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Electrospun TiO_2 Microspheres with Enhanced Activity for Photocatalytic Degradation of Methylene Blue

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TiO_2 microspheres were synthesized by electrospinning technique. The morphology, structure and photocatalytic performance in the degradation of methylene blue under UV light irradiation were characterized by scanning electron microscopy, X-ray diffraction spectroscopy and UV-visible absorption spectrophotometer. The results show that TiO_2 microspheres have a high anatase phase content and their surface is assembled by large quantities of TiO_2 nanoparticles, resulting in a porous structure. These TiO_2 microspheres exhibit an excellent photocatalytic performance with a maximum degradation rate of 95.6 %, much higher than that for TiO_2 rods (77.9 %) synthesized by electrospinning technique.

Key Words: TiO_2, Electrospinning, Photocatalysis, Microsphere.

INTRODUCTION

Nowadays, TiO_2 has attracted tremendous attention as a promising photocatalyst for widespread environmental applications owing to its intriguing optical and electric properties[1-11]. The photocatalytic performance of TiO_2 is strongly affected by its crystal structure and morphology, which are determined by synthetic methods[12,13]. So far, numerous synthetic strategies such as sol-gel, hydrothermal, solvothermal, electrochemical anodization, electrodeposition and template assisted routes have been employed for the formation of TiO_2 in the form of particles, tubes, fibers, wires, belts, rods, hollow spheres, microsphere, *etc.*[14-28]. Among various TiO_2 structures, TiO_2 microspheres with TiO_2 nanoparticles assembled on the surface is a novel structure which show excellent photoactivity due to their large surface area and highly crystallized porous wall. Many studies on TiO_2 microspheres have been reported recently. Naldoni *et al.*[29] synthesized highly-crystalline porous TiO_2 microspheres using ultrasonic spray pyrolysis in the presence of colloidal silica as a template and investigated their activity in the degradation of nitrogen oxides (NO_x) in the gas phase. Liu *et al.*[30] fabricated hollow mesoporous TiO_2 microspheres by a sol-gel process, these microspheres exhibit excellent photocatalytic performance in the decomposition of methylene orange with a 90 % degradation rate in 100 min under UV light irradiation. Dwivedi *et al.*[31] reported mesoporous TiO_2 microspheres synthesized by the sol-gel templating method for the degradation of methylene blue and about 70 % of methylene blue (MB) was decomposed in 120 min under UV light irradiation.

The electrospinning technique is a well-established, simple, versatile, cost-effective and scalable means to produce different structured materials. Since its first patent describing the basic operation principle in 1934, this method was employed widely to fabricate various advanced materials including TiO_2[32-36]. Recently, many studies have been reported to fabricate different TiO_2 nanostructures by electrospinning method for photocatalytic application, such as multichannel hollow fibers[37], mesoporous fibers[38], rice grain-shaped TiO_2[39], nanowires[40], nanotubes[41-43] and network[44]. However, as promising photocatalyst, porous TiO_2 microspheres with excellent photocatalytic activity fabricated by electrospinning method has seldom been reported up to now.

In this study, we fabricated TiO_2 microspheres with nanoparticles assembled on the surface using electrospinning technique and investigated their photocatalytic performance in the degradation of methylene blue. These TiO_2 microspheres exhibit excellent photocatalytic performance with a maximum methylene blue degradation rate of 95.6 % under UV light irradiation.

EXPERIMENTAL

Fabrication: The precursor solution was composed of 1 g PVP, 4.7 g titanium(IV) butoxide, a certain amount of urea (0 g and 0.237 g, respectively) and 4 mL glacial acetic acid (Sinopharm Chemical Reagents Co. Ltd.) in 16 mL ethanol. After vigorous stirring at room temperature for 10 h, the solution was then loaded into a syringe connected to a 22 gauge stainless steel needle. The applied voltage was 20 kV and the distance from the tip of the needle to copper collector was 10 cm. The flow rate of solution was 1 mL h^{-1}. The electrospinning was carried out in enclosed plexiglass at room temperature at about 40 % relative humidity. Then the samples were exposed to atmospheric moisture in ambient condition for 1 h. The products were sintered at 500 ºC in an air atmosphere for 0.5 h. The TiO_2 samples fabricated using precursor solution without urea and with urea were named as TiO_2-1 and TiO_2-2, respectively.

Characterization: The surface morphology, structure and composition of the samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), X-ray diffraction spectroscopy (XRD, Holland Panalytical PRO PW3040/60) with Cu-K_α radiation (V = 30 kV, I = 25 mA) and energy dispersive X-ray spectroscopy (EDS, JEM-2100), respectively. The UV-visible absorption spectra were recorded using a Hitachi U-3900 UV-visible spectrophotometer.

Photocatalytic experiments: The samples (2 g L^{-1}) were dispersed in 80 mL methylene blue aqueous solutions (5 mg L^{-1}). The mixed suspensions were first magnetically stirred in the dark for 0.5 h to reach the adsorption-desorption equilibrium. Under ambient conditions and stirring, the mixed suspensions were exposed to UV light irradiation produced by an 8 W UV lamp (λ_{max} = 254 nm). At certain time intervals, 2.5 mL of the mixed suspensions were extracted and all the aliquots withdrawn from the solutions were centrifuged to remove the photocatalyst. The filtrates were analyzed by recording UV-visible spectra of methylene blue using a Hitachi U-3900 UV-visible spectrophotometer.

The photocatalytic reaction kinetics was studied using Langmuir-Hinshelwood model. The pseudo-first-order equation is employed to fit the experimental data and can be formulated as[45]:

$$\ln(C_i / C_0) = -kt$$

where t and k are the photocatalysis time (min) and the reaction rate constant (min^{-1}), respectively. C_0 and C_i are the initial concentration and the concentration of methylene blue at time t (mg L^{-1}), respectively.

RESULTS AND DISCUSSION

Fig. 1(a) and (b) show the FESEM images of TiO_2-1 and TiO_2-2. It is obvious that the morphology of TiO_2-2 is different from that of TiO_2-1. TiO_2-1 consists of short rods and TiO_2-2 displays porous microsphere structure. Fig. 1(c) is the high-magnification FESEM image of TiO_2-2. It can be clearly observed that highly rough surface of microspheres is assembled by large quantities of nanosized TiO_2 particles, resulting in a porous structure. Such a structure can facilitate the adsorption of more pollutants and thus improves the photocatalytic performance[46]. The existence of TiO_2 in the both samples has been proved by the peaks of Ti and O in EDS data shown in Fig. 1(d) and the peak of N is not found. It indicates that the introduction of urea in the precursor solution does not alter the composition of TiO_2 but changes its structure.

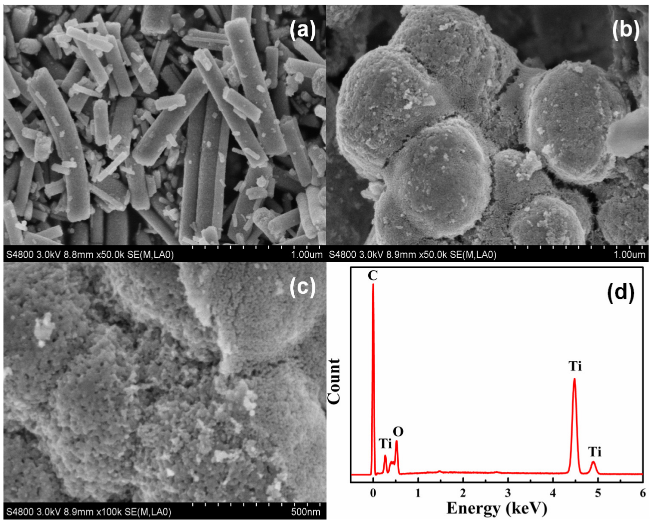

Fig. 1. Surface morphologies of (a) TiO_2-1, (b) and (c) TiO_2-2 by FESEM; (d) EDS spectrum of TiO_2-2 (TiO_2-1 has a similar EDS spectrum)

The XRD patterns of TiO_2-1 and TiO_2-2 are shown in Fig. 2. It can be observed that both samples exhibit several diffraction peaks at 25.3º, 37.8º, 48.0º, 53.9º, 55.1º, 62.7º, 68.8º, 70.3º and 75.0º, which are indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes of anatase TiO_2 (JCPDS#21-1272), respectively. Three additional peaks at 27.4º, 36.1º and 41.2º are assigned to (110), (101) and (111) crystal planes of rutile TiO_2 (JCPDS#77-0441), respectively. No typical diffraction peaks of nitrogen species are observed in the XRD pattern. Furthermore, it should be noticed that the diffraction peaks of rutile phase in TiO_2-2 are weaker than those in TiO_2-1 relative to anatase phase. Using the well-known formula, the anatase phase content in crystalline TiO_2 powder is calculated[47]:

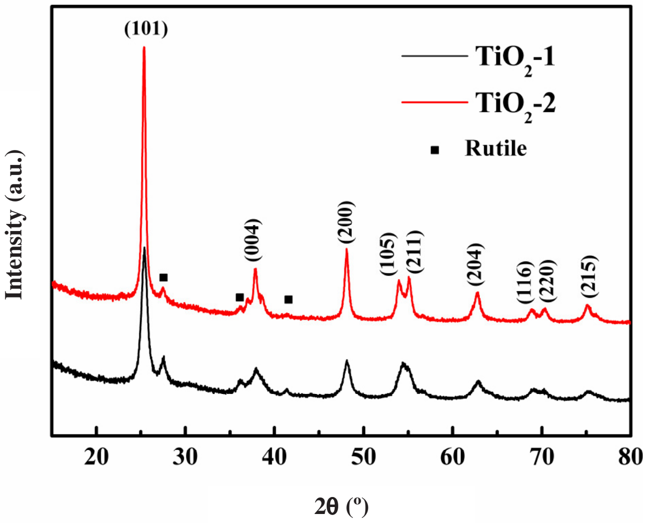

Fig. 2. XRD patterns of TiO_2-1 and TiO_2-2

$$X_A = \left(1 + 1.265\frac{I_R}{I_A}\right)^{-1}$$

where X_A is the mass fraction of anatase in the TiO_2 powders and I_A and I_R are the integrated intensities of the (101) reflection of anatase and the (110) reflection of rutile, respectively. The calculation results are given in Table-1. It can be seen that the anatase phase content in TiO_2-2 is higher than that in TiO_2-1. It is well known that crystalline phase of TiO_2 has an important influence on its photocatalytic activity. It has been reported that anatase phase is more effective than rutile phase in the photocatalytic decomposition of organic compounds and the improvement of anatase phase content can enhance the photocatalytic performance[48-53]. Therefore, the as-spun TiO_2-2 should show better photocatalytic performance than TiO_2-1.

TABLE-1
PHASE CONTENT IN AS-SPUN TiO_2 POWDER

Material	Anatase phase (%)	Rutile phase (%)
TiO_2-1	71.9	28.1
TiO_2-2	90.0	10.0

The UV-visible absorbance of methylene blue with the time variation during 0.5 h adsorption-desorption equilibrium and subsequent photocatalytic process is shown in Fig. 3. As observed from Fig. 3a and c, the rapid decrease of the methylene blue absorbance indicates the good adsorption of methylene blue by both TiO_2-1 and TiO_2-2 and the equilibrium arrives in 0.5 h. Furthermore, it can be obviously found that TiO_2-2 shows better adsorption of methylene blue compared with TiO_2-1. When TiO_2-1 and TiO_2-2 photocatalysts are used, the UV-visible absorption peak of methylene blue, related to the methylene blue concentration in the solution, becomes weak and shifts to short wavelength gradually with the increase of the time under UV light irradiation, as shown in Fig. 3b and d. The peak shift should be due to the demethyleneation occurring at the catalyst surface[54].

Fig. 4 shows the photocatalytic degradation rate of methylene blue with the time variation by TiO_2-1 and TiO_2-2. The normalized temporal concentration changes (C/C_0) of methylene blue during the photocatalytic process are proportional to the normalized maximum absorbance (A/A_0). It can be observed that TiO_2-2 exhibits higher photocatalytic degradation rate (95.6 %) than TiO_2-1 (77.9%) in 4 h. The enhancement of the photocatalytic performance should be ascribed to the increase of anatase phase content and the adsorption of pollutants in TiO_2-2[48-53,55-59]. Fig. 5 displays the linear fitting using the pseudo-first-order kinetic equation to the experimental data for TiO_2-1 and TiO_2-2. The values of k can be obtained directly from the fitted straight-line plots of ln (C_i/C_0) *versus*

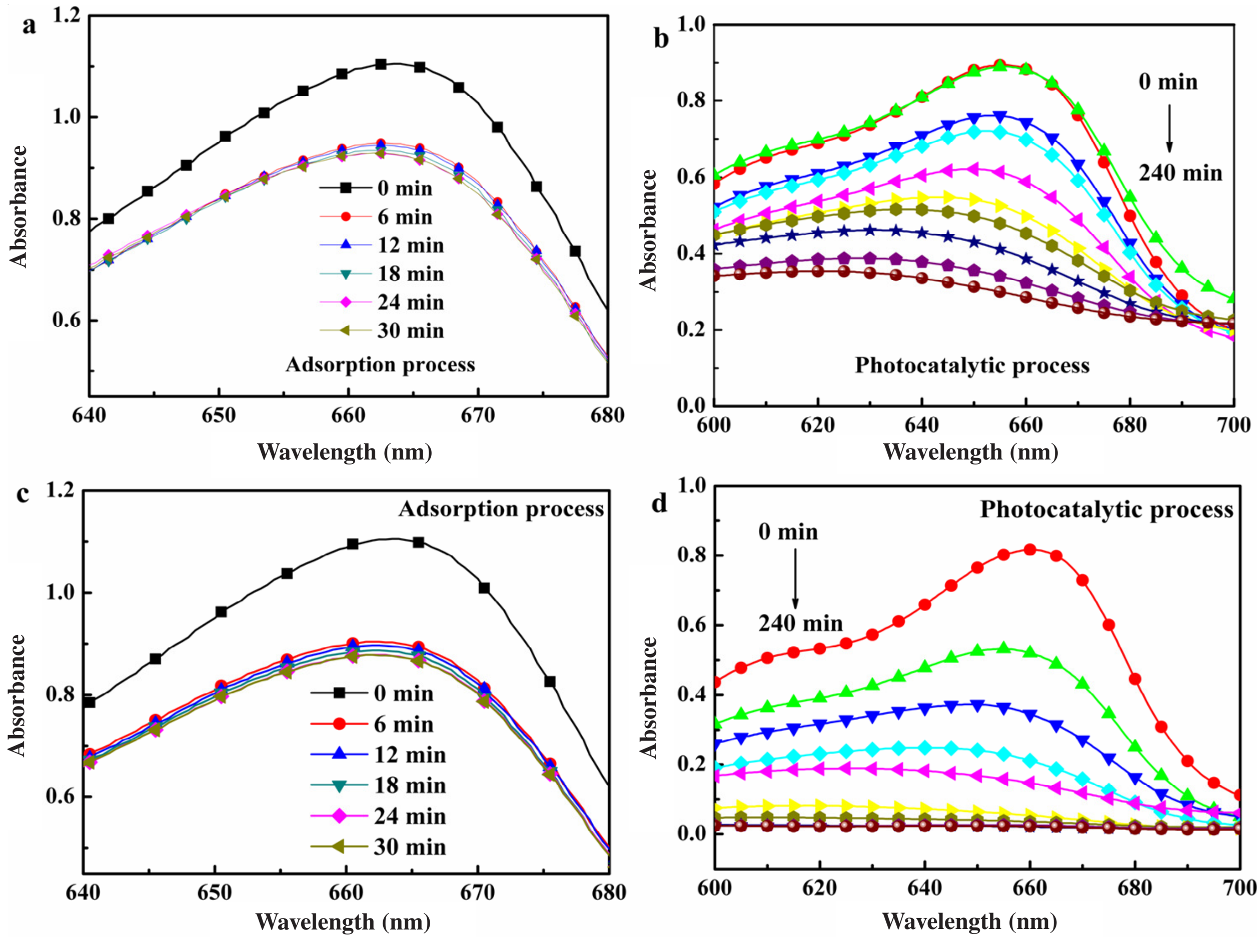

Fig. 3. UV-visible absorbance of methylene blue with the time variation during 0.5 h adsorption-desorption equilibrium and subsequent photocatalytic process: (a) and (b) TiO_2-1, (c) and (d) TiO_2-2

reaction time and follow the order: TiO_2-2 (0.01772 min^{-1}) > TiO_2-1 (0.00503 min^{-1}). TiO_2-2 exhibits better photocatalytic activity with a rate constant much high than that of TiO_2-1 under UV irradiation.

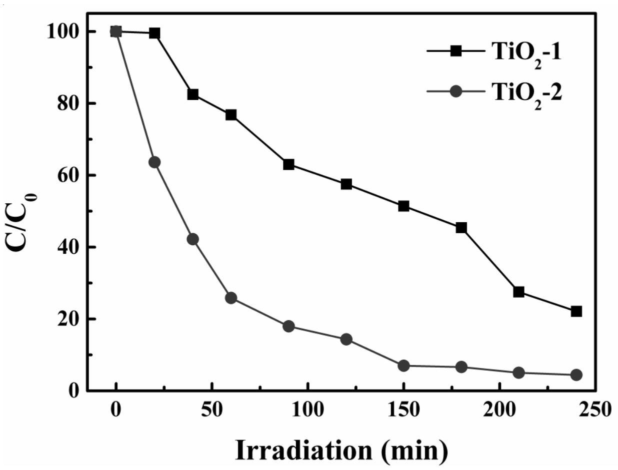

Fig. 4. Photocatalytic degradation of methylene blue by TiO_2-1 and TiO_2-2 under UV irradiation. The concentrations of methylene blue and the photocatalyst are 5 mg L^{-1} and 2 g L^{-1}, respectively

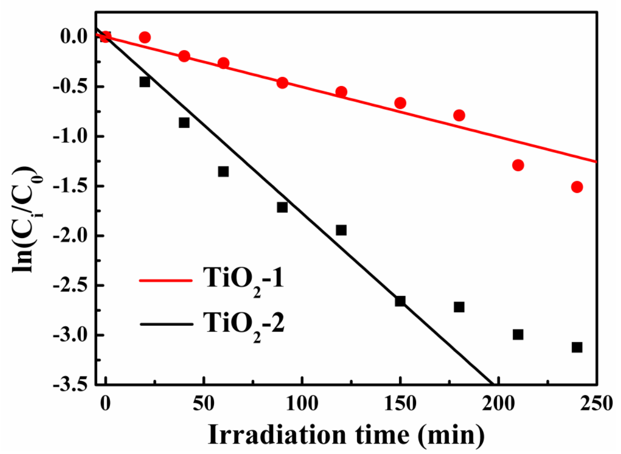

Fig. 5. Photocatalytic reaction kinetics of methylene blue with reaction time

Conclusion

TiO_2 nanostructures were successfully synthesized *via* electrospinning technique and their photocatalytic performance in the degradation of methylene blue was investigated. The experimental results indicate that

(i) The introduction of urea in the precursor solution does not alter the composition of as-prepared TiO_2 but changes the structure from rods to microspheres and increases the anatase phase content.

(ii) The surface of TiO_2 microspheres is assembled by large quantities of TiO_2 nanoparticles, resulting in a porous structure. Such a structure facilitates the adsorption of more pollutants.

(iii) The TiO_2 microspheres exhibit an excellent photocatalytic performance with a maximum degradation rate of 95.6 %, much higher than that for TiO_2 rods (77.9 %); (iv) Electrospun TiO_2 microspheres should be a promising photocatalyst for treating dye wastewater.

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