Effects of Cu doping on the phase transition and photocatalytic activity of anatase/rutile mixed crystal TiO₂ nanocomposites

Mao Tang¹, Daixiong Yang¹, Juan Wang¹, Qin Zhou¹, Xiaodong Zhu¹* and Yu Jiao²

¹ School of Mechanical Engineering, Chengdu University, Chengdu 610106, People’s Republic of China
² School of Science, Xichang College, Xichang 615013, People’s Republic of China
* Author to whom any correspondence should be addressed.

Keywords: anatase/rutile mixed crystal TiO₂, Cu doping, photocatalytic activity, sol-gel method

Abstract

Pure and Cu doped anatase/rutile mixed TiO₂ nanomaterials were fabricated through sol-gel method. The obtained photocatalysts were characterized by XRD, SEM, TEM, XPS, PL and DRS, and the influences of Cu doping on the structure and photocatalytic property were studied. The results show that when the molar ratios of Cu/Ti are 1% and 2%, Cu doping promotes anatase → rutile phase transformation. When the molar ratio of Cu/Ti is 4%, the phase transformation is inhibited. Cu element coexists in the form of Cu⁺ and Cu²⁺, and Cu doping facilitates the separation of photogenerated electrons and holes. TEM image shows that copper oxides are dispersed on TiO₂ particles surface, which significantly reduces the optical absorption of ultraviolet region. The photocatalytic experiment results show that the photocatalytic activity of Cu–TiO₂ is lower than pure TiO₂, and the higher doping concentration, the lower photocatalytic activity.

1. Introduction

Using TiO₂ photocatalytic materials to degrade harmful substances is an available route to solve pollutants problem [1–5]. Ion doping introduces impurity levels in forbidden band thus increases the visible light absorption of TiO₂. In addition, it also affects the crystallinity, introduces surface defects, and improves quantum efficiency [6–8]. Fan et al. [9] found that the crystallite size decreases and the specific surface area enhances after Ce doping. Moreover, the absorptions of both ultraviolet and visible regions are enhanced, and the recombination of photogenerated charges reduces, consequently, the photocatalytic activity is improved by Ce doping.

It is generally believed that there are more surface defects and oxygen vacancies in anatase compared to rutile, which is conducive to charges separation and photocatalytic performance [10]. Meanwhile, a growing number of studies have shown that when the anatase and rutile mixed crystal structure is formed, it is possible to promote the migration of photogenerated electrons and holes in phase interface, improve quantum efficiency and show better photocatalytic property than single crystal structure [11–13]. The phase ratio in anatase/rutile mixed crystal is a key role to photocatalytic activity. The mixed crystal effect is not fully exerted when the rutile content is at low level, however, high rutile content will damage the performance because the photocatalytic activity of single rutile phase is low. Therefore, seeking the optimum ratio is the focus and hot spot of mixed crystal TiO₂ [12, 13]. It is a common method to control the phase ratio by heat treatment temperature [14–16]. Chetia et al. [14] calcined the precursor at 500 °C and 800 °C to obtain anatase/rutile mixed crystals. As the temperature increases, the grain size increases and the specific surface area decreases. Meanwhile, the absorption of visible light increases and the recombination of photogenerated charges reduces with the increasing temperature. The mixed crystal calcined at 800 °C shows the highest photocatalytic activity. In addition, the phase content in mixed crystal can also be adjusted by controlling the calcination time [17] and the reactants ratio [18, 19].

It is documented that Cu doping improves the photocatalytic performance of TiO₂ [20–24]. The grain size of TiO₂ is reduced from 21 nm to 9 nm, the spectral absorption band is extended to 470 nm, and the photocatalytic activity is significantly improved through Cu doping in Khairy et al.’s work [23].
The phase transformation of TiO$_2$ will be affected by ion doping. Our previous work has shown that Sn doping promotes the transition from anatase to rutile [1]. In the present study, the effect of Cu doping on phase transition from anatase to rutile was utilized to control phase content, and the structure and photocatalytic performance of Cu doped mixed crystal TiO$_2$ were investigated systematically.

2. Experimental

2.1. Sample preparation
Solution A was obtained via mixing anhydrous ethanol and butyl titanate with a volume ratio of 3:2. Solution B was gained by mixing deionized water, glacial acetic acid and absolute ethanol in a volume ratio of 4:4:15, which was added to solution A dropwise to form a gel. After drying, the precursor was heat treated at 550 °C for 1 h to gain pure TiO$_2$. CuSO$_4$·5H$_2$O was added into solution B to prepare Cu-doped TiO$_2$. The Cu/Ti molar ratios are 1%, 2% and 4%. 1%Cu-doped TiO$_2$ is labeled as 1%Cu–TiO$_2$ and the rest are similar.

2.2. Sample characterization
DX-2700 x-ray diffractometer was used to analyze the crystal structure (XRD). FEI-Inspect F50 scanning electron microscope and FEI–Tecnai G2 F20 transmission electron microscope were used to observe the morphology (SEM and TEM). XSAM800 multifunctional surface analysis system was used to study the element composition and chemical state (XPS). F-4600 fluorescence spectrometer was used to analyze the photoinduced electron-hole recombination rate (PL). UV-3600 ultraviolet-visible photometer was used to test the optical absorption.

2.3. Photocatalysis experiment
The photocatalytic activity of pure TiO$_2$ and Cu–TiO$_2$ was assessed by the decoloration of rhodamine B (RhB). 0.1 g photocatalyst powder was added into 100 ml RhB solution (10 mg l$^{-1}$) to form a mixture, which was stirred for 20 min in dark to reach the equilibrium of adsorption and desorption. Then turn on a 250 W xenon lamp as light source, and sample was taken every 20 min to measure the absorbance. The degradation degree of RhB is calculated by the formula $(A_0 - A_t)/A_0 \times 100\%$, where $A_0$ and $A_t$ represent the initial and t time absorbance.

3. Results and discussion

3.1. Crystal structure
Figure 1 shows the XRD patterns of TiO$_2$ and Cu–TiO$_2$. The peaks of pure TiO$_2$ around 25.3°, 37.8°, 48.1°, 62.8° correspond to the anatase (101), (004), (200), (204) crystal planes [9]. The peaks around 27.4°, 36.0°, 41.2°, 54.3°, 56.6° correspond to the rutile (110), (101), (111), (211), (220) crystal planes [25]. Pure TiO$_2$ is a mixed crystal structure composed of anatase and rutile, in which anatase is 59.6% and rutile is 40.4%. For 1%Cu–TiO$_2$
and 2% Cu–TiO₂, the intensity of rutile diffraction peak is higher than pure TiO₂, indicating that more rutile forms, and the rutile contents are 69.7% and 44.0%, respectively. The anatase → rutile phase transformation is promoted by 1% and 2% Cu doping. The Cu³⁺/Cu⁺ ion radii are 0.073/0.077 nm, which are slightly larger than Ti⁴⁺ ion radius (0.0605 nm). It is possible that Ti⁴⁺ ions are replaced by Cu²⁺/Cu⁺ ions as they are able to enter TiO₂ lattice, which does not generate new crystal phase. The substitution by Cu²⁺/Cu⁺ ions will cause lattice distortion, forming oxygen vacancies, which makes Ti–O easier to fracture, and accelerates the nucleation and growth of rutile phase [26]. It is worth noting that when the Cu/Ti molar ratio is 4%, rutile peaks intensity decreases, and the proportion of rutile is 20.6%, which is lower than pure TiO₂. High content of Cu doing will retard the phase transformation [27]. At high doping level, copper oxides may be formed on the surface of TiO₂ particles, hindering the migration of Ti and O atoms at the interface, which is adverse to the nucleation and growth of rutile [28]. The crystal structure and crystallite size of samples are summarized in table 1.

3.2. Morphology
The SEM images of pure TiO₂ and 4% Cu–TiO₂ are shown in figure 2. Both the two samples display a certain degree of agglomeration, and it is difficult to distinguish single particle.

To observe the morphology more clearly, TEM test was further implemented and the images are presented in figure 3. In figure 3(a), the particle size of pure TiO₂ is about 30–40 nm. It is can be observed that the particle size is 30–50 nm and copper oxide particles with the size of 5–10 nm disperse on TiO₂ matrix in figure 3(b). The crystal plane spacing in figure 3(c) is 0.349 nm, which can be ascribed to anatase (101) plane. The interplanar spacing 0.248 nm corresponds to rutile (101) plane, indicating that pure TiO₂ is a mixed crystal structure composed of anatase and rutile. The marked interplanar spacing in 4% Cu–TiO₂ (figure 3(d)) is 0.366 nm, ascribing to anatase (101) plane, which is larger than pure TiO₂. The radius of Cu ion is larger than Ti⁴⁺, and the replacement of Ti⁴⁺ by Cu ions will cause lattice expansion, increasing the interplanar spacing [29]. The marked interplanar spacing 0.322 nm corresponds to rutile (110) plane, indicating that 4% Cu–TiO₂ is a mixed crystal structure. The crystal plane spacing 0.232 nm corresponds to the (111) plane of CuO [30]. XRD results show that no Cu-related diffraction peak is detected in Cu–TiO₂. It may be that Cu ions enter into TiO₂ lattice to replace Ti ions when Cu content is low, which does not form new phase [31]. On the other hand, copper oxides disperse on TiO₂ particles at high doping level [28].

3.3. Element composition and state
Figure 4 shows the XPS results of 4% Cu–TiO₂. The characteristic peaks of Ti 3p, Ti 3s, Cu 3p, C 1s, Ti 2p, O 1s, Ti 2s and Cu 2p appear in the full spectrum. The C 1s peak may come from the oil contamination of instrument. Figure 4(b) shows the high-resolution spectrum of Ti 2p. Peaks at 464.6 eV, 458.9 eV, 463.2 eV and 457.7 eV
correspond to Ti$^{4+}$ 2p$_{1/2}$, Ti$^{4+}$ 2p$_{3/2}$, Ti$^{3+}$ 2p$_{1/2}$ and Ti$^{3+}$ 2p$_{3/2}$ [16, 32], indicating that Ti element exists as Ti$^{4+}$ and Ti$^{3+}$. The characteristic peaks in figure 4(c) are located at 529.6 eV and 530.9 eV, ascribing to lattice oxygen (O$^{2-}$) and surface hydroxyl (OH$^{-}$), separately [4, 33]. The characteristic peaks of Cu$^{2+}$ 2p$_{3/2}$ and Cu$^{2+}$ 2p$_{1/2}$ in figure 4(d) appear at 933.0 eV and 952.9 eV, respectively [34]. A characteristic peak of Cu$^{+}$ appears at 963.3 eV and a characteristic peak appears at 942.6 eV which is related to the vibration of CuO [35, 36], indicating that Cu element coexists in the form of +1, +2 valence.

3.4. Optical property

Figure 5 shows the PL spectra of samples. Cu–TiO$_2$ samples show lower peak intensity than pure TiO$_2$, indicating that the photogenerated electron-hole pair recombination rate is reduced by Cu doping. Cu ions entry into crystal lattice causes lattice defects and introduces oxygen vacancies, which trap photogenerated charges, improving the separation of carriers [3, 37, 38]. XPS results show that Cu element coexist in the form of +1 and +2 valence, and Cu$^{2+}$ ions capture photogenerated electrons to form Cu$^{+}$ ions, which is also conducive to inhibiting recombination [39].

The UV-visible absorption spectra of samples are shown in figure 6. The absorption edge shows a certain degree of red shift after Cu doping. Cu ions enter into TiO$_2$ lattice, introducing impurity levels in forbidden band, reducing forbidden band width [7, 40]. Remarkably, the absorption of Cu–TiO$_2$ in ultraviolet region is quite different from pure TiO$_2$. With the increasing Cu doping concentration, the absorption in ultraviolet region gradually decreases and 4%Cu–TiO$_2$ shows the lowest UV absorption. TEM results show that Cu is dispersed and distributed on the surface of TiO$_2$ particles in the form of oxide, which will affect the optical absorption of TiO$_2$. As the doping concentration increases, copper oxides will precipitate on TiO$_2$ particles.
surface, hindering the absorption of UV light [41]. The higher Cu doping concentration, the more precipitated copper oxides, and the more decrease in UV radiation absorption.

3.5. Photocatalytic activity
The photocatalytic performance of samples is evaluated by the degradation degree of RhB, and the results are shown in figure 7. After 80 min of reaction, the degradation degree of pure TiO₂, 1% Cu–TiO₂, 2% Cu–TiO₂ and
4%Cu–TiO₂ are 40.1%, 36.2%, 29.2% and 16.0%, respectively. The degradation degree gradually decreases as Cu doping concentration increase. The kinetic curves are shown in figure 7(b). The first order reaction rate constants of pure TiO₂, 1%Cu–TiO₂, 2%Cu–TiO₂ and 4%Cu–TiO₂ are 0.0061 min⁻¹, 0.0050 min⁻¹, 0.0035 min⁻¹ and 0.0012 min⁻¹. The results show that Cu doping inhibits the photocatalytic activity of TiO₂.

Some researchers believe that the photocatalytic activity is related to the doping concentration, and low concentration is conducive to charges separation. When the concentration at high level, excess defects and oxygen vacancies will be introduced, which generates new recombination centers of photogenerated electrons and holes, decreasing the photocatalytic activity [42, 43]. In the present study, 4%Cu–TiO₂ shows lower PL peak intensity than pure TiO₂ yet, thus the decrease of photocatalytic activity should not be ascribed to the generation of new recombination centers due to the high Cu doping content.

The TEM results show that copper oxides particles are dispersed and distributed on the surface of TiO₂. When the surface of TiO₂ particles is covered with other substances, its optical absorption will be affected [40, 41]. The ultraviolet-visible absorption spectra show that pure TiO₂ exhibits higher absorption in ultraviolet region and the absorption decreases after Cu doping. The higher Cu concentration, the more oxides precipitated, and the more obvious decrease in ultraviolet region absorption. The absorption in ultraviolet region decreases significantly, which is not conducive to photocatalytic performance. This is also consistent with the higher concentration, the lower photocatalytic activity.
4. Conclusions

The pure and Cu doped mixed crystal TiO$_2$ nanomaterials with different concentrations were prepared by sol-gel method and characterized by XRD, SEM, TEM, XPS, PL and DRS. The results show that when the molar ratios of Cu/Ti are 1% and 2%, Cu doping promotes the transformation from anatase to rutile, and inhibits the transformation when the molar ratio of Cu/Ti is 4%. Cu element coexists in the form of $+1$ and $+2$ valence, and the photoinduced charges recombination decreases after Cu doping. Copper oxides disperse and precipitate on TiO$_2$ surface, which significantly reduces the optical absorption of ultraviolet region. The photodegradation degrees of Cu–TiO$_2$ are lower than pure TiO$_2$, and the higher Cu concentration, the lower photodegradation degree. The first-order reaction rate constant decreases from 0.0061 min$^{-1}$ for pure TiO$_2$ to 0.0012 min$^{-1}$ for 4% Cu–TiO$_2$.

Acknowledgments

This work was supported by the Training Program for Innovation of Chengdu University (S202011079053, CDU-CX-2021134, CDU-CX-2021527).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Xiaodong Zhu @ https://orcid.org/0000-0001-6787-4878

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