on the other hand, the C-doping could benefit to sufficiently narrow the band gap with N-doping.

In this manuscript, carbon and nitrogen-codoped nanocrystalline titanium dioxides were synthesized by a microemulsion–hydrothermal process. In the microemulsion system, Triton X-100 was used as the surfactant, *n*-hexanol as the cosurfactant, cyclohexane as the continuous oil phase, and tetrabutyltitanate dissolved in nitric acid (5 mol/L) as the aqueous phase. Triethylamine was chosen as the additional nitrogen source, and the mole ratio of N/Ti varied from 0, 1, 2, and 4, corresponding prepared TiO_2 denoted as TiO_2–C, TiO_2–C–N–1, TiO_2–C–N–2, and TiO_2–C–N–4, respectively.

In order to investigate the chemical states of C and N atoms incorporated into TiO_2, C1s and N1s binding energies were measured by X-ray photoemission spectroscopy (XPS). The results were showed in Figure 1. As could be seen in Figure 1a, there were two peaks around 285.8 and 288.6 eV, which contributed two states of carbon species. The lower binding energy was associated with the adventitious elemental carbon[3,10] or the carbon absorbed on the surface of TiO_2 as a contaminant (contamination of organic residues on their surfaces),[4] which did not contribute to the improvement of photocatalytic activity. The latter peak around 288.6 eV suggested the presence of a carbonate species.[2–4,10] Our study suggested that the appearance of this peak was a consistent feature for the carbonate species substitution in TiO_2, which could shift the absorption edge of TiO_2 to the longer wavelength region. There was some discrepancy with Kamisaka's report[11] in that different preparation method and conditions played an important role in determining the carbon oxidation states and effects.[2]

It could be seen in Figure 1b that there was a broad peak from 397 to 403 eV, which was in the range (396–404 eV) observed by several other researchers and was typical of nitrogen-doped titanium dioxide.[5–8] After fitting the curve, two peaks were obtained at 399.4 (peak 1) and 401.4 eV (peak 2), respectively. We attributed the peak 1 to the anionic N^- in O–Ti–N linkages, which was consistent with the characteristics reported in other literatures.[6–8] The binding energy of this peak was higher than that of TiN appeared at ≤ 397.5 eV, which might be because that nitrogen doping into the TiO_2 lattice reduced the electron density on the nitrogen because of the high electronegativity of oxygen. Thus, changes in the nitrogen environment could produce significant difference in the nitrogen 1s XPS spectra region. The other peak was attributed to the formation of oxynitride, which was further testified by the O1s XPS spectra (not shown). An additional peak appeared at about 532 eV in the O1s spectra and previously was attributed to the presence of Ti–O–N bonds.[12,13] From the above observations, it could be concluded

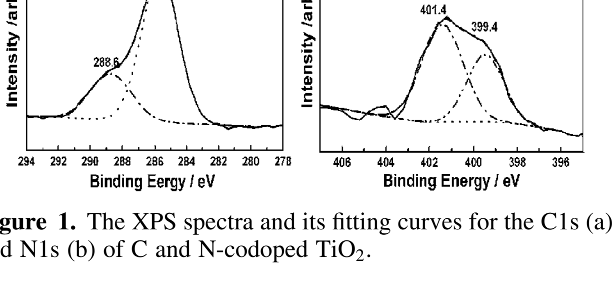

Figure 1. The XPS spectra and its fitting curves for the C1s (a) and N1s (b) of C and N-codoped TiO_2.

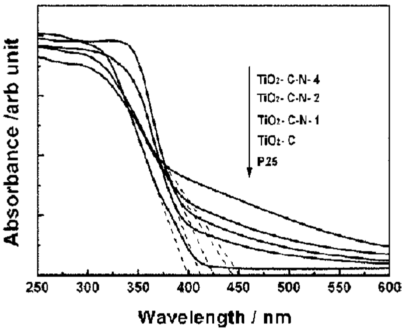

Figure 2. The diffuse reflectance spectra of different samples.

that the chemical states of the nitrogen doped into TiO_2 might be various and coexist in the form of N–Ti–O and Ti–O–N.

Figure 2 showed UV–vis diffuse reflection spectra of various samples. The samples, P25, TiO_2–C, TiO_2–C–N–1, TiO_2–C–N–2, and TiO_2–C–N–4, showed the band-gap absorption onset at 400, 412, 425, 447, and 451 nm, corresponding to energy band gaps 3.04, 2.95, 2.86, 2.72, and 2.70 eV, respectively. The optical absorption edge of the codoped samples shifted to the lower-energy region, possibly owing to the narrow band-gap resulted by carbon and nitrogen codoping. Meanwhile, the C and N-codoped TiO_2 showed drastic and stronger photoabsorption in the range of wavelengths from 400 to 550 nm compared with pure TiO_2 and also higher than C-doped sample. In addition, with the increase of addition content of triethylamine, the absorption of photocatalysts in visible-light region gradually strengthened.

Photocatalytic activity of the C and N-codoped TiO_2 powders was evaluated by measuring the decomposition rates of Rhodamine B (20 mg/L) in an aqueous solution (50 mL) containing 50 mg of the TiO_2 photocatalyst. As the photocatalyst, C and N-codoped TiO_2 or pure TiO_2 powder (P-25) was used. A 1000-W halogen lamp was used as the light source of the home-made photoreactor, surrounded with a water circulation facility at the outer wall. The short-wavelength components ($\lambda < 420$ nm) of the light were cut off using a glass optical filter. For a typical photocatalytic experiment, a portion of 0.05-g catalyst powders was added into 50 mL of the Rhodamine B solution above in a quartz tube. Prior to irradiation, the suspensions were magnetically stirred in dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium. As showed in Figure 3, C and N-codoped TiO_2 photocatalysts showed higher photocatalytic activities than P-25 and C-doped TiO_2. Furthermore, when the N/Ti ratio was 2, the photocatalyst had the highest photocatalytic activity, and the Rhodamine B could be completely decomposed after 1 h, probably due to the highest actual nitrogen-doping concentration. So the mole ratio of 2 was regarded as the optimal value for the best photocatalytic activity. In addition, we also evaluated the decomposition of 2,4-dichlorophenol (100 mg/L), the decomposition rate by TiO_2–C and TiO_2–C–N–2 could reach 31.3 and 55.0%, irradiating for 5 h at the same experiment conditions (see Supporting Information).

On the basis of Asahi's theory and our experiments, we considered that C and N-codoping would produce a synergistic effect, which coincided with our hypothesis. Firstly, the states of N-doping could connect with the states of C-doping and available overlap with the band states of TiO_2 so as to satisfy the condition iii of Asahi submitted; furthermore, the C-doping could benefit to sufficiently narrow the band gap together with the N-doping. Subsequently, the band gap was further narrowed by C and N-codoping, which was attributed to the improvement of photocatalytic activity in the visible light.

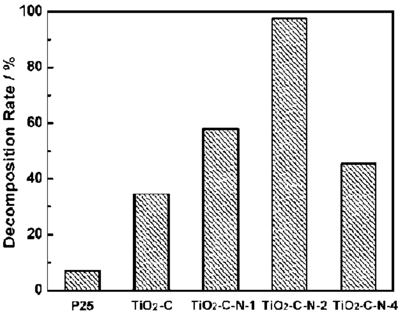

Figure 3. Photocatalytic activity of decomposition of Rhodamine B on different samples after irradiation for 1 h.

In conclusion, C and N-codoped TiO_2 powders were successfully synthesized and could efficiently decompose Rhodamine B and 2,4-dichlorophenol under visible light. There was a synergistic effect by C and N-codoping to result stronger absorption in visible-light region and commendable photocatalytic activity.

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