

Hydrothermal Synthesis of Flower-like Hierarchical TiO₂ Microspheres from Titanium Sulfate and Hexafluorosilicic Acid

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Abstract: Flower-like hierarchical TiO₂ microspheres assembled by nanosheets with exposed {001} facets were prepared through a cost-effective hydrothermal synthesis method, using cheap Ti(SO₄)₂ as the feedstock and hexafluorosilicic acid as the capping agent. These hierarchical microspheres were assembled by numerous and cross-linked nanosheets. The fine structure of hierarchical microspheres could be easily controlled by adjusting the concentration of hexafluorosilicic ions. The growth process of the microspheres was examined through XRD and SEM characterizations, and a possible formation mechanism was proposed. Compared with other solvothermal synthesis methods, this cost-effective hydrothermal synthesis route is attractive and can be potentially applied in the production of flower-like TiO₂ hierarchical microspheres in large scale. The as-prepared flower-like TiO₂ hierarchical microspheres exhibit good photocatalytic ability to degrade methyl orange dye.

Key words: flower-like; hydrothermal synthesis; crystal growth; hierarchical structure

Inorganic materials with hierarchical nanostructures based on nano-units have attracted great attention because of their distinctive properties^[1-4]. Among them TiO₂ is one of the most studied materials owing to its nontoxicity, structural stability and broad applications in photocatalysis, photovoltaic cells, photonic crystals and sensors^[5]. Recently, hierarchically structured TiO₂ materials (assembled by nanotubes, nanorods, nanosheets, and nanothorns) are of great interest because of its improved property^[6-8]. However, flower-like TiO₂ hierarchical microspheres (1–3 μm) assembled by TiO₂ nanosheets (thickness of 7–20 nm) with exposed {001} facets are mainly prepared by a solvothermal route at 180°C for 8–20 h, and expensive organic solvents (diethylene glycol or isobutyl alcohol/isopropyl alcohol) and Ti sources (TiF₄ or titanium butoxide) are often used^[9-11]. In this paper, we reported a cost-effective hydrothermal synthesis of flower-like TiO₂ hierarchical microspheres using cheap Ti(SO₄)₂ as the feedstock and hexafluorosilicic acid as the capping agent. The hierarchical structure can be conveniently adjusted by controlling the concentration of hexafluorosilicic ions. In addition, the growth process of these microspheres was examined and a possible formation mechanism was proposed.

1 Experimental

The flower-like TiO₂ microspheres were hydrothermally synthesized from the precursor hydrogel in Teflon-lined stainless steel autoclaves at 180°C for 24 h. In a typical synthesis, the precursor hydrogel was prepared by dissolving 4.8 g of titanium sulfate (96%, Sinopharm Chemical Reagent Co., Ltd.) in 5.4 mL distilled water, followed by adding 5 mL of hexafluorosilicic acid (30%–32%, Sinopharm Chemical Reagent Co., Ltd.) under magnetic stirring. The molar composition of the final hydrogel was 1Ti⁴⁺: 4.5F⁻: 15H₂O. After the hydrothermal crystallization, the solid product was collected by filtration, followed by washing and drying at 100°C overnight.

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance powder diffractometer using a Ni-filtered Cu Kα radiation source at 40 kV and 20 mA. The morphology of samples was observed on a field emission scanning electron microscope (FESEM, HITACHI S-4800). The high-resolution transmission electron microscope (HRTEM) observation was performed on a JEOL JEM-2010UHR instrument at an acceleration voltage of 200 kV. The nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 instrument at the liquid nitrogen temperature. The pore size distribution was

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calculated using the BJH model from desorption data.

The photocatalytic decomposition of mixed methyl orange (MO) dyes was conducted in aqueous solution containing the selected titania sample under UV-light irradiation at ambient temperature. Briefly, 10 mg of the sample was dispersed in 10 mL of mixed MO (10 mg/L) aqueous solution in a 50 mL quartz tube. A 150 W 365 nm UV lamp (Shanghai Bilon Instrument Co. LTD; 5 cm around the tube) was used as a light source. The concentration of MO was monitored by a UV-2550 UV-visible spectrophotometer (Shimadzu, Japan). UV-Vis diffuse reflectance spectra (DRS) were determined by a UV-Vis spectrophotometer (Shimadzu UV-2550).

2 Results and Discussion

Figure 1(a) shows the XRD pattern of the resulting flower-like TiO_2 hierarchical microspheres from the synthesis hydrogel with a composition of $1\text{Ti}^{4+}:4.5\text{F}^-:15\text{H}_2\text{O}$. The diffraction peaks at 2θ of 25.3° , 37.8° , and 48.5° can be obviously observed, corresponding to (101), (004) and (200) planes of the anatase TiO_2 phase (JCPDS 21-1272). The diffraction peak of the (200) plane is significantly more intense than that of the (004) plane, indicating a domain crystalline growth along the a axis^[9]. As shown in Fig. 1(b), these hierarchical microspheres also exhibit the uniform morphology, and the particle size ranges from 2.2 μm to 3.7 μm (average diameter of 2.8 μm). Close

observation (shown in Fig. 1(c)) presents that the microspheres are assembled by numerous cross-linked nanosheets with a thickness of ~ 50 nm. From a broken microsphere we can easily see that the nanosheets are inserted inward to the center and regularly packed together, forming a symmetrical spherical structure (Fig. 1(d)). This hierarchical structure assembled by nanosheets was also evidenced through the TEM observation (Fig. 1(e)). A representative higher-resolution TEM image of a single nanosheet (Fig. 1(f)) shows two sets of the lattices with an equal fringe spacing of 0.19 nm and an interfacial angle of 90° , which are in well agreement with the (200) and (020) planes of anatase TiO_2 ^[12]. The corresponding fast Fourier transform (FFT) pattern (the inset in Fig. 1(f)) can be indexed to diffraction spots of the [001] zone^[13]. Thus, the percentage of exposed {001} facets ($EF(\%)$) of the TiO_2 nanosheets shown in Fig. 1(e) is estimated to be 90% according to eqt. (1)^[14]. Above characterization results indicate that flower-like TiO_2 hierarchical nanostructures constructed by TiO_2 nanosheets with highly exposed {001} facets can be synthesized using cheap $\text{Ti}(\text{SO}_4)_2$.

$$EF(\%) = \frac{a^2}{\frac{(b^2 - a^2)}{\cos \theta} + a^2} \times 100\% \quad (1)$$

Where, a is the side length of {001} facet, b is the bottom edge of {101} facet and θ is the value for the angle between the {101} and {001} facets.

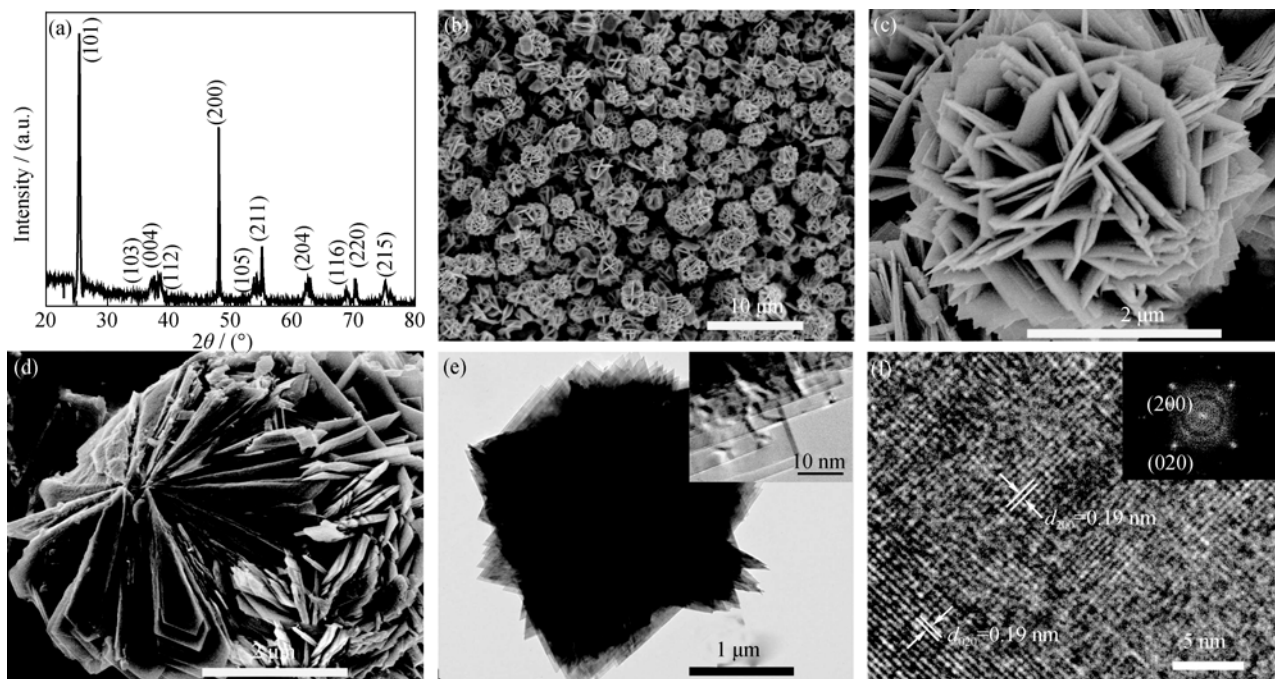


Fig. 1 XRD pattern (a), FESEM images with low (b) and high (c) magnifications, FESEM image (d) of a broken sample, low-magnification (e) and high-resolution (f) TEM image of the flower-like TiO_2 microspheres. The insets in (e) and (f) show the TEM image of the nanosheet at high magnification and FFT pattern, respectively.

We also found that the concentration of hexafluorosilicic acid in the precursor hydrogel plays crucial role in controlling the fine structure of resultant TiO₂ hierarchical microspheres. When the molar ratio of F⁻/Ti⁴⁺ ranged from 0.3–3, the resulting microspheres exhibit the wool-woven ball-like structures assembled by densely packed nanosheets (Fig. 2(a)–(c)). In addition, both the thickness of the nanosheets and the diameter of the whole microspheres slightly increase with the concentration of F⁻. While the microspheres present the flower-like structure assembled by nanosheets as the molar ratio of F⁻/Ti⁴⁺ increases to 6, and the diameter of the microspheres increases to ~6 μm (Fig. 2(d)). Irregular-shaped microspheres with aggregated nanosheets are prepared when the molar ratio of F⁻/Ti⁴⁺ was further increased to 9 (Fig. 2(e)). On the contrary, microspheres with smooth surface are obtained without the addition of hexafluorosilicic acid (Fig. 2(f)).

Comparison experiments through substitution of hexafluorosilicic acid by other fluorides were further conducted at Ti⁴⁺: F⁻: H₂O molar ratio of 1: 0.75: 15, in order to explore the effect of F⁻ source on the morphology of final microspheres. Only distributed regular-shaped TiO₂ crystals are prepared by hydrofluoric acid and potassium fluoride, but flower-like TiO₂ hierarchical microspheres assembled by nanosheets can be prepared by ammonium fluorosilicate (data not shown). These results indicate that SiF₆²⁻ plays a critical role in the formation of the flower-like TiO₂ hierarchical structure.

In order to explore the growth mechanism of the flower-

like hierarchical structures TiO₂ microspheres, time- dependent experiments with molar composition of 1Ti⁴⁺: 4.5F⁻: 15H₂O were carried out. We found that the sample only exhibits weak XRD diffraction peak at 25.3° and 48.5°, corresponding to the (101) and (200) planes (Fig. 3(a)), as the crystallization time was 2 h. It means that only small amount of crystalline phase is formed in the products. This is further evidenced by the FESEM image that amorphous materials are mainly existed in the products (Fig. 4(a)). When the crystallization time is prolonged to 3 h, the relative diffraction intensities of XRD peaks at 25.3° and 48.5° become much stronger (Fig. 3(b)). The corresponding FESEM image (Fig. 4(b)) shows formation of spherical structure constructed by less than 10 sheets with thickness of 50 nm, with accumulation of some nanoparticles between the nanosheets. XRD patterns shows that the products crystallized for 4–5 h have already owned the well anatase TiO₂ structure (Fig. 3(c) and (d)). All these microspheres show the flower-like morphology (Fig. 4(c) and (d)), but exhibit obvious defects and untransformed particles, indicating the kinetic process for the formation of flower-like TiO₂ hierarchical microspheres are not finished. When the crystallization time is further prolonged to 12 h, the diffraction intensity of the (200) plane becomes stronger (Fig. 3(e)) and flower-like and cross-linked TiO₂ hierarchical microspheres are formed (Fig. 4(e)). The above formation process is quite similar to that of the flower-like Fe₃O₄ microspheres^[15], and thus the growth mechanism can be also considered as three steps: fast nucleation of primary nanoparticles, oriented attachment and coarsening, and finally Ostwald ripening.

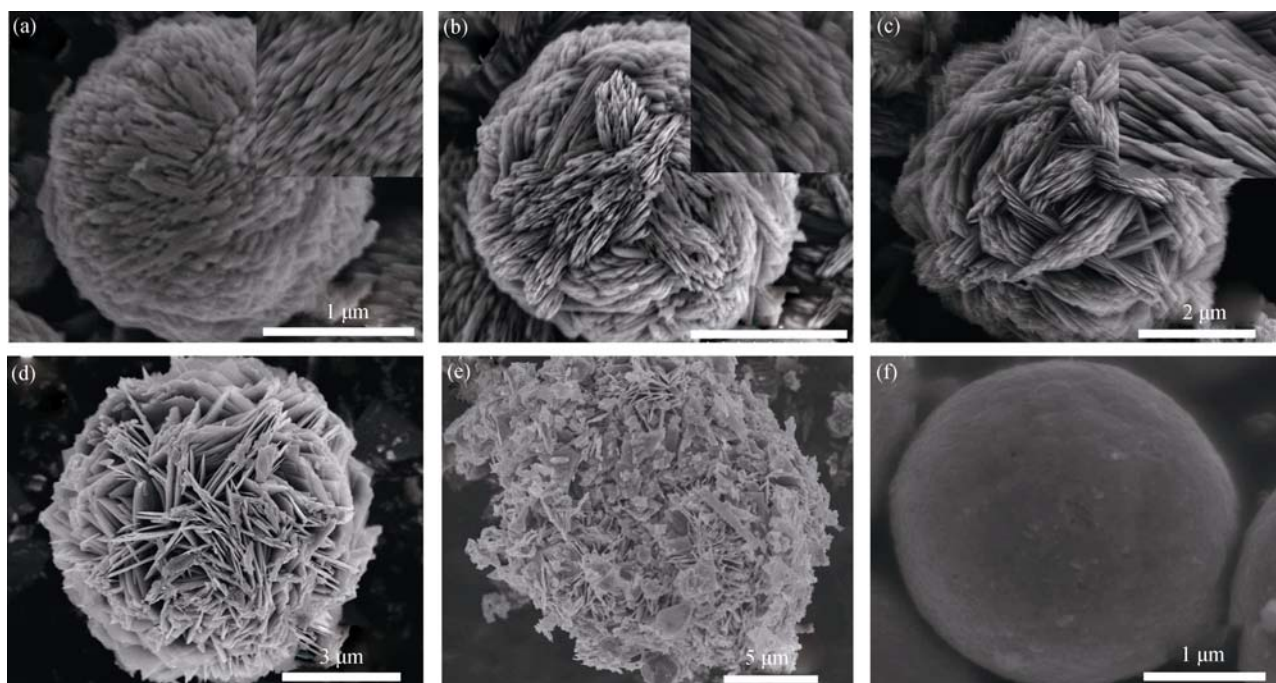


Fig. 2 FESEM images of the samples prepared with precursor hydrogel of different $n(\text{Ti}^{4+}): n(\text{F}^-): n(\text{H}_2\text{O})$

(a) 1: 0.3: 15; (b) 1: 1.5: 15; (c) 1: 3: 15; (d) 1: 6: 15; (e) 1: 9: 15; (f) 1: 0: 15

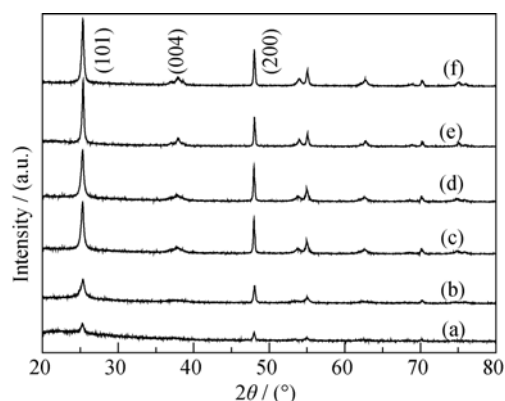


Fig. 3 XRD pattern of the samples prepared with a molar composition of $1\text{Ti}^{4+}: 4.5\text{F}^{-}: 15\text{H}_2\text{O}$ at 180°C for different time (a) 2 h; (b) 3 h; (c) 4 h; (d) 5 h; (e) 12 h

Figure 5(a) presents the nitrogen adsorption-desorption isotherm and BJH pore size distribution curve (inset) of the hierarchical flower-like TiO₂. The isotherm shows a type IV isotherm a long range hysteresis loop at P/P_0 with values from 0.5 to 1.0. This indicates that the TiO₂ possesses a high proportion of mesopores, which are distributed mainly in 2–4 nm as well as in 20–50 nm. The BET surface area is $5.3\text{ m}^2/\text{g}$. The optical property of the hierarchical flower-like TiO₂ is investigated by UV-Vis diffuse reflectance spectrum (Fig. 5(b)), which shows higher UV light absorption than those of other TiO₂ flower-like microspheres^[8]. Obviously, the UV-Vis absorption would be affected considerably by the morphological changes of the TiO₂, and the hierarchical flower-like TiO₂ can allow multi-

ple reflections of UV light, which enhances light-harvesting and thus increases the quantity of photogenerated electrons and holes available to participate in the photocatalytic decomposition process.

UV-Vis spectra of MO aqueous solution in the presence of hierarchical flower-like TiO₂ under UV light irradiation illustrated in Fig. 6(a) show high photocatalytic efficiency for the degradation of MO in aqueous solution. More than 94% of MO was degraded within 120 min. The fitting of absorbance maximum plot versus time over the hierarchical flower-like TiO₂ shown in Fig. 6(b) indicates an exponential decay. The photodegradation of MO dye catalyzed by the hierarchical flower-like TiO₂ fits pseudo first-order reaction, *i.e.*, $\ln(C_0/C)=kt$, where C_0 and C are the initial and actual concentration of MO dye, respectively, and k is the apparent rate constant of the degradation. In our experiment, k is found to be 0.023. The results suggest the as-prepared hierarchical flower-like TiO₂ show good catalytic activity for the degradation of MO dye.

3 Conclusion

In summary, flower-like TiO₂ hierarchical microspheres assembled by nanosheets with exposed {001} facets were successfully synthesized in the $\text{Ti}(\text{SO}_4)_2\text{-H}_2\text{SiF}_6\text{-H}_2\text{O}$ hydrothermal system. The fine structure of the flower-like TiO₂ microspheres can be easily controlled by adjusting the concentration of SiF_6^{2-} , which is critical in determining the flower-like structure. Classic nucleation and Ostwald

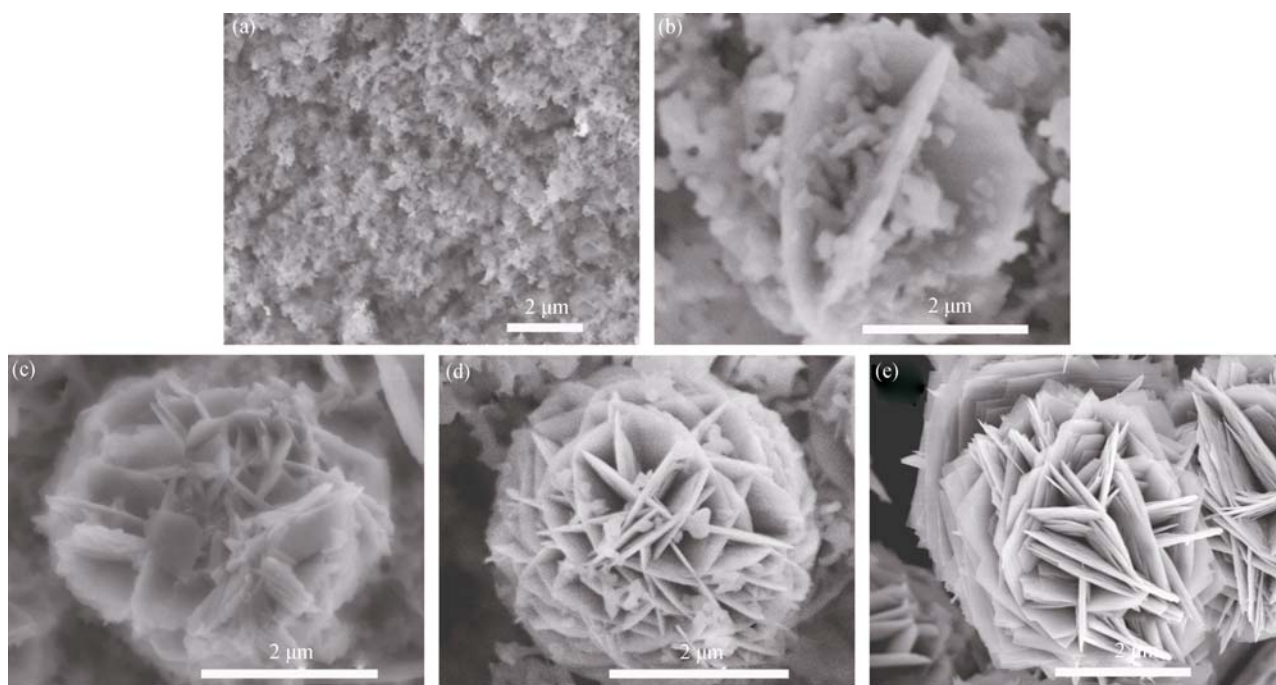


Fig. 4 FESEM images of the samples prepared with a molar composition of $1\text{Ti}^{4+}: 4.5\text{F}^{-}: 15\text{H}_2\text{O}$ at 180°C for different time (a) 2 h; (b) 3 h; (c) 4 h; (d) 5 h; (e) 12 h

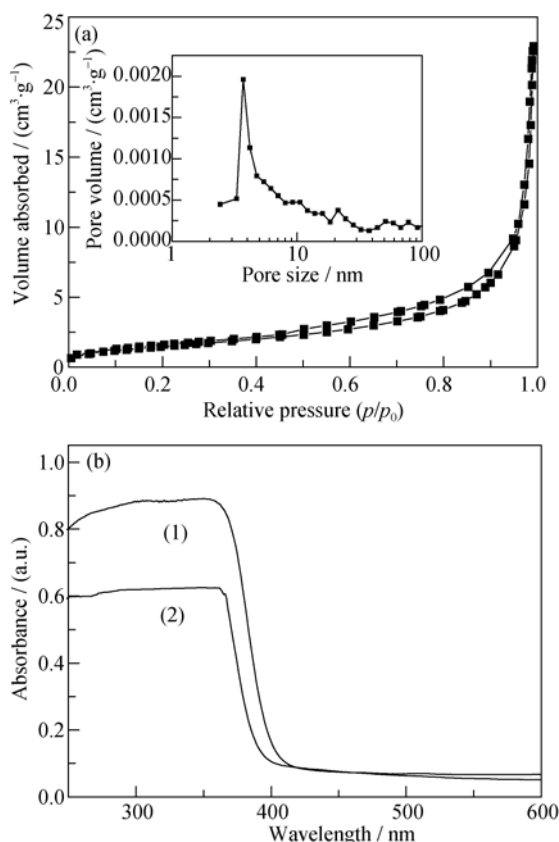


Fig. 5 N₂ adsorption-desorption isotherm and pore size distribution curve (a) and UV-visible absorption spectra (b) of hierarchical flower-like TiO₂

(1) As-prepared; (2) From the literature^[8]

ripening growth mechanism were also identified through the time-dependent experiments. The TiO₂ hierarchical microspheres can be used for photocatalytic degradation of MO in aqueous solution, with more than 94% of MO degraded within 120 min. This cost-effective synthesis route makes this novel method attractive in preparing TiO₂ hierarchical nano-structures in large scale.

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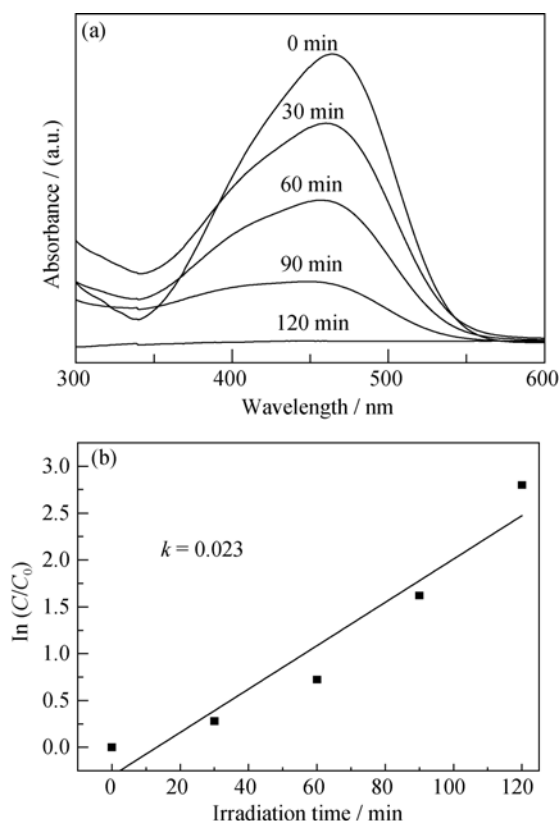


Fig. 6 UV-Vis spectra of MO aqueous solution in the presence of hierarchical flower-like TiO₂ under UV light irradiation (a) and the fitting of absorbance maximum plot vs time over the hierarchical flower-like TiO₂ (b)

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以硫酸钛和氟硅酸水热法制备花状多级 TiO_2 微球

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摘 要: 以廉价的硫酸钛为原料和氟硅酸为结构控制剂, 用成本低效益好的水热法制备暴露 {001} 面纳米片组装的花状多级 TiO_2 微球。这些多级微球是由许多交联的纳米片组装。通过调变氟硅酸根离子的浓度可以容易地控制多级微球的精细结构。通过 XRD 和 SEM 表征来检测微球的生长过程, 并提出了可能的形成机理。与其他溶解热合成法相比, 这种成本低效益好的水热合成法有望应用于大批量生产花状多级 TiO_2 微球。这种精制的花状多级 TiO_2 微球展现了很好的光催化降解甲基橙的能力。

关 键 词: 花状; 水热合成; 晶体生长; 多级结构

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