

## The Cactus-like Organic-grafted Silica Balls as the Supporter of TiO<sub>2</sub> Photocatalyst

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Cactus-like organic-grafted silica balls synthesized by *m*-XDI, APTES, and PDMS was used as supporter of anatase TiO<sub>2</sub> to improve the separation of TiO<sub>2</sub> photocatalyst.

To construct the organized nanoscale, microscopic, and bulk inorganic materials from molecular components, the synthetic chemistry is of great interest<sup>1</sup> and the produced materials may be applied in electronics, catalysis, magnetism, sensory devices, and mechanism design. To all known, TiO<sub>2</sub> nanocrystals can provide excellent UV-photocatalysis<sup>2</sup> but suffer from the difficult separation. So great attention has been directed to the support of TiO<sub>2</sub> nanocrystals on some macroscopic particles easy to be separated, such as the active carbon and the molecular sieves.<sup>3</sup> In the present work, the cactus-like organic-grafted silica balls (XAP) was synthesized by *m*-xylenediisocyanate (*m*-XDI), aminopropyltriethoxysilane (APTES), and hydroxyl-terminated polydimethylsiloxane (PDMS). Then the anatase TiO<sub>2</sub> nanocrystals were successfully supported onto these balls to improve the separation of TiO<sub>2</sub> photocatalyst.

A typical synthesis of organic-grafted silica ball XAP included two reactions. The first reaction between *m*-XDI and APTES was carried out in tetrahydrofuran (THF) under dry nitrogen protection. The molar ratio of *m*-XDI to APTES was 1:1. APTES was very slowly dripped into the THF solution of *m*-XDI with a speed of five drops per minute. As a result, there was an unreacted N=C=O group on the intermediate XA shown in Figure 1 (the FTIR spectrum of XA can be found in the Supporting Information). The second reaction between XA and PDMS was also under dry nitrogen protection. PDMS (average molecular weight 6000) was added into the THF solution of XA in order to react N=C=O of XA with the terminal Si-OH of PDMS. The concentration of PDMS was 5 wt % in the final solution. Three days later, water was added to hydrolyze the Si-OC<sub>2</sub>H<sub>5</sub> groups of XA brought by APTES. The final solution was kept 60 °C for two weeks and white precipitate came into being. After washing the precipitate with THF and anhydrous ethanol and drying at 60 °C, a loose powder XAP was obtained. The surface area of XAP is 210 m<sup>2</sup>/g measured by N<sub>2</sub> adsorption. The atom composition of Si, C, H, O, and N is 9.7, 20.5, 57.5, 11.2, and 1.1%, respectively, which is close to the synthesis composition.

The supporting of TiO<sub>2</sub> nanocrystals on XAP was as follows. XAP was immersed into the ethonal solution of titanium(IV) *n*-butoxide (TB) for 2 h. XAP with adsorbed TB was washed with ethonal, filtered and then transferred into a Teflon-lined autoclave to undergo a hydrothermal process at 140 °C for 10 h. The hydrothermal product, XAP-Ti, was the final assembly of TiO<sub>2</sub> nanocrystals with XAP.

The SEM of XAP shows the spheric cactus-like morphology with about 20 μm diameter (see Figure 2a). TEM in a thorn of a

cactus ball shows large uneven continuous phase (see Figure 2b). In the first reaction, APTES molecules can quickly react with the half of the N=C=O groups to form the intermediate XA. The another half of N=C=O groups reacts with the terminal Si-OH groups of PDMS chains, and, a PDMS chain can link two XA intermediates (see Figure 1). Thus, one hydrophobic PDMS chain with two hydrophilic ends composes of a Bola molecule. These Bola molecules can construct reverse micelle in THF solvent. The hydrophilic ends in the core of reverse

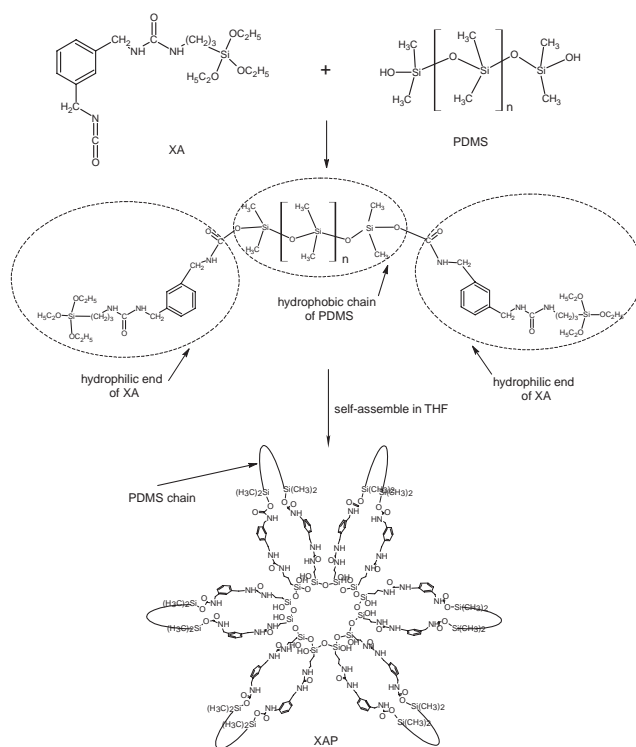


Figure 1. Schematic presentation of the formation of XAP.

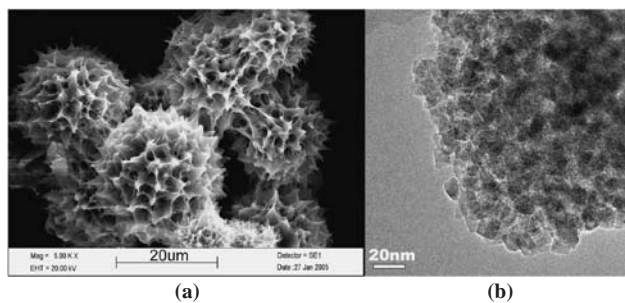
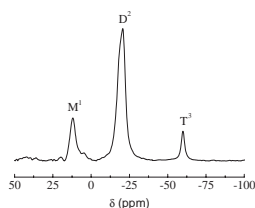


Figure 2. SEM and TEM of XAP.



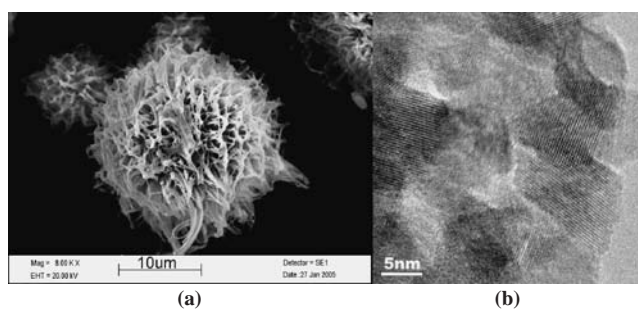
**Figure 3.**  $^{29}\text{Si}$  MAS NMR spectrum of XAP.

micelle hydrolyze and condense into silica matrix (see Figure 1). So the formation of the cactus-like spheric morphology underwent a complex process of reaction and self-assembly.

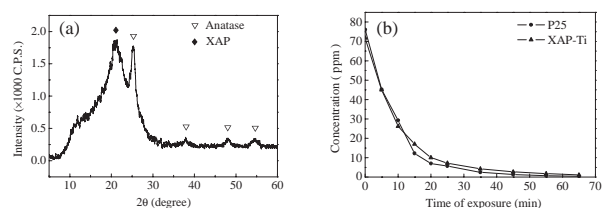
Figure 3 shows the  $^{29}\text{Si}$  MAS NMR spectrum of XAP. Three obvious NMR resonance peaks can be found in Figure 3. Symbols  $M^n$ ,  $D^n$ , and  $T^n$  denote monofunctionalized, difunctionalized, and trifunctionalized silicon atoms, respectively, where  $n$  is the number of Si–O–Si bridges attached to Si atom. In XAP, resonance peaks  $M^1$ ,  $D^2$ , and  $T^3$  should result from  $-\text{C}(\text{O})\text{OSi}^*(\text{CH}_3)_2\text{OSi}-$  at the terminal of PDMS chain,  $-\text{SiOSi}^*(\text{CH}_3)_2\text{OSi}-$  in PDMS chain, and  $(\text{SiO})_3\text{Si}^*(\text{CH}_2)_3\text{NH}-$  produced by the hydrolysis and condensation of  $\text{Si}(\text{OC}_2\text{H}_5)_3$  of XA (see Figure 1). All these NMR peaks indicate that intermediate XA has been successfully translated into XAP.

Figure 4 shows that the SEM and HRTEM of assembly XAP–Ti. SEM of XAP–Ti display an obvious difference in morphology from XAP (see Figure 2a and Figure 4a). The clear cactus-like surface of XAP is covered by many long strips that may be composed of  $\text{TiO}_2$ . By HRTEM investigation (see Figure 4b), these strips are found to be crystalline. The interlayer distance is about 0.353 nm that is consistent with the [101] face of anatase  $\text{TiO}_2$ . Figure 5a shows the powder XRD pattern of XAP–Ti. It can be easily found that anatase  $\text{TiO}_2$  exists in the assembly XAP–Ti. The EDS (energy diffusion spectrum) of a random strip on XAP–Ti shows high Ti atom content of about 43 mol % (the EDS result can be found in the Supporting Information). Therefore, during the hydrothermal process of XAP with adsorbed TB, anatase  $\text{TiO}_2$  has been crystallized on the surface of XAP and formed lots of crystalline strips. From the HRTEM results, the size of anatase crystal grain is about 5–10 nm that is consistent with the calculation from XRD pattern with the Sherrer formula.

The assembly XAP–Ti is mainly used to improve the separation of  $\text{TiO}_2$  nanocrystals that is generally used in UV photocatalysis. With the micrometer-class size of XAP–Ti, only general filter paper is needed to separate XAP–Ti from its dispersion system. To investigate the UV-photocatalysis activity of XAP–Ti, the aqueous solution of methylene blue (MB) was photodecomposed under 300 W high-pressure mercury vapor lamp.



**Figure 4.** SEM and HRTEM of XAP–Ti.



**Figure 5.** (a) XRD patterns and (b) photocatalysis activity of XAP–Ti.

The MB original concentration was 100 ppm. Prior to the UV irradiation, the suspension of XAP–Ti in MB solution was stirred in the dark for 30 min to ensure the adsorption–desorption equilibrium. The concentration of MB at this point was used as the initial value for the kinetic treatment of the photodecomposition process. Samples were collected from the reactive system at regular intervals and centrifuged to analyze MB concentration by a UV–vis spectrophotometer. Figure 5b shows the decrease of MB concentration with the UV exposing time, photocatalyzed by XAP–Ti and P25, respectively. P25 (produced by Degussa Co. German and is made up of 80 wt % anatase and 20 wt % rutile) is considered as the best commercially available UV photocatalyst up to now, and usually used as a comparison. The initial concentrations of MB are 71.5 and 76.4 ppm for XAP–Ti and P25, respectively. From Figure 5b, it can be seen that, during the initial 10 min, the decreasing speed of MB concentrations is very close for XAP–Ti and P25. But after that, the MB concentration decreases slightly slower for XAP–Ti than that for P25. About 92–94% of total MB can be decomposed within 35 min for the two catalysts. So the photocatalysis performance of XAP–Ti is also similar to that of P25. After thus reaction, the morphology of XAP–Ti was observed again by SEM and no significant change was found, which indicated the organic-grafted silica balls were not destroyed by the photocatalytic oxidation.

In summary, this kind of organic-grafted silica ball with cactus-like morphology may be used as the supporter of  $\text{TiO}_2$  photocatalyst and may provide a compatible solution to both the photocatalysis performance and the easy separation of nano  $\text{TiO}_2$  at the same time.

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