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Article

Strong visible absorption and excellent photocatalytic performance of brown TiO₂ nanoparticles synthesized using one-step low-temperature process

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ABSTRACT

We report a facile and modified sol-gel approach to synthesize brown TiO₂ nanoparticles at low temperature (100–600 °C). The TiO₂ nanoparticles dried at 180 °C (TiO₂-180°C) possessed a small particle size (5.0 nm), large specific surface area (213.45 m²/g), and efficient response to broadband light over the entire ultraviolet-visible spectrum with a narrow band gap of 1.84 eV. In addition, TiO₂-180°C exhibited the optimal reaction rate constant for the degradation of methylene blue (0.08287 mg/(L·min)), which is six times higher than that of the mixed rutile/anatase phase TiO₂ photocatalytic standard P25 (0.01342 mg/(L·min)). Furthermore, cycling photodegradation experiments confirmed the stability and reusability of this catalyst. The unique physicochemical properties resulting from the low-temperature preparation of TiO₂-180°C, including its broadband visible absorption associated with a high concentration of oxygen vacancies, large surface area, and enriched surface –OH/H₂O may be responsible for this excellent photocatalytic performance. The use of as-prepared TiO₂-180°C for practical applications is expected after further optimization.

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1. Introduction

Photocatalysis is a promising method for the degradation of various organic compounds in wastewater treatment, environmental-pollution reduction, and solar-energy conversion [1–5]. Of the various photocatalysts developed, TiO₂ is considered one of the most promising candidates because of its low toxicity, good physical and chemical stability, non-corrosiveness, and low cost [6,7] and has recently been intensively studied [8–10]. However, the low activity of TiO₂ under visible light, which results from its wide bandgap energy of 3.2 eV, and its low quantum efficiency due to the recombination of electron-hole pairs limits its solar-energy-conversion capabilities as well as its practical applications. Because visible light accounts for a large proportion of solar energy, considera-

ble efforts have been devoted to enhancing the visible-light response of TiO₂ [11–13].

Enhancement of the photocatalytic activity of TiO₂ under visible light has been achieved by doping with noble metals [14,15] or nonmetals [16–19] or via recombination with other semiconductors [20]. The absorption edge of TiO₂ in these studies was usually red-shifted to the visible-light range; however, the visible absorption intensity remained insufficient (Table 1). Moreover, these strategies also lead to other problems, such as thermal instability, increased carrier recombination centers [21,22], decreased photodegradation activity, and the formation of hazardous by-products [23]. The emergence of black TiO₂ with a narrow band gap has received significant attention [24,25]. Its strong absorption in the visible-light range and superior photocatalytic performance make it prom-

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Table 1
Physical parameters of TiO₂ previously studied in the literature.

Material	Preparation method	Absorption edge (nm)	Band gap (eV)	Size (nm)	S _{BET} (m ² /g)	Ref.
Cu-TiO ₂	Sol-Gel	—	2.74	35	35.6	[14]
S-TiO ₂	Sol-Gel	435	2.85	9.5	—	[16]
O-TiO ₂	Hydrolysis method	420	2.95	10.3	78.7	[18]
Pt-S-TiO ₂	Immersion	—	3.20	20	49.0	[19]
TiO ₂ /WO ₃	Citric acid complexation	475	2.61	300	37.1	[20]

ising in the photocatalysis field. Two major preparation methods are used to synthesize black TiO₂, a high-H₂-pressure process and hydrogen-gas annealing [26,27]. The former requires troublesome reaction conditions such as a high-pressure H₂ atmosphere for long times, whereas the formation of irregular TiO₂ is likely using the latter [28]. Therefore, a more facile route to prepare TiO₂ with efficient visible-light absorption and excellent photocatalytic activity is needed.

Based on this understanding, we developed a convenient modified sol-gel synthetic route to prepare TiO₂ nanoparticles with strong visible-light response at low temperature. The synthetic TiO₂ nanoparticles were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), surface area and porosity analysis, ultraviolet-visible (UV-vis) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR) spectroscopy. Furthermore, the photocatalytic activity of TiO₂ for the degradation of methylene blue (MB) was validated under visible-light irradiation.

2. Experimental

2.1. Materials

Tetrabutyl titanate (Ti(OC₄H₉)₄, 98%) was used as the titanium precursor. Anhydrous ethanol (C₂H₅OH, 99.7%) was used as the solvent and reactant. Hydrochloric acid (HCl, 36.0%–38.0%) and sodium hydroxide (NaOH, 96%) were used to adjust the pH of the solution. Degussa P25, a mixed rutile/anatase phase TiO₂ photocatalytic standard, was used as the control catalyst. All the reagents and solvents were used directly without further purification.

2.2. Synthesis of TiO₂ nanoparticles

The typical preparation procedure was as follows. First, 5 mL of Ti(OC₄H₉)₄ was slowly added into 20 mL of C₂H₅OH under stirring, followed by the addition of 0.75 mL of HCl solution. Then 10 mL of the mixed H₂O and C₂H₅OH solution (1:1, V/V) was added dropwise under continuous stirring to obtain sol A. The TiO₂ samples were designated as TiO₂-x°C, where x indicates the drying or calcination temperature. For 100 ≤ x ≤ 200, the obtained sol A was dried at x °C for 4 h in an oven to obtain

dry crystals. These dry crystals were washed with water and ethanol, dried at 80 °C for 4 h, and ground in a mortar to obtain powder samples. For 300 ≤ x ≤ 600, the obtained sol A was dried at 100 °C for 4 h in an oven and then calcined at x °C for 2 h in a muffle furnace.

2.3. Structural characterization

Structural characterization of the samples was performed using XRD (Rigaku, D/max-RB) with Cu K_α radiation (λ = 0.15406 nm); conditions of 36 kV and 20 mA and a scan speed of 4°/min were employed. The morphologies of samples were examined using TEM (TECNAI-10, Philips) or HRTEM (H-7650, Hitachi). N₂ adsorption-desorption isotherms of the samples were obtained using a surface area and porosity analyzer (Tristar 3000, Micromeritics) with a liquid nitrogen adsorbent at 196 °C, and the specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05–0.3. The surface states of samples were determined using FTIR spectroscopy (Nicolet 6700, Thermo) on KBr disks. EPR data were obtained on an EPR spectrometer (Elexsys E500, Bruker) using an X-band (9.44 GHz, 2.17 mW) microwave with sweeping magnetic field at 110 K in cells. The XPS measurements were performed on an X-ray photoelectron spectrometer (ESCALAB 250, Thermo Fisher Scientific) using an Al K_α monochromatic X-ray source (1486.6 eV, 15 kV, and 150 W). Raman spectra were obtained on a micro-Raman spectrometer (inVia Reflex, Renishaw) using the back-scattering geometry with a diode-pumped solid-state laser (20 mW, 532 nm) as the excitation light source. Diffuse reflectance spectra were obtained using a UV-vis spectrophotometer (Cary 5000, Varian) with BaSO₄ as the reference. Absorption spectra were measured using a double-beam UV-vis spectrophotometer (TU-1900, Persee).

2.4. Photoactivity measurements

The photocatalytic performances of the TiO₂ samples were evaluated based on the degradation of MB under visible-light irradiation. The TiO₂ catalysts were dispersed in 50 mL of MB solution (10 mg/L) in a glass beaker under magnetic stirring. The light source consisted of a 300-W xenon lamp equipped with a cut-off filter (400 nm) or three 18-W light-emitting diode (LED) lamps of different colors (blue: 410–480 nm; green: 480–560 nm; red: 600–650 nm). Before visible-light irradiation, the MB solution containing catalysts was kept in the dark for 30 min to establish an adsorption-desorption equilibrium. Concurrently, the light source was preheated for 30 min to achieve a stable light output. In the photocatalysis experiments, 4 mL of the MB solution were removed at certain intervals and centrifuged, and its absorbance at 664 nm was measured. The degradation rate (*D*%) of the MB solution was determined using the absorbance data and Eq. (1):

$$D\% = (1 - C_t/C_0) = (1 - A_t/A_0) \times 100\%, \quad (1)$$

where *C*₀ and *A*₀ are the initial concentration and absorbance of the MB solution, respectively, and *C*_{*t*} and *A*_{*t*} are the concentration and absorbance of the MB solution at irradiation time *t*,

respectively. The dynamic process of the photocatalytic degradation of MB over TiO₂ can be described using first-order kinetics [29]. Consequently, the reaction rate constant (k) was determined based on Eq. (2) by plotting $-\ln(C_t/C_0)$ as a function of t :

$$-\ln(C_t/C_0) = kt. \quad (2)$$

3. Results and discussion

3.1. Characterization of photocatalysts

3.1.1. XRD analysis

Fig. 1 presents the XRD patterns for P25 and the TiO₂ nanoparticles prepared at various temperatures. The peaks at 25.7°, 38.3°, 48.5°, 54.4°, 55.6°, 63.2°, 70.8°, and 75.6° can be attributed to the (101), (004), (200), (105), (211), (204), (220), and (215) crystal planes of the anatase phase [JCPDS No. 21-1272], respectively [30,31]. Meanwhile, the peaks at 27.8°, 36.6°, 39.9°, 41.8°, 44.8°, 54.9°, 57.1°, 64.6°, 69.4°, and 70.4° correspond to the (110), (101), (200), (111), (210), (211), (220), (310), (301), and (112) crystal planes of the rutile phase [JCPDS No. 21-1276], respectively [32]. The phase transition temperature (600 °C) is consistent with that reported in Ref. [33]. The main phase of P25 is anatase, with a small amount of the rutile phase. The intense and sharp diffraction peaks indicate its highly crystalline structure. In contrast, the diffraction peaks for the TiO₂- $x^\circ\text{C}$ ($100 \leq x \leq 200$) nanoparticles are weak and broad, suggesting that their particles sizes were rather small. According to Serpone *et al.* [34], the sample must contain at least 5% crystalline material to form a discernible pattern; therefore, we deduced that a mass of amorphous component was present in the TiO₂ crystal. The crystallinities of the TiO₂ samples calculated using Jade software ranged between 60% and 80%, confirming this deduction. The peaks become relatively stronger and sharper for the TiO₂- $x^\circ\text{C}$ ($300 \leq x \leq 600$) nanoparticles, accompanied by a progressive phase transition from the anatase to rutile phase. The narrowing of the diffraction peaks indicates an increase in crystal size and crystallinity, with the crystallinity of the TiO₂-600°C nanoparticles reaching 100%. The crystallite sizes of the TiO₂ nanoparticles were calculated using the Scherer equation ($D = 0.9\lambda/\beta\cos\theta$), and the

results are presented in Table 2. Based on the XRD results, it was concluded that the preparation temperature plays a key role in the phase composition of TiO₂ nanoparticles.

3.1.2. TEM analysis

The morphologies of the TiO₂ nanoparticles prepared at various temperatures were examined using TEM and HRTEM. As observed in Fig. 2(a)–(d), TiO₂- $x^\circ\text{C}$ ($100 \leq x \leq 200$) consisted of aggregated or nonaggregated spherical nanoparticles (< 10 nm in diameter), whereas only aggregated particles are observed for TiO₂- $x^\circ\text{C}$ ($300 \leq x \leq 600$) in Fig. 2(e)–(h). These findings indicate that the particle aggregation increased significantly with increasing preparation temperature. The HRTEM image in Fig. 2(i) shows that TiO₂-180°C contained uniform spherical particles with an average diameter of 5.0 nm, which is consistent with the particle size calculated from the XRD data. The lattice fringes of TiO₂-180°C have a spacing of 0.33 nm (Fig. 2(j)), which is attributed to the (101) planes of anatase [32].

3.1.3. Specific surface areas and pore size distributions

The specific surface area is an important indicator of catalyst performance. As observed in Table 2, the TiO₂- $x^\circ\text{C}$ ($100 \leq x \leq 200$) nanoparticles had larger specific surface areas than P25. The TiO₂-140°C nanoparticles had the highest specific surface area (243.76 m²/g), which was almost five times that of P25 (53.07 m²/g). The specific surface areas gradually decreased with increasing preparation temperature. Apparently, a high preparation temperature induced an increase of crystallinity but decrease of the surface area.

The N₂ adsorption-desorption isotherm curves and pore size distributions (PSDs) of the TiO₂ nanoparticles are presented in Fig. 3. According to the International Union of Pure and Applied Chemistry (IUPAC) classification [14], the isotherm curves of TiO₂-100°C can be classified as Type-II isotherms; its adsorption curve overlapped well with the desorption curve for the entire pressure range, which indicates vast quantities of micropores in the TiO₂-100°C nanoparticles. The TiO₂- $x^\circ\text{C}$ ($140 \leq x \leq 200$) nanoparticles showed Type-IV isotherms with H2-type hysteresis in the relative pressure range of 0.4–0.6 (Fig. 3(a)), which revealed the presence of mesopores. The isotherm curves of TiO₂- $x^\circ\text{C}$ ($300 \leq x \leq 600$) can also be classified as Type-IV with the typical H2-type hysteresis, with the hysteresis loops appearing at relatively higher pressure (Fig. 3(b)), indicating the existence of mesopores and/or

Fig. 1. XRD patterns of TiO₂ nanoparticles prepared at various temperatures.

Table 2

Physicochemical properties of synthesized TiO₂ nanoparticles.

Sample	Band gap (eV)	Size (nm)	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
P25	3.20	22.0	53.07	7.8054	0.1036
TiO ₂ -100°C	2.97	4.3	211.86	2.3089	0.1223
TiO ₂ -140°C	2.54	4.5	243.76	2.5587	0.1559
TiO ₂ -180°C	1.84	5.0	213.45	2.6566	0.1418
TiO ₂ -200°C	2.04	5.4	184.84	2.8643	0.1312
TiO ₂ -300°C	2.31	6.1	149.06	3.6667	0.1366
TiO ₂ -400°C	2.87	11.6	78.74	6.8195	0.1342
TiO ₂ -500°C	2.91	20.9	57.02	10.2684	0.1434
TiO ₂ -600°C	3.01	27.3	17.23	14.1630	0.1341

Fig. 2. TEM images of TiO_2 nanoparticles. (a) TiO_2 -100°C; (b) TiO_2 -140°C; (c) TiO_2 -180°C; (d) TiO_2 -200°C; (e) TiO_2 -300°C; (f) TiO_2 -400°C; (g) TiO_2 -500°C; (h) TiO_2 -600°C; HRTEM image (i) and lattice fringes (j) of TiO_2 -180°C.

Fig. 3. N_2 adsorption-desorption isotherms (a, b) and pore size distributions (c, d) of TiO_2 nanoparticles.

macropores. The formation of mesopores and macropores might be the consequence of the reunion of TiO_2 nanoparticles at higher temperature.

In Fig. 3(c) and 3(d), the TiO_2 - $x^\circ\text{C}$ ($100 \leq x \leq 200$) nanoparticles show monomodal PSDs with the pore size ranging between 1.9 and 7.6 nm, suggesting a small fraction of micropores (< 2 nm in diameter) and large fraction of mesopores (2–50 nm in diameter). The TiO_2 - $x^\circ\text{C}$ ($300 \leq x \leq 600$) nanoparticles showed a unimodal PSD with a large fraction of pore size diameters in the mesoporous range. The peak location clearly shifted toward larger diameters, indicating that the pore diameter increased with increasing preparation temperature of the TiO_2 samples.

3.1.4. FTIR analysis

FTIR spectroscopy was used to characterize the surface states of the TiO_2 samples. As observed in Fig. 4, the TiO_2 - $x^\circ\text{C}$ ($x = 100, 140, 180, 400$) nanoparticles showed similar FTIR spectra modes. The broad peaks at 3600–2900 cm^{-1} can be attributed to the O–H stretching and bending vibration of surface-adsorbed water molecules, whereas the absorption peaks at 1608 and 1385 cm^{-1} are attributed to the bending vibration of H–O–H [35]. The strong and wide absorption in the lower energy region of 800–400 cm^{-1} can be attributed to the stretching vibration of Ti–O from the TiO_2 lattice [36].

Fig. 4. FTIR spectra of TiO₂ nanoparticles.

3.1.5. XPS analysis

To further investigate the surface chemical composition and elemental chemical states, XPS measurements of the TiO₂-x°C ($x = 100, 140, 180, 400$) nanoparticles were performed, and the results are presented in Fig. 5. For all the experiments, C 1s (284.8 eV) was used as a standard for the energy scale. The core levels of O 1s, Ti 2p, Cl 2p, and C 1s can be clearly observed in the XPS survey spectra (Fig. 5(a)). In the high-resolution spectra of Ti 2p, the two peaks centered at 458.55–459 and 464.45–464.7 eV are assigned to the binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} in the Ti⁴⁺ chemical state, respectively [18]. No characteristic binding energy assigned to Ti³⁺ was observed, which is consistent with the EPR data. The peak areas expanded gradually with increasing preparation temperature, indicating the rise of the relative Ti⁴⁺ content. The atomic ratio of O:Ti was far greater than 2.0 in TiO₂-100°C (Table 3) and decreased with increasing preparation temperature, implying that the surface of the as-prepared TiO₂ nanoparticles was covered by large amounts of -OH/H₂O.

The high-resolution O 1s spectra in Fig. 5(c) all contain wide and asymmetric peaks. These spectra were fitted using the software XPS Peak with application of Gaussian fitting to the three peaks at binding energies of 529.8–530.05, 531.2–531.5, and 532.2–532.7 eV, which were attributed to lattice oxygen from TiO₂ (O-Ti-O), surface hydroxyl oxygen groups (-OH),

Table 3

XPS data for TiO₂ nanoparticles.

Sample	Binding energy (eV)			Atomic content (%)		
	O 1s	Ti 2p _{3/2}	Ti 2p _{1/2}	O	Ti	O:Ti
TiO ₂ -100°C	529.8	458.55	464.45	52.62	2.98	17.66
TiO ₂ -140°C	530.05	458.8	464.55	51.93	13.14	3.95
TiO ₂ -180°C	530.0	458.8	464.55	51.35	18.51	2.77
TiO ₂ -400°C	530.2	459.0	464.70	50.69	23.53	2.15

and adsorbed H₂O, respectively [14]. It is apparent that the relative areas of lattice oxygen increased with increasing preparation temperature, whereas those of the adsorbed water decreased, which is in good agreement with the variation of Ti⁴⁺ content shown in Fig. 5(b). Note that the variation of the relative area of hydroxyl oxygen groups shows a substantially different trend. As observed in Fig. 5(c), the relative area of hydroxyl oxygen groups increased with increasing preparation temperature until 180 °C and then decreased.

3.1.6. Raman analysis

To examine the structural properties of the TiO₂-x°C ($x = 100, 140, 180, 400$) nanoparticles and the presence of oxygen vacancies (Vo), Raman spectroscopy measurements were performed. P25 was also analyzed as a reference under the same measurement conditions. Four characteristic Raman-active modes of anatase phase centered at 143, 396, 515, and 638 cm⁻¹ are detected in Fig. 6, which is consistent with the reported Raman frequencies [37,38]. Compared with P25, the E_g peak at 143 cm⁻¹ for the TiO₂ nanoparticles obviously displays a certain degree of blue-shift, with E_g shifted from 139 to 144, 150, 152, 154, and 146 cm⁻¹ accompanied by peak broadening. As previously reported, lattice disorder or localized defects related to oxygen vacancies may cause the shifting and broadening of the E_g mode in Raman spectra [39,40]. In the present case, the information from Raman spectroscopy unambiguously supported the presence of Vo.

In addition, the blue-shift of the E_g mode of TiO₂ nanoparticles increased with increasing preparation temperature until 180 °C and then decreased, suggesting the change in the Vo concentration. This result supports the conclusion that the Vo concentration can be controlled by the preparation tempera-

Fig. 5. XPS survey spectra of TiO₂ nanoparticles (a); High-resolution XPS spectra of Ti 2p (b) and O 1s (c).

Fig. 6. Raman spectra of P25 and TiO₂ nanoparticles. Inset: high-resolution E_g mode.

ture, as evidenced by the EPR and DRS data discussed in the following sections.

3.1.7. EPR spectra

EPR measurements were conducted to further verify the presence of Vo. The black line representing P25 in Fig. 7 shows a negligible EPR signal. Under the same EPR measurement conditions, the TiO₂- $x^\circ\text{C}$ ($x = 100, 140, 180, 400$) nanoparticles exhibited varied EPR signal intensities at $g = 2.003$, corresponding to unpaired electrons trapped by oxygen vacancies [41]. However, the representative signal of Ti³⁺ usually appearing at $g \approx 1.961$ was not observed, confirming the absence

Fig. 7. EPR spectra of P25 and TiO₂ nanoparticles. Inset: EPR spectra of Ti³⁺.

of Ti³⁺ in the as-prepared TiO₂ samples, which is consistent with the XPS data [37]. Furthermore, the maximum intensity was observed for the TiO₂-180°C nanoparticles, which indicates that these nanoparticles contained the highest concentration of oxygen vacancies, confirming the Raman spectra analysis.

3.1.8. Absorption properties

The optical properties of the TiO₂ nanoparticles were characterized by UV-vis diffuse reflectance spectroscopy (DRS). Fig. 8(a) presents the absorption spectra of P25 and the TiO₂ nanoparticles. The absorption edge of P25 was detected at ap-

Fig. 8. (a) UV-vis DRS spectra for TiO₂ nanoparticles; (b) $(\alpha h\nu)^2$ vs. photon energy of TiO₂ nanoparticles; (c) Images of TiO₂ nanoparticles.

proximately 400 nm because of the intrinsic absorption of anatase TiO_2 (3.20 eV) [14]. Compared with P25, the absorption edge of TiO_2 -100°C red-shifted to 700 nm and the UV-vis absorption showed a slight enhancement. The visible absorption was remarkably enhanced for TiO_2 - $x^\circ\text{C}$ ($140 \leq x \leq 180$) and gradually declined at higher temperature. The TiO_2 -180°C nanoparticles exhibited extensive absorption covering the entire UV-vis spectrum. The absorption spectra of TiO_2 - $x^\circ\text{C}$ ($x \geq 500$) were in accordance with those in the literature [14,18]. A Tauc plot of the KM function vs. energy is plotted in Fig. 8(b), from which the bandgap energies of the samples were deduced; the results are also presented in Table 2. All the TiO_2 nanoparticles exhibited narrower bandgap energies compared with P25, with TiO_2 -180°C having the narrowest band gap of 1.84 eV. Color differences are apparent among the TiO_2 samples in Fig. 8(c); the depths of the colors agreed well with their absorption intensities in the visible range. More importantly, the color of the TiO_2 -180°C nanoparticles remained unchanged for 8 months under ambient condition, suggesting that its stability is satisfactory.

The intense absorption in the visible range could result from oxygen vacancies [37,38]. In the study on black TiO_2 performed by Chen *et al.* [24], TiO_2 samples were hydrogenated at 500 °C to introduce oxygen vacancies or surface defects, which can generate two tails at the top of the valence band (VB) and bottom of the conduction band (CB) to narrow the bandgap (E_g) by destroying the lattice periodicity. In our above EPR and Raman

analyses, the presence of Vo was detected in the TiO_2 -180°C nanoparticles; a high concentration of Vo would lead to disorder of the surface state of the TiO_2 nanoparticles and generate a new vacancy band below the CB, yielding a decrease of the bandgap energy [26,37].

In conclusion, the preparation temperature was the critical factor affecting the properties of the TiO_2 samples. TiO_2 -180°C exhibited both a large surface area and strong visible absorption, making it highly promising for photocatalytic degradation under visible-light irradiation.

3.2. Photocatalytic performance

3.2.1. Effect of initial pH

The initial pH of the MB solution has a great effect on the absorption equilibrium between organic molecules and the photocatalyst, thereby affecting the photocatalytic degradation process [42]. Therefore, the effect of the initial pH of the MB solution was investigated. Fig. 9(a) and 9(b) show the photocatalytic activities of the TiO_2 -180°C catalyst at different initial pH values. The maximum degradation rate of 99.03% and the maximum reaction rate constant of 0.07036 $\text{mg}/(\text{L}\cdot\text{min})$ were obtained for an initial pH of 4 under visible-light irradiation for 80 min (Fig. 9(b) and (d)). This degradation rate was far greater than that of a blank experiment, in which 10.74% of MB molecules degraded in the absence of a catalyst after 120 min. A good linear correlation is observed between $\ln(C_t/C_0)$ and

Fig. 9. (a) Photocatalytic activities of TiO_2 -180°C at different initial pH values; (b) Degradation rates; (c) Kinetic linear simulation curves; (d) Reaction rate constants.

Fig. 10. Photocatalytic activities (a); Degradation rates (b); Kinetic linear simulation curves (c) and reaction rate constants (d) of TiO_2 -180°C at different loadings; (e) Real-time absorption spectra of MB solution during the photodegradation process. Inset: photographs of MB solution in real-time.

the reaction time (t) in Fig. 7(c), indicating that the degradation process of MB over the TiO_2 photocatalyst was consistent with first-order kinetics. The results indicate that faintly acid solution is favorable for the photocatalytic degradation process, which is reasonable because faintly acid solution is favorable for the migration of electrons to the surface of the photocatalyst and their reaction with O_2 to form H_2O_2 , generating free $\cdot\text{OH}$ radicals and leading to an increase of the photocatalytic efficiency [43]. Thus, the initial pH was set to 4 in the following experiments.

3.2.2. Effect of catalyst loading

To investigate the effect of catalyst loading on the photocatalytic degradation process, experiments with TiO_2 loadings ranging from 0.04 to 0.10 g were performed; P25 was also analyzed for comparison. The degradation rates of MB increased with TiO_2 loading until 0.07 g and then decreased (Fig. 10(a) and (b)). Adequate catalyst loading can provide a sufficient number of active sites, leading to a sufficient concentration of electron-hole pairs, and thus enhanced degradation rate. However, excess catalyst loadings may promote the recombination of electron-hole pairs on the TiO_2 surface, reducing the photocatalytic activity of catalysts [44,45]. At a TiO_2 loading of 0.07 g, the degradation rate reached 99.33% under visible-light irradiation for 40 min, far higher than that of P25 (53.87%). Note that the maximum reaction rate constant of TiO_2 -180°C (0.08287 $\text{mg}/(\text{L}\cdot\text{min})$) was almost six times that of P25 (0.01342 $\text{mg}/(\text{L}\cdot\text{min})$), suggesting the enhancement of photocatalytic activity. Fig. 10(e) presents the real-time absorption spectra of MB solution with 0.07 g TiO_2 loading during the degradation process.

We also studied the degradation rates of TiO_2 - $x^\circ\text{C}$ ($100 \leq x \leq 600$) catalysts at the optimal pH and catalyst loadings (Fig. 11). Their photocatalytic activity was roughly consistent with their

visible-light responses. However, TiO_2 -400°C exhibited an apparently lower degradation rate than TiO_2 -100°C despite their similar absorption properties. A plausible explanation is that the TiO_2 -100°C nanoparticles exhibited larger specific surface area than TiO_2 -400°C nanoparticles. Moreover, the TiO_2 -140°C nanoparticles had larger specific surface area than the TiO_2 -180°C nanoparticles but resulted in a lower degradation rate because TiO_2 -180°C produced a stronger visible-light intensity. These results clearly suggest that the photocatalytic activity of the catalyst was not only affected by its visible-light response, but also related to its particle size and specific surface area. The specific surface area can directly affect the adsorption between the catalyst and target molecules on the surface of the catalyst; a larger specific surface area was conducive to improving surface adsorption, thus improving the photocatalytic reaction rate. The large BET surface area, high response to visible light, and strong adsorption between MB molecules and the catalyst led to the higher photocatalytic ac-

Fig. 11. Degradation rates of MB with different TiO_2 nanoparticles under visible-light irradiation.

Fig. 12. Degradation rates of MB with TiO₂-180°C and P25 under visible-light irradiation.

tivity of TiO₂-180°C.

3.2.3. Photocatalytic performance under LED lamp irradiation

To investigate the dependence of the irradiation light used during the photocatalytic degradation of MB, LED lamps of different colors were used as the light source, and the results are presented in Fig. 12. P25 was also evaluated for comparison. In the blank experiments, the degradation rates of MB were always lower than 13% for all the lamps in the absence of TiO₂-180°C for 240 min. Under the dark stirring condition, approximately 21.63% and 14.62% of MB molecules degraded over the P25 and TiO₂-180°C catalysts, respectively. Conversely, in the presence of the TiO₂-180°C catalyst, the degradation rates increased to 95.10%, 53.36%, and 41.58% for the blue, green, and red LED irradiation, respectively. Under the same conditions, only 42.32%, 26.30%, and 28.54% of MB molecules degraded over P25, respectively. These results indicate that P25 exhibited weak photocatalytic activity under blue-light irradiation and no photocatalytic activity under green- and red-light irradiation, whereas the TiO₂-180°C catalyst exhibited excellent photocatalytic activity under blue-light irradiation and moderate photocatalytic activity under green- and red-light irradiation. The photocatalytic activities under different light irradiation were consistent with the light response of

TiO₂-180°C in the DRS spectra in Fig. 8(a).

3.2.4. Stability of TiO₂ catalyst

In addition to the photocatalytic activity, the stability of catalyst is another crucial factor for a high-quality catalyst [16]. To examine the stability of the TiO₂-180°C catalyst, three cycles of photodegradation experiments under visible-light irradiation were performed, and the results are presented in Fig. 13. The degradation rate of MB decreased slightly in the cycling degradation experiments. After three successive cycles, the TiO₂-180°C catalyst still resulted in a 92.20% degradation rate. The XRD spectrum of the TiO₂-180°C catalyst did not change significantly after the cycling degradation experiments. Although most nanomaterials with small particle size exhibit poor stability, the stability of the present TiO₂-180°C catalyst was satisfactory and is believed to be promising for industrial application after further optimization.

3.2.5. Quenching experiments

Electron-hole pairs and generated free radicals have been shown to play an important role in the photocatalytic degradation process [46]. Their effects can be deduced from radical quenching experiments. The radical quenching experiments were conducted by adding isopropanol (IPA, an efficient ·OH scavenger), *p*-benzoquinone (BQ, a superoxide radicals ·O₂⁻ quencher), or disodium edetate dihydrate (EDTA-2Na, a scavenger of h⁺) to the MB solution. The results are presented in Fig. 14. Although IPA, BQ, and EDTA-2Na all suppressed the photocatalytic degradation, the inhibition effect of IPA was most significant, indicating that ·OH, ·O₂⁻, and h⁺ were all involved in the photocatalytic degradation with ·OH being predominant.

3.2.6. Reaction mechanism

Based on the above results, we proposed a mechanism to explain the enhancement of photocatalytic activity of TiO₂-180°C nanoparticles (Fig. 15). Because of the narrow energy gap of TiO₂-180°C nanoparticles (1.84 eV), its electrons can generally be easily excited from the VB to the CB under visible-light irradiation, producing electron-hole pairs. The electron-hole pairs are then separated and migrate to the sur-

Fig. 13. (a) Degradation rates of three cycles of photodegradation of MB under visible-light irradiation; (b) XRD patterns of TiO₂-180°C before and after photocatalytic reaction.

Fig. 14. Effect of quencher on the degradation of MB under visible-light irradiation.

face of TiO_2 -180°C, reacting with H_2O , $-\text{OH}$, and adsorbed O_2 on the surface to form $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, which are strong oxidizers and tend to react with MB molecules to form CO_2 and H_2O .

The reasons for the enhancement of the photocatalytic activity of TiO_2 -180°C nanoparticles can be summarized as follows. First, the high surface area and microporous structure of the TiO_2 -180°C nanoparticles contribute to the contact and collision between MB molecules and the catalyst. Next, the high concentration of Vo in the TiO_2 -180°C crystal lattice enhance its visible-light absorption, thereby promoting the generation of electron-hole pairs, resulting in high efficiency of the degradation reaction and photocatalytic activity. Finally, quenching experiments confirmed that $\cdot\text{OH}$ was the key factor in the photocatalytic degradation process. Because abundant adsorbed

H_2O and $-\text{OH}$ covered the surface of the TiO_2 -180°C molecules, containing more adsorbed H_2O and $-\text{OH}$ is favorable for the formation of the active species of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ in the photocatalytic reaction, thereby improving the photocatalytic activity. These unique physical and chemical properties led to the enhancement of the photocatalytic activity of the TiO_2 -180°C nanoparticles for MB degradation.

4. Conclusions

A facile modified sol-gel method was developed for the synthesis of TiO_2 nanoparticles at low temperature. The physico-chemical properties of the TiO_2 nanoparticles prepared at different temperatures were characterized, and their photocatalytic performances were assessed. The TiO_2 -180°C nanoparticles had a small particle size of 5.0 nm and large specific surface area of $213.45 \text{ m}^2/\text{g}$ and exhibited efficient absorption over the entire UV-vis range. Moreover, these nanoparticles exhibited excellent photodegradation activity under visible-light irradiation, resulting in the highest degradation rate of 99.33% and highest reaction rate constant of $0.08287 \text{ mg}/(\text{L}\cdot\text{min})$ at the optimized initial pH of 4 and catalyst loading of 0.07 g. This excellent performance may be attributed to the combined contribution of the small particle size, large surface area, enhanced optical properties associated with the high Vo concentration, and enriched surface $-\text{OH}/\text{H}_2\text{O}$. This work provides an alternative approach for the preparation of TiO_2 photocatalysts with controllable morphological structure and visible absorption intensity. The as-prepared TiO_2 nanoparticles should be promising candidates for applications in solar cells, water splitting, and other light-harvesting systems after further modification.

Fig. 15. Mechanism for the photodegradation of MB by TiO_2 .

Graphical Abstract

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Strong visible absorption and excellent photocatalytic performance of brown TiO₂ nanoparticles synthesized using one-step low-temperature process

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Brown TiO₂ nanoparticles synthesized using a modified sol-gel approach at 180 °C exhibited small particle size, large surface area, enhanced visible-light response, and enriched surface -OH/H₂O, leading to the enhancement of their photocatalytic activity.

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一步低温法制备可见光响应的棕色纳米TiO₂及其光催化性能

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摘要: 光催化作为一种具有前景的技术, 被广泛运用于有机物降解、废水处理、空气净化、抗菌、太阳能电池等领域。在众多的光催化材料中, 纳米TiO₂因具有性质稳定、耐腐蚀、廉价和无毒等优点而受到广泛关注。但纳米TiO₂禁带宽度较大(3.2 eV)、只对紫外光有响应及电子-空穴对易复合等特性限制了它的应用。因此, 提高纳米TiO₂的可见光响应一直是研究的热点。本文发展了一种在低温下制备棕色纳米TiO₂的改良溶胶-凝胶法。该法以钛酸四丁酯为钛源, 无水乙醇为溶剂, 形成溶胶后无需陈化和高温高压, 在简单温和的条件下即可制备出棕色纳米TiO₂。比较了低温干燥和高温焙烧两种处理方法, 结果表明, 随着制备温度的升高, 样品的粒子尺寸增大, 比表面积减小, 颜色从白色转变为棕色, 在更高的温度又变浅。样品的可见光吸收在180 °C时达到最大, 随后减弱。在优化温度180 °C下制备的TiO₂-180 °C纳米粒子不仅具有较小的粒径(5.0 nm), 较大的比表面积(213.45 m²/g), 且在整个紫外-可见光区都具有较强的吸收, 其禁带宽度低至1.84 eV。X-射线光电子能谱结果表明, TiO₂粒子表面的-OH/H₂O含量随制备温度升高而先增加后下降。Raman光谱中E_g峰的移动和变宽表明TiO₂晶格可能存在缺陷或氧空位, 而TiO₂-180 °C纳米粒子的电子顺磁共振图谱的g值在2.003左右, 对应氧空位中的未成对电子, 验证了以上推测。其中TiO₂-180 °C纳米粒子呈现为最强的EPR信号, 表明其晶格内存在最高浓度的氧空位, 这是其具有强可见光吸收的原因。光催化实验结果表明, 在可见光照射下, TiO₂-180 °C可高效降解亚甲基蓝(MB)。当C_(MB) = 10 mg/L, pH = 4, 催化剂添加量为0.07 g时, TiO₂-180 °C催化剂的光催化活性达到最佳, 光照1 h后MB降解率达到99.33%, 反应速率常数(0.08287 mg/(L·min))约为同条件下P25(0.01342 mg/(L·min))的6倍。同时, TiO₂-180 °C催化剂在不同单色光下的光催化活性与它对单色光的光响应大致相符。循环降解实验证明TiO₂-180 °C催化剂具有很好的稳定性。光猝灭实验表明, ·OH在光催化降解过程占主导作用, 而TiO₂-180 °C样品表面含有较多的-OH, 有利于·OH的产生, 乃至光催化反应。研究表明, 晶格内高浓度的氧空位导致的强可见光响应, 得益于低温制备条件而保留了大量-OH/H₂O的纳米粒子表面以及更大的比表面积, 共同促成了TiO₂-180 °C优越的光催化活性。所制备的棕色纳米TiO₂经过进一步修饰后有望运用于实际应用中。

关键词: 二氧化钛; 可见光; 宽谱带吸收; 氧空位; 光催化降解

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