

## A Highly Photoactive Nanocrystalline TiO<sub>2</sub> Aerogel Prepared by a Non-Alkoxide Sol-Gel Method

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**Abstract** The nanocrystalline TiO<sub>2</sub> aerogel was prepared by a novel epoxide-mediated non-alkoxide sol-gel method and the catalyst was characterized by X-ray diffraction, N<sub>2</sub> adsorption and transmission electron microscopy. The influence of the preparation conditions on the textural properties of the TiO<sub>2</sub> aerogels was investigated and the catalyst activity was tested by using phenol degradation as the model reaction. When H<sub>2</sub>O/TiCl<sub>4</sub> molar ratio is 3, the prepared TiO<sub>2</sub> aerogel has the smallest crystallite size and the biggest surface area, and the catalyst shows the highest activity for phenol degradation.

**Key words:** titanium dioxide; aerogel; phenol; degradation; propylene epoxide; sol-gel

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TiO<sub>2</sub> is one of the most widely studied semiconductor materials for photocatalytic reactions due to its low cost, ease of handling, and high resistance to photoinduced decomposition<sup>[1~6]</sup>. An important aspect in the preparation of TiO<sub>2</sub> as photocatalysts for environmental applications is the development of nanostructured TiO<sub>2</sub> powders with small crystallite size, high surface area, controlled porosity, and tailored pore size distribution<sup>[3~6]</sup>. Among the methods developed for preparing nanocrystalline TiO<sub>2</sub> materials, the sol-gel method has attracted considerable attention for preparing TiO<sub>2</sub> materials with a three-dimensional open porosity<sup>[6~11]</sup>. But the conventional sol-gel method commonly requires highly reactive alkoxide precursors and complex solvent/ligand systems<sup>[5~12]</sup>. We report here the synthesis of highly photoactive TiO<sub>2</sub> aerogels with tailored structural properties by an epoxide-mediated sol-gel method using TiCl<sub>4</sub> as the titanium precursor, and its photocatalytic activity was tested using phenol degradation as the model reaction.

The procedure to prepare the TiO<sub>2</sub> aerogels is as follows. Briefly, a specific amount of TiCl<sub>4</sub> was dissolved in a water-ethanol solution (1 ml H<sub>2</sub>O+40 ml EtOH) with various H<sub>2</sub>O/TiCl<sub>4</sub> molar ratios, and then propylene oxide (Ti/epoxide molar ratio fixed at 1/6) was added dropwise under stirring. The gelation occurred in 1~6 min, after which the clear monolithic gel was aged for another 12 h at room temperature.

The resultant alcogel was then subjected to a series of solvent exchanges in anhydrous ethanol for 3 days followed by drying with CO<sub>2</sub> under supercritical conditions ( $T_c = 304$  K,  $p_c = 7.38$  MPa) to obtain a crack-free titania monolithic aerogel sample that takes the shape of the reaction vessel. This was further calcined at 673 K for 4 h to remove organic materials.

Transmission electron microscopy (TEM) was performed on a JEOL 2011 electron microscope operating at 200 kV. X-ray powder diffraction (XRD) was carried out on a Bruker D8 Advance X-ray diffractometer using nickel filtered Cu K<sub>α</sub> radiation with  $2\theta = 20^\circ \sim 70^\circ$ , and a voltage of 40 kV and current of 20 mA. The photodegradation of phenol was carried out in a quartz reactor. Before the reaction, the prepared suspension was magnetically stirred for about 30 min under the condition of oxygen bubbling (50 ml/min) in dark to achieve the adsorption/desorption equilibrium. The reaction conditions were 50 mg catalyst, 100 ml phenol solution containing the photocatalyst ( $c_0 = 0.60$  mmol/L, pH=7), 298 K, 32 W mercury lamp as light source, stirring rate of 400 r/min, and irradiation time of 2 h. The product was analysed by high performance liquid chromatography using a SPHERISORB ODS column (25 m×0.46 cm), 50% methanol-water mobile phase, and UV detector.

Fig 1 shows the XRD patterns of the calcined TiO<sub>2</sub> aerogel samples prepared with different H<sub>2</sub>O/

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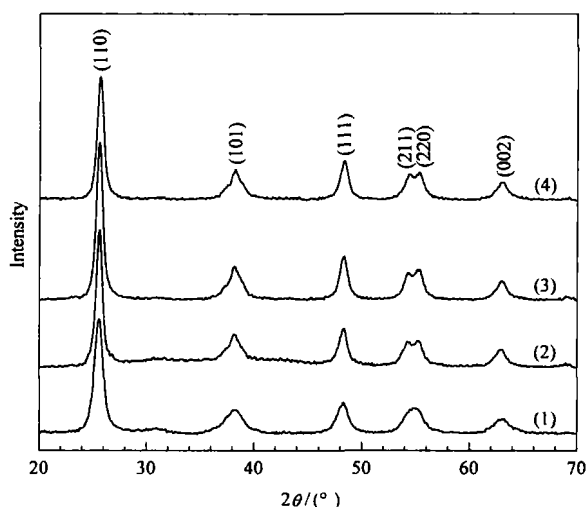


Fig 1 XRD patterns of the calcined  $\text{TiO}_2$  aerogels prepared with  $\text{H}_2\text{O}/\text{TiCl}_4$  molar ratios of 3 (1), 5 (2), 7 (3), and 10 (4)

$\text{TiCl}_4$  ratios. Prior to the calcination, the as-prepared aerogel samples were completely amorphous (data not shown). All calcined samples exhibited a well-crystallized anatase phase and no appreciable difference in the intensity of the corresponding reflection peaks was observed, implying that the  $\text{H}_2\text{O}/\text{TiCl}_4$  ratio has little influence on the crystallinity and phase transformation of the  $\text{TiO}_2$  samples. The average anatase crystallite

size ( $d$ ) of the calcined  $\text{TiO}_2$  aerogels estimated by the Scherrer equation is tabulated in Table 1. With increasing  $\text{H}_2\text{O}$  content during the synthesis process, there was a progressive increase in the average size of the anatase crystallites, which showed that a partial control of the nanocrystal size can be achieved by varying the  $\text{H}_2\text{O}/\text{TiCl}_4$  ratio.

Fig 2 shows the TEM images and selected area electron diffraction (SAED) pattern of the  $\text{TiO}_2$  aerogel samples with a  $\text{H}_2\text{O}/\text{TiCl}_4$  molar ratio of 3. It was found that the as-prepared sample (Fig 2(a)) is highly porous and consists of clusters of cross-linked particles smaller than 5 nm. After calcination at 673 K, loosely aggregated spherical nanoparticles with a particle size of 8 ~ 10 nm were observed. The high-resolution transmission electron microscopy image (Fig 2(b), inset (1)) shows sets of lattice fringes, which is evidence of the highly crystalline nature of the particles. The SAED pattern (Fig 2(b), inset (2)) of the calcined sample is indexed to anatase<sup>[3]</sup>, which is in good agreement with the XRD result.

Table 1 summarizes the structural properties of the  $\text{TiO}_2$  aerogels and the photocatalytic activity of the calcined samples. It is seen that the  $\text{H}_2\text{O}/\text{TiCl}_4$  ratio plays a key role in determining the structural properties as well as the photocatalytic activity. The

Table 1 Structural characteristics and photocatalytic activity of the  $\text{TiO}_2$  aerogel samples for phenol degradation

Catalyst	$n(\text{H}_2\text{O})/n(\text{TiCl}_4)$	Gelation time (min)	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_p/(\text{cm}^3/\text{g})$	$D_p/\text{nm}$	$d/\text{nm}$	Degradation efficiency (%)
$\text{TiO}_2$ aerogel	3	5	116 (464)	0.62 (2.06)	9.0	8.6	89
	5	3	71 (479)	0.17 (0.34)	5.2	11.0	81
	7	1	80 (532)	0.20 (0.75)	4.5	11.6	79
	10	1	101 (558)	0.18 (0.58)	4.5	12.4	70
Degussa P-25	—	—	55	0.25	—	20	72

The numbers in parentheses are the data of the as-prepared  $\text{TiO}_2$  aerogel samples prior to calcination.

$D_p$  — Average pore size of the  $\text{TiO}_2$  aerogel samples estimated from  $\text{N}_2$  adsorption data.

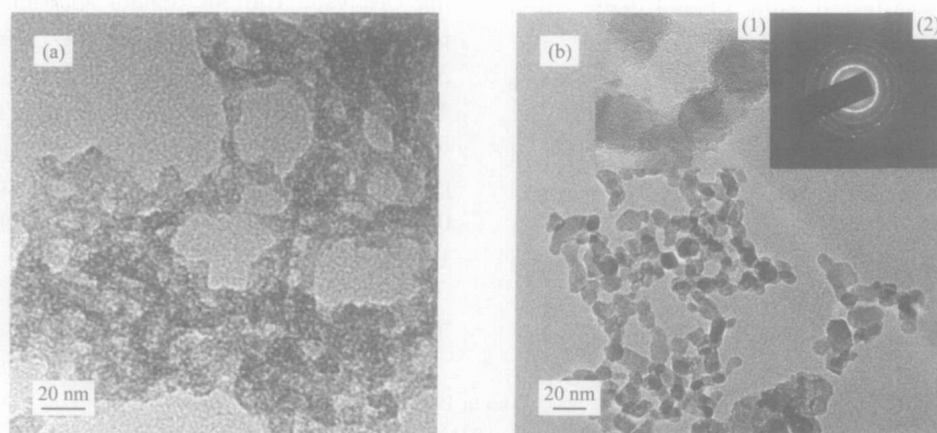


Fig 2 TEM images of the as-prepared (a) and calcined (b)  $\text{TiO}_2$  aerogel samples prepared with a  $\text{H}_2\text{O}/\text{TiCl}_4$  molar ratio of 3

as-prepared sample with a H<sub>2</sub>O/TiCl<sub>4</sub> ratio of 3 has the smallest surface area (464 m<sup>2</sup>/g), but it is interesting to note that the biggest surface area and pore volume are shown by its calcined counterpart. All the calcined TiO<sub>2</sub> aerogel samples were highly active during the photocatalytic degradation of phenol. This is due to their high surface area and the formation of a highly crystalline anatase phase. It should be noted that the TiO<sub>2</sub> aerogel sample with the biggest surface area and pore volume shows the highest catalytic activity, and its catalytic performance is superior to that of the commercial photocatalyst Degussa P-25. The higher activity can be attributed to the better textural properties and the smaller crystallite size.

In summary, we have successfully synthesized nanocrystalline TiO<sub>2</sub> aerogels with controllable structure and superior photocatalytic activity by adapting a facile and straightforward epoxide-mediated sol-gel procedure that uses TiCl<sub>4</sub> as the titanium precursor. This versatile route may also find applications in the preparation of composite or doped TiO<sub>2</sub>, thus providing new opportunities for the tailoring of a new generation of TiO<sub>2</sub>-based highly efficient photocatalytic materials.

It is worth noting that the key to obtaining a gel free of precipitates is the sol-gel processing of the aqueous/alcohol solution of titanium chlorides in the presence of an appropriate amount of propylene epoxide additive and water. The TiO<sub>2</sub> aerogels prepared with this unique approach are formed through the generation of a continuous mesoporous network to provide favorable textural and structural properties for good photocatalytic activities. The H<sub>2</sub>O/TiCl<sub>4</sub> ratio plays a key role. The rigid alcogels free of precipitates

can be produced at H<sub>2</sub>O/TiCl<sub>4</sub> ratios higher than 3 during the initial sol-gel process. When the H<sub>2</sub>O/TiCl<sub>4</sub> ratio is lower than 3, there is only a rapid formation of a gel-like precipitate. Similar phenomena were reported by Gash *et al*<sup>[13]</sup> when they studied the epoxide-mediated gelation behavior of a FeCl<sub>3</sub>/H<sub>2</sub>O system.

## References

- 1 Fox M A, Dulay M T. *Chem Rev*, 1993, **93**(1): 341
- 2 Ohtani B, Ogawa Y, Nishimoto S. *J Phys Chem B*, 1997, **101**(19): 3746
- 3 Dagan G, Tomkiewicz M. *J Phys Chem*, 1993, **97**(49): 12651
- 4 Kapoor P N, Uma S, Rodriguez S, Klabunde K J. *J Mol Catal A*, 2005, **229** (1-2): 145
- 5 Li H X, Zhu J, Li G Sh, Wan Y. *Chem Lett*, 2004, **33** (5): 574
- 6 Kolen'ko Y V, Garshev A V, Churagulov B R, Boujday S, Portes P, Colbeau-Justin C. *J Photochem Photobiol A*, 2005, **172**(1): 19
- 7 Schneider M, Baiker A. *Catal Today*, 1997, **35**(3): 339
- 8 Suh D J. *J Non-Cryst Solids*, 2004, **350**(1): 314
- 9 Campbell L K, Na B K, Ko E I. *Chem Mater*, 1992, **4** (6): 1329
- 10 Zhang Y H, Xiong G, Yao N, Yang W, Fu X. *Catal Today*, 2001, **68**(1-3): 89
- 11 Navío J A, Colón G, Mañas M, Real G, Litter M I. *Appl Catal A*, 1999, **177**(1): 111
- 12 Niederberger M, Bartl M H, Stucky G D. *Chem Mater*, 2002, **14**(10): 4364
- 13 Gash A E, Tillotson T M, Satcher J H Jr, Poco J F, Hrubesh L W, Simpson R L. *Chem Mater*, 2001, **13** (3): 999

## 非钛醇盐溶胶-凝胶法制备高光活性纳米晶 TiO<sub>2</sub> 气凝胶

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摘要: 以 TiCl<sub>4</sub> 为前驱体, 采用环氧丙烷快速成胶法合成了具有高光催化活性的纳米晶 TiO<sub>2</sub> 气凝胶。利用 X 射线衍射、N<sub>2</sub> 物理吸附和透射电镜等手段考察了 H<sub>2</sub>O/TiCl<sub>4</sub> 摩尔比和热处理等制备参数对 TiO<sub>2</sub> 气凝胶织构性质的影响, 并以苯酚的光催化降解为模型反应评价了样品的光催化活性。结果表明, H<sub>2</sub>O/TiCl<sub>4</sub> 摩尔比为 3 时体系的成胶过程较为缓慢, 制备的纳米晶 TiO<sub>2</sub> 气凝胶样品具有最小的晶粒尺寸及最大的比表面积和孔容, 并且具有最佳的光催化活性。

关键词: 二氧化钛; 气凝胶; 苯酚; 降解; 环氧丙烷; 溶胶-凝胶

(Ed YHM)