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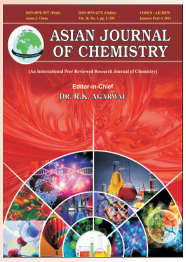

Fabrication of C-N Co-Doped TiO_2 with Visible-Light Responsive Photocatalytic Activity in Degradation of 2,4,6-Trichlorophenol

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A one-step, hydrothermal method for the synthesis of C-N co-doped titanium dioxide photocatalysts is demonstrated. The incorporation of nitrogen from ammonia and carbon from alcohols with different chain length (methanol, ethanol, isopropanol) used as carbon precursors was confirmed by XRD, UV-visible and XPS analyses. The results indicated that C and N doped into the TiO_2 crystal lattice simultaneously by hydrothermal process. The photocatalytic performance in the degradation of 2,4,6-trichlorophenol indicated that C and N co-doped TiO_2 showed much higher photocatalytic activity than pure TiO_2 and single doped samples under visible light. The possible mechanism was proposed.

Keywords: TiO_2, Photocatalysis, C-N Co-doping, Carbon precursors, Degradation.

INTRODUCTION

Titanium dioxide has attracted many attentions since it served as a functional material for the decomposition of organic compounds. The irradiation of TiO_2 with band gap photons produce electron-hole couples which after migration to the surface of the solid may be trapped by surface reducible species and adsorbed water to produce superoxide anion radicals and hydroxyl radicals. Subsequent reactions of these radicals between themselves and with adsorbed molecules lead to oxidation/reduction reactions which in turn may degrade aqueous/air pollutants.

Most of the researches focused on two issues: on one hand, the decrease of energy gap of TiO_2 was explored to modify the optical response in visible light range not only ultraviolet[1], on the other hand, how to prevent photogenerated electrons and holes from recombination and improve the photocatalytic activity[2]. Asahi *et al.*[3] reported the TiO_2, which was doped with N element, exhibited a high photocatalytic activity under visible light. The result revealed that doping was an effective way to solve the above problems. Further study has shown that TiO_2 powders doped with two different elements, such as F-N[4], B-N[5], S-C[6], and C-N[7] have better photocatalytic properties than single nonmetal doping. Recently, the C-N co-doped TiO_2 has attracted many attentions for its excellent photocatalytic properties under visible light. Yin *et al.*[8] prepared N and C co-doped titania by a mechano-chemical method revealed high photocatalytic activity for nitrogen monoxide degradation under visible light irradiation, possessing two absorption edges around 400 nm and 540 nm. Chen *et al.*[7] synthesized TiO_2 photocatalysts with different amounts of carbon and nitrogen by the sol-gel method. The increase of photocatalytic degradation of methylene blue under visible light irradiation was ascribed to the synergistic effect of C and N atoms in agreement with other researchers. Zhang and Song[9] proposed that the degradation of methylene blue under visible light was the results of partial replacement of oxygen atoms on the TiO_2 surface with nitrogen, whereas the carbon atoms formed a mixed layer of deposited carbon and C-O band species on the surface of the TiO_2 particles.

In the present work, a one-step, hydrothermal method for the synthesis of C-N co-doped titanium dioxide photocatalysts is demonstrated. The prepared co-doped TiO_2 catalysts were tested in the photocatalytic degradation of 2,4,6-trichlorophenol (TCP) under visible light. A possible mechanism for the photocatalysis was proposed.

EXPERIMENTAL

Titanium dioxide was co-doped with C and N by a one-step process with different alcohols (methanol, ethanol, isopropanol) as carbon precursors and in the presence of ammonia water vapors as the nitrogen precursor. 4 g of P25 and 5 mL of the selected alcohol were placed inside the reactor vessel, 5 mL of ammonia solution was added and the reactor was closed and heated up to 100 °C. The system was kept at this temperature for 4 h. After the thermal treatment was completed the reactor was cooled down slowly to room temperature. Subsequently, the N-C co-doped TiO_2 photocatalysts were dried for 24 h at 105 °C in a muffle furnace and denoted as TiNC(x), where x stands for the carbon number of alcohol. For comparison, carbon doped TiO_2, TiC, was prepared by the same percedure but in the absence of ammonia solution. When deionized water was used to replace alcohol following the same procedure as the synthesis of TiNC(3), the product, nitrogen doped TiO_2, is denoted as TiN.

XRD patterns of the prepared TiO_2 samples were recorded on a Rigaku D/max-2400 instrument using Cu-K_α radiation (λ = 1.54 Å). UV-visible spectroscopy measurement was carried out on a JASCO V-550 model UV-visible spectrophotometer, using $BaSO_4$ as the reflectance sample. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al K_α radiation as the exciting source. The binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect.

Suspensions were prepared in deionized water by mixing TiO_2 catalyst with appropriate solutions of 2,4,6-trichlorophenol. In a typical procedure, 0.1 g TiO_2 powders were dispersed in 100 mL solution of 2,4,6-trichlorophenol (initial concentration $C_0 = 60 \times 10^{-6}$ g mL^{-1}) in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor, and stirred for 0.5 h in darkness to achieve the adsorption equilibrium. In the photoreaction under visible light irradiation, the suspension was exposed to a 110-W high-pressure sodium lamp with main emission in the range of 400-800 nm and air was bubbled at 130 mL/min through the solution. The UV light portion of sodium lamp was filtered by 0.5 M $NaNO_2$ solution. All runs were conducted at ambient pressure and 30 °C. The conversion of 2,4,6-trichlorophenol was determined using an Agilent 1100 series HPLC operated in isocratic mode under the following conditions: methanol-water (80 %:20 %); flow rate 1 mL min^{-1}; temperature 25 °C; Column Phenomenex Luna 10 µ Phenyl-Hexyl, 4.6 mm × 250 mm; detector UV at 254 nm; injection volume 5 µL.

RESULTS AND DISCUSSION

It is reported that the phase composition and particle size of TiO_2 have significant influence on its photocatalytic activity[1]. The XRD patterns of prepared TiO_2 catalysts (Fig. 1) indicate that all TiO_2 samples were mixtures of anatase and rutile phases. The phase contents and the particle sizes of the catalysts were calculated by their XRD patterns according to the method of Spurr and Myers[10] and Debye-Scherrer equation[11], respectively. The results showed that the particle sizes and anatase contents for P25, TiC, TiN and TiNC (3) were 25.5 nm and 75 %, 26.4 nm and 75.2 %, 26.2 nm and 75.5 %, 26.1 nm and 74.9 %. This indicated that no obvious changes in phase composition and particle sizes between P25 and doped TiO_2 catalysts.

To study the optical response of C-N codoped TiO_2 samples, the UV-visible spectra were measured and shown in Fig. 2. P25 did not absorb visible-light, whereas two doped catalysts extended the absorption edges to visible light region, which must result from nitrogen and carbon doped into TiO_2 lattice. In order to calculate the onsets of absorption edges, a tangent was drawn on absorption spectra and was extrapolated. The intercept on the wavelength axis was obtained. Using this wavelength, the band gaps of the TiO_2 catalysts were calculated according the method of Oregan and Gratzel[12]. The results shown that the band gaps for P25 and TiC were 3.06 and 2.9 eV. For TiNC(3), two band gaps, 2.86 and 2.3 eV were observed. Thus, it is deduced that carbon doping located the energy level 0.2 eV above the valence band whereas for interstitial N-doped TiO_2, the visible light response arises from occupied π^* character N-O localized states above the valence band edge (0.76 eV). This is consistent with the theoretical evidence calculated by Valentin *et al.*[13] For co-doped samples using alcohols with different chain length as carbon source, the band gap energies were 2.4, 2.36 and 2.3 eV for TiNC(1), TiNC(2) and TiNC(3). This indicated that the chain length of alcohols influence the light absorption ability of catalysts, which probably affect the photocatalytic activity.

XPS has become an increasingly available and powerful tool for understanding the nature of many different types of surfaces. It can provide information about the actual composition

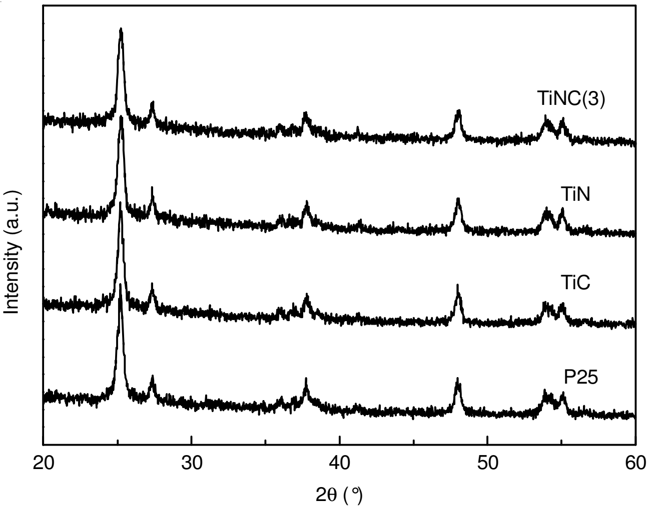

Fig. 1. XRD patterns of the prepared catalysts

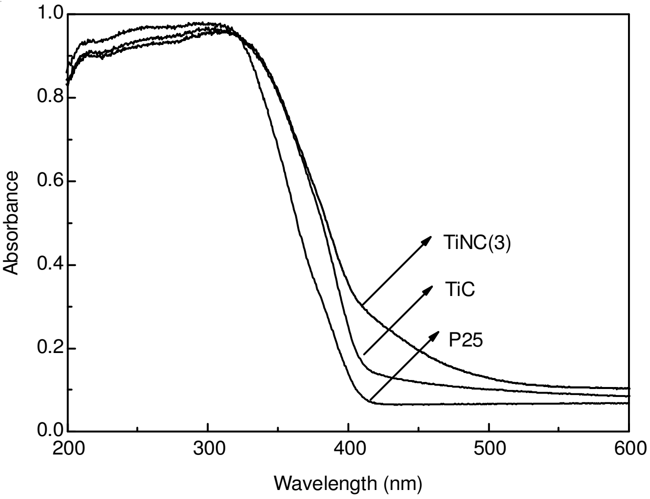

Fig. 2 UV-visible diffuse reflectance spectra of prepared catalysts

and chemical state of surfaces and interfaces that dominate properties of nanostructured materials. Generally speaking, the binding energy of the element is influenced by its electron density. An increase of binding energy implies the lowering of the electron density. Fig. 3 shows the XP spectra of prepared samples in the region of C 1s and N 1s. In the spectrum of C 1s region, three peaks were observed, which located at 284.6, 286.2 and 288.4 eV, respectively. The peaks located at 284.6 and 286.2 eV were atributed to the C-C and C-O bonds of alcohol. Another peak located at 288.6 eV may be attributed to the electron deficiency of the C atom in the Ti-O-C structure, according to the previous reports[14,15]. This indicated that carbon was doped into the TiO_2 lattice. Besides, it is noted that the peak intensity which located at 288.6 eV decreased with decrease the chain length of alcohols, indicating the doping C content decreased. The doping C contents in three catalysts were determined by XP spectra data. The results showed that the doping C content for TiNC(1), TiNC(2) and TiNC(3) were 0.45 %, 0.98 % and 1.55 %. This indicated that the chain length of alcohols influence the carbon doping content remarkably. In the spectrum of N 1s region, two peaks were observed for TiNC(3), which located at 396 and 400 eV.

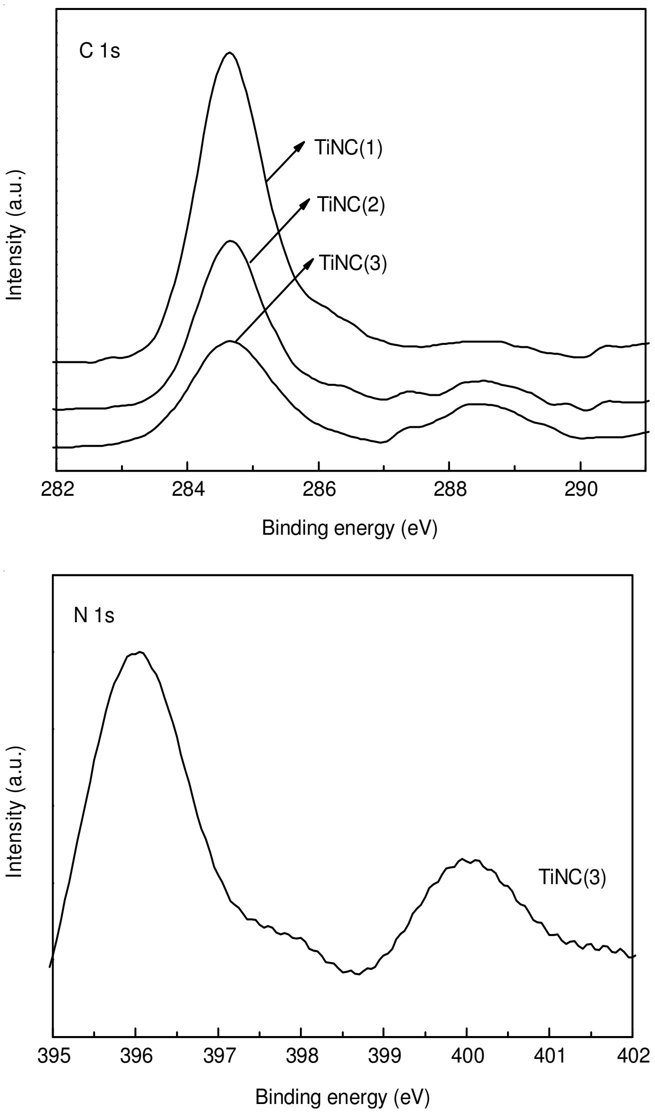

Fig. 3. XP spectra of prepared samples in the region of C 1s (a) and N 1s (b)

According to the literatures[16,17], the peaks around 396 and 400 eV are attributed to the formation of Ti-N bond and other surface N species such as N-N and N-O bond. Therefore, it is indicated that carbon and nitrogen were doped into TiO_2 lattice simultaneously.

Fig. 4 shows the photocatalytic activities of P25, TiC, TiN and TiNC(3) under visible light. Obviously, P25 shows almost no photocatalytic activity for the degradation of 2,4,6-trichlorophenol under visible light, whereas TiC, TiN and TiNC(3) exhibited much higher photocatalytic activities than P25. This must result from the doping of carbon and nitrogen narrowed the band gap, leading to the increased visible light absorption. Fig. 4 showed that the TiNC(3) exhibited much higher activity than that of single doped TiN and TiC. Such high photocatalytic activity of TiNC(3) is mainly ascribed to the synergetic effects of N-C co-doping. First, the C-N codoping results in the absorption increase at the visible-light region. This implies that TiNC(3) can be activated by visible light and more photogenerated electrons and holes can be created and participate in the photocatalytic reactions. It was reported that nitrogen doping can create intra-band-gap states close to the valence band edges, which induces visible light absorption[18]. Furthermore, the carbonaceous species formed by doped C atoms acted as a photosensitizer, which can be excited and inject electrons into the conduction band of TiO_2, then the electron is transferred to the molecular oxygen adsorbed on the surface of TiNC(3), producing $\cdot O^{2-}$ and $\cdot OH$. These reactive species are capable of degrading 2,4,6-trichlorophenol[19].

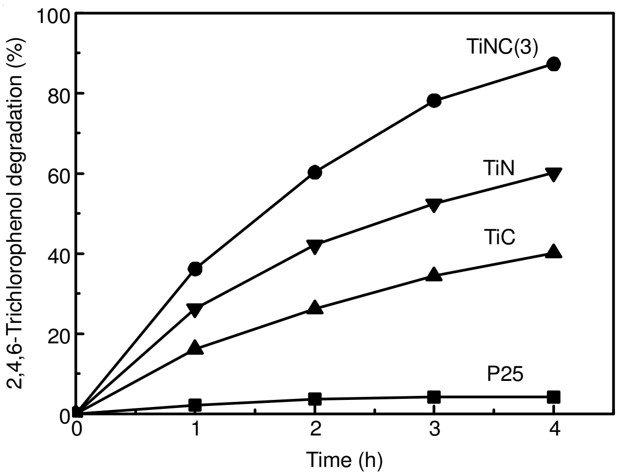

Fig. 4. Photocatalytic activities of P25, TiC, TiN, and TiNC(3) under visible light

Fig. 5 shows the photocatalytic activities of prepared C-N co-doped TiO_2 under visible light. The photocatalytic activities follows the order: TiNC(1) < TiNC(2) < TiNC(3). This indicated that the chain length of alcohols influence the activity remarkably. The XPS results showed that the doping C content decreased with decrease the chain length of alcohol, which is the main reason for the decreased activity. Moreover, the chain length of alcohols influence the light absorption ability of cataltsys, as shown in Fig. 2. Besides, the higher surface adsorbed carbon species (shown in XP spectrum) lead to the lower adsorption ability of 2,4,6-trichlorophenol, thus decreased the photocatalytic activity of TiNC(1) and TiNC(2).

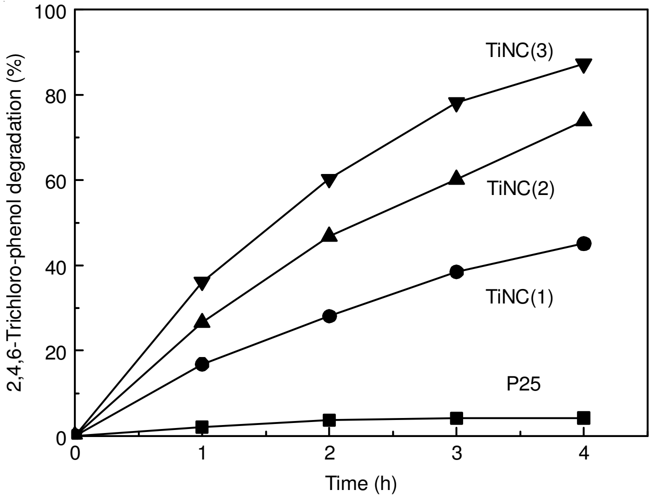

Fig. 5. Photocatalytic activities of prepared C-N co-doped TiO_2 under visible light

Conclusion

A one-step, hydrothermal method for the synthesis of C-N co-doped titanium dioxide photocatalysts is reported. No obvious changes in phase composition and particle sizes between P25 and doped TiO_2 catalysts, whereas the band gap energy was narrowed to 2.3 eV by C-N co-doping. The chain length of alcohols influence the light absorption ability of catalysts. XPS results indicated that carbon and nitrogen doped into TiO_2 lattice, simultaneously. The chain length of alcohols influence the carbon doping content remarkably. The C-N co-doped TiO_2 catalyst exhibited much higher activity for the degradation of 2,4,6-trichlorophenol under visible light than that of P25 and single doped samples. The chain length of alcohols influenced the activity of prepared catalysts obviously.

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