A Novel Synthetic Route to Carbon Nanotubes Supported $\text{ZrO}_2/\text{TiO}_2$ Nanoparticles†

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In this study, $\text{ZrO}_2/\text{TiO}_2$ nanoparticles were synthesized and loaded upon carbon nanotubes with TiCl_4 , ZrOCl_2 and HNO_3 , using hydrothermal synthetic method. Prepared particles were then subjected to structural characterization with XRD and TEM. Our XRD results suggest that, in the $\text{ZrO}_2/\text{TiO}_2$ -carbon nanotubes complexes, phase transition of TiO_2 crystallites occurs from rutile to anatase as the doped ZrO_2 content increases. TEM results indicate that, $\text{ZrO}_2/\text{TiO}_2$ particles can be supported homogeneously on the surface of carbon nanotubes only when the complex has 10 % ZrO_2 , under our experimental conditions.

Key Words: Hydrothermal synthesis, Zirconium oxide, Titanium oxide, Carbon nanotubes.

INTRODUCTION

Compared with most single-component oxide, the $\text{ZrO}_2/\text{TiO}_2$ nanoparticle complex has larger relative surface area and has been regarded as better catalyst carrier in reactions like hydrogenation, desulfurization and eliminating NO_x from automobile exhaust. Carbon nanotubes (CNTs) have high adsorbing capability and have been widely used as supporting materials in nanoparticle preparation. Under certain conditions, oxide nanoparticles in catalysts can be loaded upon carbon nanotubes, further increasing the catalytic efficiency with extra relative surface areas¹⁻³.

In this study, we applied hydrothermal synthetic method in preparing $\text{ZrO}_2/\text{TiO}_2$ -carbon nanotubes nanoparticle complexes. Hydrothermal synthesis is a method with relatively low cost and little pollution for nanoparticle preparation⁴⁻⁷. Using this method, crystallized oxide can be prepared at relatively low temperature (*ca.* 200 °C) in water solution and dried at 80 °C, therefore bypassing technical hurdles such as particle agglomeration and argon protection during high temperature calcination.

Based on the remarkable adsorbing capability of carbon nanotubes, we also evaluated the influence of different doping ratio of ZrO_2 to TiO_2 on nanoparticle complexes formation and investigated preliminarily into the underlying mechanisms.

EXPERIMENTAL

ZrOCl_2 solution (24.0 mL, 0.25 mol/L) was used as precursor. HNO_3 (4.0 mL, 16 mol/L) was added into the precursor. The whole reaction mixture was transferred to tubular stainless steel autoclave for reaction at *ca.* 200 °C for 8 h. Reaction products were washed with ethanol for 5-6 times and dried at 80 °C for 2 h.

ZrOCl_2 solution (12.0 mL, 0.25 mol/L) was used as precursor. Sodium dodecylbenzenesulfonate (1.0 mL, 5 g/L) and carbon nanotubes (0.5 g) were sequentially added into the precursor solution. The reaction mixture was stirred vigorously at room temperature for 0.5 h, added with HNO_3 (4.0 mL, 16 mol/L) and then transferred to tubular stainless steel autoclave for reaction at 200 °C for 12 h. Reaction products were washed with ethanol for 5-6 times and dried at 80 °C for 2 h. Fine ZrO_2 -carbon nanotubes complexes were obtained.

Certain amount (Table-1) of ZrOCl_2 solution (0.25 mol/L) was mixed with TiCl_4 (0.9 mol/L) to be used as precursor, with the ZrOCl_2 : TiCl_4 molar ratio at 4:1, 1:1, 1:5-1:10, 1:100-1:1000. Sodium dodecylbenzenesulfonate (1.0 mL, 5 g/L) was added into the precursor solution (with different ZrOCl_2 : TiCl_4 molar ratio, respectively). Carbon nanotubes (0.5 g) were added into the solution, followed by ultrasonic treatment for 0.5 h. HNO_3 (16 mol/L) was then added into the mixture at certain amount (Table-1). The resultant reaction mixture was

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then transferred to tubular stainless steel autoclave (covered with polytetrafluoroethylene) for reaction at 200 °C for 7 h. Reaction products were washed with ethanol for 5-6 times and dried at 80 °C for 2 h. The ZrO₂/TiO₂-carbon nanotubes nanoparticle complexes were obtained.

The obtained samples were characterized by Y-2000 X-ray diffractometer and JEM -200CX transmission electron microscope.

TABLE-I
SUMMARY OF REAGENT AMOUNT AND
RATIO FOR SYNTHETIC REACTION

Sample	V _{ZrOCl₂} (0.25 mol/L)	V _{TiCl₄} (0.9 mol/L)	V _{HNO₃} (16 mol/L)	m _{TiCN} (g) (C.P. grade)	n _{ZrOCl₂} : n _{TiCl₄} ratio
A	1.0 mL	28.0 mL	4.8 mL	0.5 g	1:1
B	6.0 mL (0.5 mol/L)	16.7 mL	3.7 mL	0.5 g	1:5
C	18.0 mL	5.0 mL	3.8 mL	0.5 g	1:1
D	29.0 mL	2.0 mL	5.2 mL	0.5 g	4:1

RESULTS AND DISCUSSION

Crystal structure of ZrO₂, carbon nanotubes, ZrO₂-carbon nanotubes and ZrO₂/TiO₂-carbon nanotubes complexes: X-ray diffraction experiments were performed for prepared ZrO₂, carbon nanotubes and ZrO₂-carbon nanotubes particles. According to PDF card (JCPDS number 72-597), both ZrO₂ (Fig. 1) and ZrO₂-carbon nanotubes (Fig. 3) particles are monoclinic. Compared with XRD pattern of carbon nanotubes alone (Fig. 2), XRD result of ZrO₂-CNTs particles have no diffraction peak of carbon nanotubes, suggesting that carbon nanotubes is masked by ZrO₂. Consistent with XRD results, TEM image (Fig. 6, F) also indicates that the white ZrO₂ particles are adsorbed upon the surface of carbon nanotubes.

Fig. 1. XRD of ZrO₂

We also examined the XRD results of ZrO₂/TiO₂-CNTs particle complexes at other doping ratios, namely, when the molar ratio of ZrO₂: TiO₂ is at 1: 100-1:1000, 1:5-1:10, 1:1 and 4:1 (Fig. 4 A, B, C, D). Compared with standard PDF cards, it is obvious that ZrO₂/TiO₂-CNTs particle complexes, when doped at 1:100~:1000 molar ratio (ZrO₂: TiO₂, hereafter), have only rutile TiO₂ diffraction peaks (JCPDS number 21-1276, Fig. 4A), whereas complexes doped at 1:5~1:10 ratio have only anatase TiO₂ diffraction peaks (JCPDS number

21-1272, Fig. 4B). By contrast, ZrO₂/TiO₂-CNTs complexes doped at 1:1 ratio have diffraction peaks of both monoclinic ZrO₂ (JCPDS number 72-597) and anatase TiO₂ (Fig. 4C). Finally, when ZrO₂ and TiO₂ are doped at 4:1 molar ratio, only the monoclinic ZrO₂ diffraction peaks can be observed (Fig. 4D). When n(ZrO₂) : n(TiO₂) = 1:5 ~ 1:10, the relatively high content of ZrO₂ may inhibit phase transition of TiO₂ crystallites, ending up with anatase TiO₂. When n(ZrO₂) : n(TiO₂) = 1:100-1:1000, the relatively low content of ZrO₂ may fail to inhibit phase transition from anatase (Fig. 5D) to rutile (Fig. 5C) TiO₂, at relatively low temperature (200 °C).

Fig. 2. XRD of carbon nanotubes

Fig. 3. XRD of ZrO₂-carbon nanotubes

Morphologies of ZrO₂, carbon nanotubes, ZrO₂-CNTs and ZrO₂/TiO₂-CNTs complexes: In order to understand the morphological basis of the complexes' different behaviours under XRD, transmission electron microscopy (TEM) was used to visualize the ultrastructure of some of the prepared nanoparticles (Fig. 5 A, B, C and D). Carbon nanotubes alone under TEM have tubular structures (Fig. 5A) with characteris-

Fig. 4. XRD patterns of $\text{ZrO}_2/\text{TiO}_2$ -CNTs nanoparticle complexes of different composition, $n(\text{ZrO}_2):n(\text{TiO}_2)$ = (A) 1:100-1:1000, (B) 1:5-1:10, (C) 1:1 and (D) 4:1

tically dark colour, whereas ZrO_2 -CNTs complexes have white tubular structures, presumably caused by ZrO_2 adsorption upon carbon nanotubes' surface (Fig. 5B). $\text{ZrO}_2/\text{TiO}_2$ -CNTs complexes doped with 0.1 % ZrO_2 , on the other hand, have dark coloured and agglomerated columnar grains, which is typical morphology of rutile TiO_2 crystallites (Fig. 5C). In contrast, when $\text{ZrO}_2/\text{TiO}_2$ -CNTs complexes are doped with 10 % ZrO_2 , carbon nanotubes are coated homogeneous with globular $\text{ZrO}_2/\text{TiO}_2$ nanoparticles on the surface (Fig. 5D), characteristics of anatase TiO_2 crystallites. Collectively, our TEM results are consistent with our XRD data where TiO_2 is in the rutile phase when doping ratio $n(\text{ZrO}_2) : n(\text{TiO}_2)$ is less than 1:10 (Fig. 4A), while TiO_2 is in the anatase phase when the ratio is larger than 1:10 (Fig. 4B, C). Therefore, TEM images have so far supported the notion that TiO_2 in the anatase phase has larger relative surface area than rutile phase, thus is easier to be adsorbed and used as catalysts carrier.

A number of factors are involved in affecting phase transition of TiO_2^{8-10} , yet in this study our data have revealed that doping content of ZrO_2 is playing a major role under

moderate temperatures like 200 °C. When doping ratio ($n\text{ZrO}_2:n\text{TiO}_2$, hereafter) is less than 1:10, ZrO_2 dopes into TiO_2 lattice, forming stable TiO_2 solid solution. As ZrO_2 content drops, phase transition occurs from anatase TiO_2 (Fig. 4B) to rutile TiO_2 (Fig. 4A). This is probably because Zr^{4+} has similar radius (79 pm) to that of Ti^{4+} (68 pm). As proposed previously, doping cations have easier access to lattice gaps or have higher tendency to replace Ti^{4+} when they have similar radius as Ti^{4+} , giving rise to homogeneous distribution in TiO_2 crystallites. Lower content of doping Zr^{4+} diffuses among TiO_2 lattices, forming the priority nucleating center for rutile phase, thus allowing phase transition (from anatase to rutile) to occur at moderate temperature (200 °C) rather than at higher temperatures (630 °C) required for pure TiO_2 to initiate phase transition.

When doping ratio is 1:1, diffraction peaks unique to monoclinic ZrO_2 and anatase TiO_2 can be observed, suggesting the possibility that equal amount of ZrO_2 and TiO_2 form solid solution and mixed crystallites (Fig. 4C).

When doping ratio is larger than 1:1, excess ZrO_2 renders Ti^{4+} to be the doping cation, which enters into ZrO_2 lattice and

Fig. 5. TEM images of $\text{ZrO}_2/\text{TiO}_2$ -CNTs nanoparticle complexes of different composition, (A) carbon nanotubes alone (50000X), (B) ZrO_2 -CNTs (100000X), (C) $\text{ZrO}_2/\text{TiO}_2$ -CNTs complexes doped with 0.1 % ZrO_2 (70000X), (D) $\text{ZrO}_2/\text{TiO}_2$ -CNTs complexes doped with 10 % ZrO_2 (60000X)

forms ZrO_2 solid solution, giving rise to the situation where only the diffraction peaks of ZrO_2 (Fig. 4D) can be observed.

Conclusion

We have successfully prepared the $\text{ZrO}_2/\text{TiO}_2$ -CNTs nanoparticle complexes with hydrothermal synthesis under 200 °C. When $n(\text{ZrO}_2) : n(\text{TiO}_2) > 1:1$, only the diffraction peaks of ZrO_2 can be observed; When $n(\text{ZrO}_2) : n(\text{TiO}_2) = 1:1-1:10$, ZrO_2 can inhibit the phase transition of TiO_2 , giving rise to globular anatase TiO_2 , which makes it easier for $\text{ZrO}_2/\text{TiO}_2$ complex to be adsorbed to carbon nanotubes; When $n(\text{ZrO}_2) : n(\text{TiO}_2) = 1:100-1:1000$, phase transition of TiO_2 occurs under 200 °C, from anatase to rutile TiO_2 , making the $\text{ZrO}_2/\text{TiO}_2$ complex even harder to be loaded upon carbon nanotubes.

Collectively, appropriate doping of Zr^{4+} can be used for preparing TiO_2 nanoparticles in different phase. Precise control of the doping ratio is required for achieving homogeneous coating of $\text{ZrO}_2/\text{TiO}_2$ nanoparticle complexes upon the surface of carbon nanotubes.

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