

Solvothermal Synthesis of Rice-Like TiO₂ Nanocrystals Using Different Titanium Sources and Their Photocatalytic Activity for Degradation of Benzene

Fei He, Di Zhou, Tao Li and Guangxing Li

Abstract—Rice-like TiO₂ nanocrystals have been synthesized by a facile and mild solvothermal route. Transmission electron microscopic imaging reveal that these anatase TiO₂ nanocrystals are 5 nm in average width and 35 nm in length. The influence of different titanium sources on the formation of the rice-like TiO₂ nanocrystals was investigated. The photocatalytic activity of CSTWs had been carried out by the degradation of gaseous benzene. The results indicated that, comparing with commercial TiO₂ (Degussa P25), the 1D TiO₂ structure exhibited significant photocatalytic activity. A detailed reaction mechanism is proposed to explain their formation as intermediates in the reaction.

Keywords—Rice-like TiO₂ nanocrystals; Titanium sources; Solvothermal route; Photocatalytic degradation; Benzene

I. INTRODUCTION

TiO₂ has attracted more and more attention in many fields, such as photocatalysis [1-3], solar cells [4,5], and gas sensors [6,7], due to its superior properties. TiO₂ has been extensively researched for applications in environmental remediation because of its high chemical stability, low cost, and low toxicity [8-10]. Nanoparticles are the subject of intensive research not only because of the novel properties and functions associated with individual nanoparticles but also owing to the new collective properties and advanced tunable functions arising from nanoparticle ensembles. As the relative properties of the nanocrystals are largely affected by the morphology, the morphology control of nanocrystals with well-defined shape is a key challenge in modern chemistry materials. Since the discovery of carbon nanotubes in 1991 [11], one-dimensional (1D) nanostructured materials have been extensively studied because of their distinctive geometrical morphologies, novel physical and chemical properties, and potential applications in

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nanoscale optical and electric devices [12]. Among the various oxide and nonoxide 1D nanostructured materials, TiO₂ nanotubes have gained more and more attention because of their enhanced properties, cheap fabrication, high specific surface area and pore volume. In this work, we report a simple one-step hydrothermal synthesis of elongated rice-like TiO₂ nanocrystals. The photocatalytic properties of the products were evaluated by monitoring of photodegradation of gaseous

benzene. The influence of different titanium sources on the photocatalytic activity of TiO₂ nanocrystals has been studied.

II. MATERIALS AND METHODS

A. Synthesis

Rice-like TiO₂ nanocrystals were synthesized by solvothermal technique using TBT, TTIP and TiCl₄ as titanium sources, respectively. After the solvothermal treatment, the powder product was separated by centrifugation, washed with distilled water and absolute ethyl alcohol three times, respectively, and then dried at 333 K.

B. Analysis

X-Ray diffraction (XRD) patterns of all samples were recorded on an X'Pert PRO X-ray diffractometer with Cu K α radiation. Transmission electron microscopy (TEM) was taken with a Tecnai G20 transmission electron microscope using an accelerating voltage of 200 KV. Adsorbed intermediates were extracted from the used TiO₂ sample with chloroform and condensed on a rotatory evaporator. The photooxidation intermediate products were identified by analysing them with an Agilent 7890A/5975C GC-MS, which was equipped with a DB-WAX capillary column.

C. Photocatalytic activity

The photocatalytic reactor was connected to a GC-9560 gas chromatograph. The catalysts (0.5 g) were prepared by coating a glass dish, which had a diameter of 12.0 cm, with an aqueous suspension of TiO₂ powder and setting it on the bottom of the reactor. The Hg lamp was turned on until the measured concentration of CO₂ remained unchanged, which was to ensure the removal of all of the adventitious organic compounds adsorbed on the TiO₂ catalyst and to establish the adsorption-desorption equilibrium of CO₂ on the TiO₂

catalyst. Subsequently, 2 μL benzene was injected into the reactor. Prior to photocatalytic oxidation, the benzene vapour, which was diluted with air, was pre-adsorbed on the catalyst before illumination. Next, the oxidation commenced when the UV lamp was turned on. The concentration of the CO_2 produced was obtained by subtracting the initial concentration of CO_2 in the reactor from the final concentration. All of the contrast experiment was conducted under the same conditions.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD patterns of the as-grown samples synthesized using different titanium sources, such as TBT, TTIP and TiCl_4 . We found that titanium source had obvious effect on the XRD results. When using TBT and TTIP, the series of strong diffractions demonstrate only an anatase structure of TiO_2 in all samples. But, when using TiCl_4 , a series

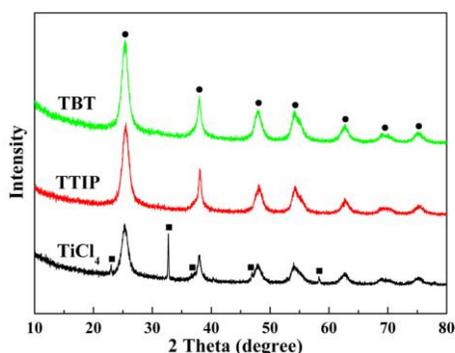


Fig. 1 XRD patterns of the samples prepared using TBT, TTIP and TiCl_4 . (●) anatase TiO_2 ; (■) $\text{TiCl}_4(\text{NH}_3)_2$.

of diffraction peak which are assigned to $\text{TiCl}_4(\text{NH}_3)_2$ appeared. On the basis of the synthetic process, we propose the $\text{TiCl}_4(\text{NH}_3)_2$ for the reaction product of titanium tetrachloride and ammonia. Because of the low solubility, although washed with distilled water and absolute ethyl alcohol several times, it still exists.

TEM image in Fig. 2 reveals that the obtained TiO_2 nanocrystals prepared using TBT exhibit a rice-like shape with an average of 5 nm in width and an average of 35 nm in length. This indicates that the hydrothermal reaction leads to the growth of anisotropic primary particle. But it is interesting that when we use TiCl_4 as the titanium source, the nanoparticles are severely agglomerated, and which don't exhibit rice-like shape.

Volatile organic compounds (VOCs) are widely used in industrial processes and domestic activities. Benzene, which is often found in industrial waste discharges, can cause serious urban air pollution. One recent report demonstrated that exposure to even 1 ppm of benzene can reduce blood cell counts and cause hematotoxicity in factory workers [13]. So, in order to improve indoor air quality (IAQ), it must be eliminated. The effect of titanium source on the photocatalytic activity was evaluated by the degradation of gaseous benzene,

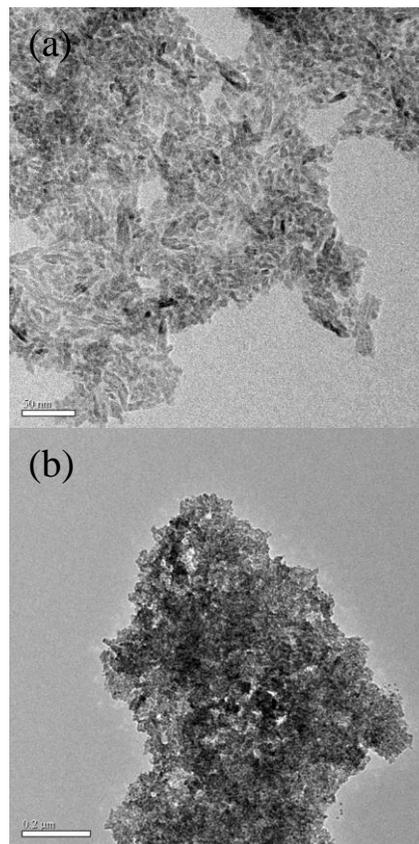


Fig. 2 TEM image of the sample prepared using TBT(a) and TiCl_4 (b).

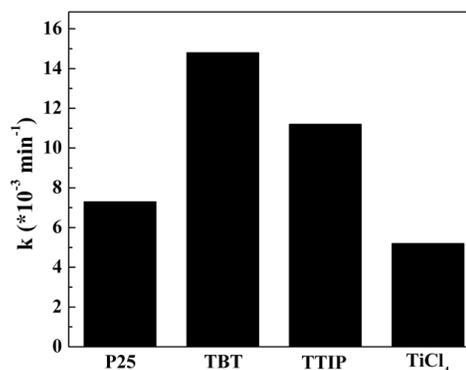


Fig. 3 The apparent rate constants of different TiO_2 samples prepared with different titanium sources.

with commercial P25 as a comparison. The results demonstrate that the sample prepared with TBT shows the highest performance in the photocatalytic process whose k is significantly higher than that of P25, which is recognized as an excellent photocatalyst [14]. We also found that the sample prepared with TiCl_4 shows lower photocatalytic performance, which could be attributed to the existence of $\text{TiCl}_4(\text{NH}_3)_2$.

In order to investigate the mechanism of photodegradation destruction of benzene, adsorbed intermediates were extracted from the used sample by chloroform and ultrasonication, the resulting solution was evaporated to concentrate any dissolved

intermediates, then the concentrated solution was analyzed by GC/MS for intermediates. Zhong et al. noted that in the case of

benzene photocatalytic oxidation, some alkyl radicals such as $\text{CH}_3\cdot$, $\text{CH}_3\text{CH}_2\cdot$ and $\text{CH}_3\text{CH}_2\text{CH}_2\cdot$ could be formed [15]. V. V. Kislov's results showed that when benzene molecule absorbs photon with enough energy, it can split apart into $\text{CH}_3\cdot$, $\text{C}_2\text{H}_3\cdot$,

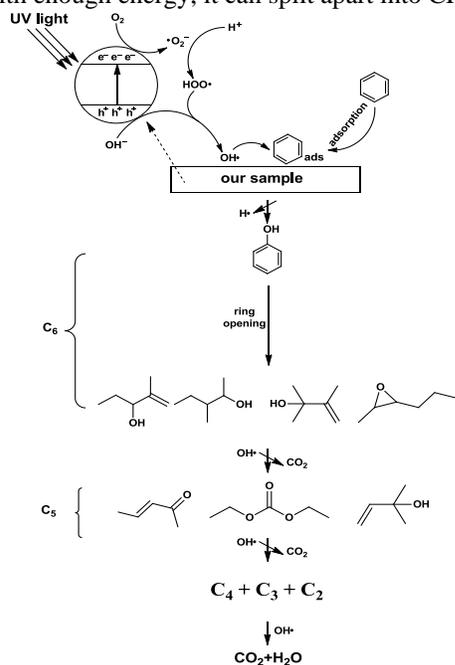


Fig. 4 Photocatalytic oxidation mechanism of benzene

$\text{C}_6\text{H}_5\cdot$ and other products after isomerization and split effect [16]. On the basis of the identified intermediates, possible photocatalytic degradation pathways of benzene are proposed in Fig. 4. When the TiO_2 particles were illuminated by photons with the appropriate energy, the valence band electrons of the TiO_2 were excited to the conduction band, creating highly reactive electron (e^-) and hole (h^+) pairs. The photogenerated electrons and holes were long-lived enough to react with adsorbed O_2 and H_2O to produce $\cdot\text{OH}$ radicals, which could cause photodegradation. In the first step, the benzene molecules were adsorbed onto the surface of the TiO_2 sample; then, the OH radicals were added to yield phenol. In our experimental conditions, the hydroxyl radicals have been regarded as a key species in the photocatalytic degradation of benzene, it can react with benzene to form various alkyl radicals, such as $\text{CH}_3\cdot$, $\text{CH}_3\text{CH}_2\cdot$ and so on, after a series of free radical reaction, the benzene molecules were degraded into ring opened products and some lower C-atomic aliphatics, finally they were mineralization to CO_2 and H_2O .

IV. CONCLUSION

In summary, we report a facile and mild solvothermal route for the synthesis of rice-like TiO_2 nanocrystal. We found that titanium source had obvious effect on the photocatalytic performance. The sample prepared using TBT exhibits a remarkable photocatalytic activity which was attributed to the 1D TiO_2 structure, intrinsic nanoporous and large surface area characteristics of the mesoscopic structured TiO_2 . A detailed

reaction mechanism is proposed to explain their formation as intermediates in the reaction. This strategy is simple, cheap and mass-productive, which may shed light on a new avenue for large-scale synthesis of 1D TiO_2 structure for catalyst, energy and other applications.

ACKNOWLEDGMENT

We acknowledge the National Basic Research Program of China (Grant Nos. 2009CB939705) and the National Natural Science Foundation of China (20973068) for financial support. We are also grateful to the Analytical and Testing Center of Huazhong University of Science and Technology, Wuhan, China.

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