A Novel Synthetic Route to Carbon Nanotubes Supported ZrO₂/TiO₂ Nanoparticles†

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In this study, ZrO₂/TiO₂ nanoparticles were synthesized and loaded upon carbon nanotubes with TiCl₄, ZrOCl₂ and HNO₃, using hydrothermal synthetic method. Prepared particles were then subjected to structural characterization with XRD and TEM. Our XRD results suggest that, in the ZrO₂/TiO₂-carbon nanotubes complexes, phase transition of TiO₂ crystallites occurs from rutile tinania to anatas as the doped ZrO₂ content increases. TEM results indicate that, ZrO₂/TiO₂ particles can be supported homogeneously on the surface of carbon nanotubes only when the complex has 10 % ZrO₂, under our experimental conditions.

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

INTRODUCTION

Compared with most single-component oxide, the ZrO₂/TiO₂ nanoparticle complex has larger relative surface area and has been regarded as better catalyst carrier in reactions like hydrogenation, desulfurization and eliminating NOₓ 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 areas[1-3].

In this study, we applied hydrothermal synthetic method in preparing ZrO₂/TiO₂-carbon nanotubes nanoparticle complexes. Hydrothermal synthesis is a method with relatively low cost and little pollution for nanoparticle preparation[4-7]. Using this method, crystallized oxide can be prepared at relatively low temperature (*ca.* 200 ℃) in water solution and dried at 80 ℃, 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 ZrO₂ to TiO₂ on nanoparticle complexes formation and investigated preliminarily into the underlying mechanisms.

EXPERIMENTAL

ZrOCl₂ solution (24.0 mL, 0.25 mol/L) was used as precursor. HNO₃ (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 ℃ for 8 h. Reaction products were washed with ethanol for 5-6 times and dried at 80 ℃ for 2 h.

ZrOCl₂ 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 HNO₃ (4.0 mL, 16 mol/L) and then transferred to tubular stainless steel autoclave for reaction at 200 ℃ for 12 h. Reaction products were washed with ethanol for 5-6 times and dried at 80 ℃ for 2 h. Fine ZrO₂-carbon nanotubes complexes were obtained.

Certain amount (Table-1) of ZrOCl₂ solution (0.25 mol/L) was mixed with TiCl₄ (0.9 mol/L) to be used as precursor, with the ZrOCl₂: TiCl₄ 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 ZrOCl₂: TiCl₄ molar ratio, respectively). Carbon nanotubes (0.5 g) were added into the solution, followed by ultrasonic treatment for 0.5 h. HNO₃ (16 mol/L) was then added into the mixture at certain amount (Table-1). The resultant reaction mixture was

then transferred to tubular stainless steel autoclave (covered with polytetrafluoroethene) for reaction at 200 ºC for 7 h. Reaction products were washed with ethanol for 5-6 times and dried at 80 ºC for 2 h. The ZrO_2/TiO_2-carbon nanotubes nanoparticle complexes were obtained.

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

TABLE-l
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_{TCN} (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 ZrO_2, carbon nanotubes, ZrO_2-carbon nanotubes and ZrO_2/TiO_2-carbon nanotubes complexes: X-ray diffraction experiments were performed for prepared ZrO_2, carbon nanotubes and ZrO_2-carbon nanotubes particles. According to PDF card (JCPDS number 72-597), both ZrO_2 (Fig. 1) and ZrO_2-carbon nanotubes (Fig. 3) particles are monoclinic. Compared with XRD pattern of carbon nanotubes alone (Fig. 2), XRD result of ZrO_2-CNTs particles have no diffraction peak of carbon nanotubes, suggesting that carbon nanotubes is masked by ZrO_2. Consistent with XRD results, TEM image (Fig. 6, F) also indicates that the white ZrO_2 particles are adsorbed upon the surface of carbon nanotubes.
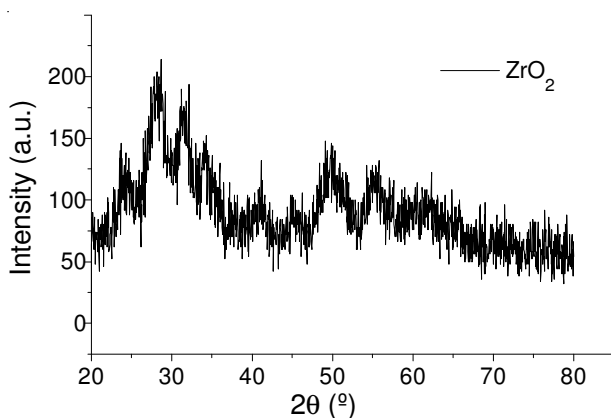

Fig. 1. XRD of ZrO_2

We also examined the XRD results of ZrO_2/TiO_2-CNTs particle complexes at other doping ratios, namely, when the molar ratio of ZrO_2: TiO_2 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 ZrO_2/TiO_2-CNTs particle complexes, when doped at 1:100~:1000 molar ratio (ZrO_2: TiO_2, hereafter), have only rutile TiO_2 diffraction peaks (JCPDS number 21-1276, Fig. 4A), whereas complexes doped at 1:5~1:10 ratio have only anatase TiO_2 diffraction peaks (JCPDS number

21-1272, Fig. 4B). By contrast, ZrO_2/TiO_2-CNTs complexes doped at 1:1 ratio have diffraction peaks of both monoclinic ZrO_2 (JCPDS number 72-597) and anatase TiO_2 (Fig. 4C). Finally, when ZrO_2 and TiO_2 are doped at 4:1 molar ratio, only the monoclinic ZrO_2 diffraction peaks can be observed (Fig. 4D). When $n(ZrO_2)$: $n(TiO_2)$ = 1:5 ~ 1:10, the relatively high content of ZrO_2 may inhibit phase transition of TiO_2 crystallites, ending up with anatase TiO_2. When $n(ZrO_2)$: $n(TiO_2)$ = 1:100-1:1000, the relatively low content of ZrO_2 may fail to inhibit phase transition from anatase (Fig. 5D) to rutile (Fig. 5C) TiO_2, at relatively low temperature (200 ºC).
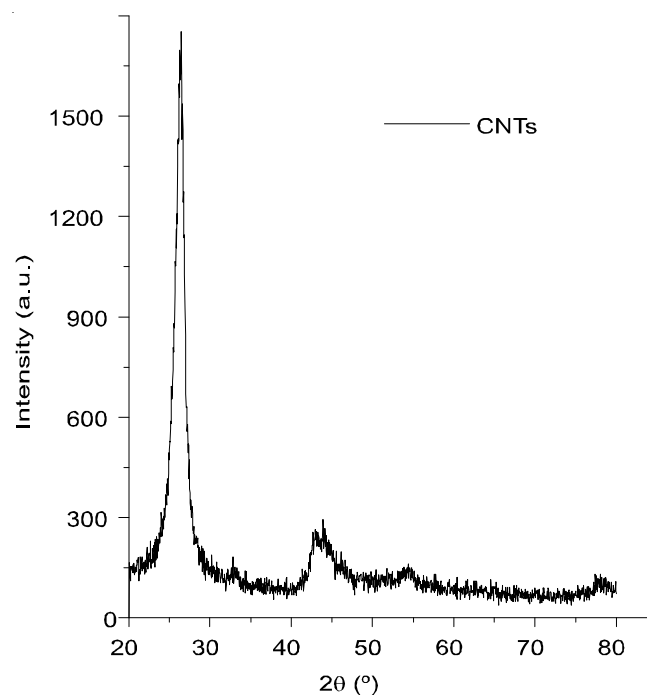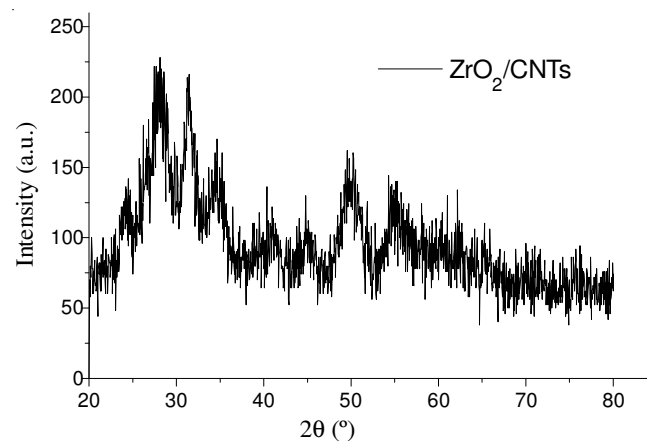

Fig. 2. XRD of carbon nanotubes

Fig. 3. XRD of ZrO_2-carbon nanotubes

Morphologies of ZrO_2, carbon nanotubes, ZrO_2-CNTs and ZrO_2/TiO_2-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-
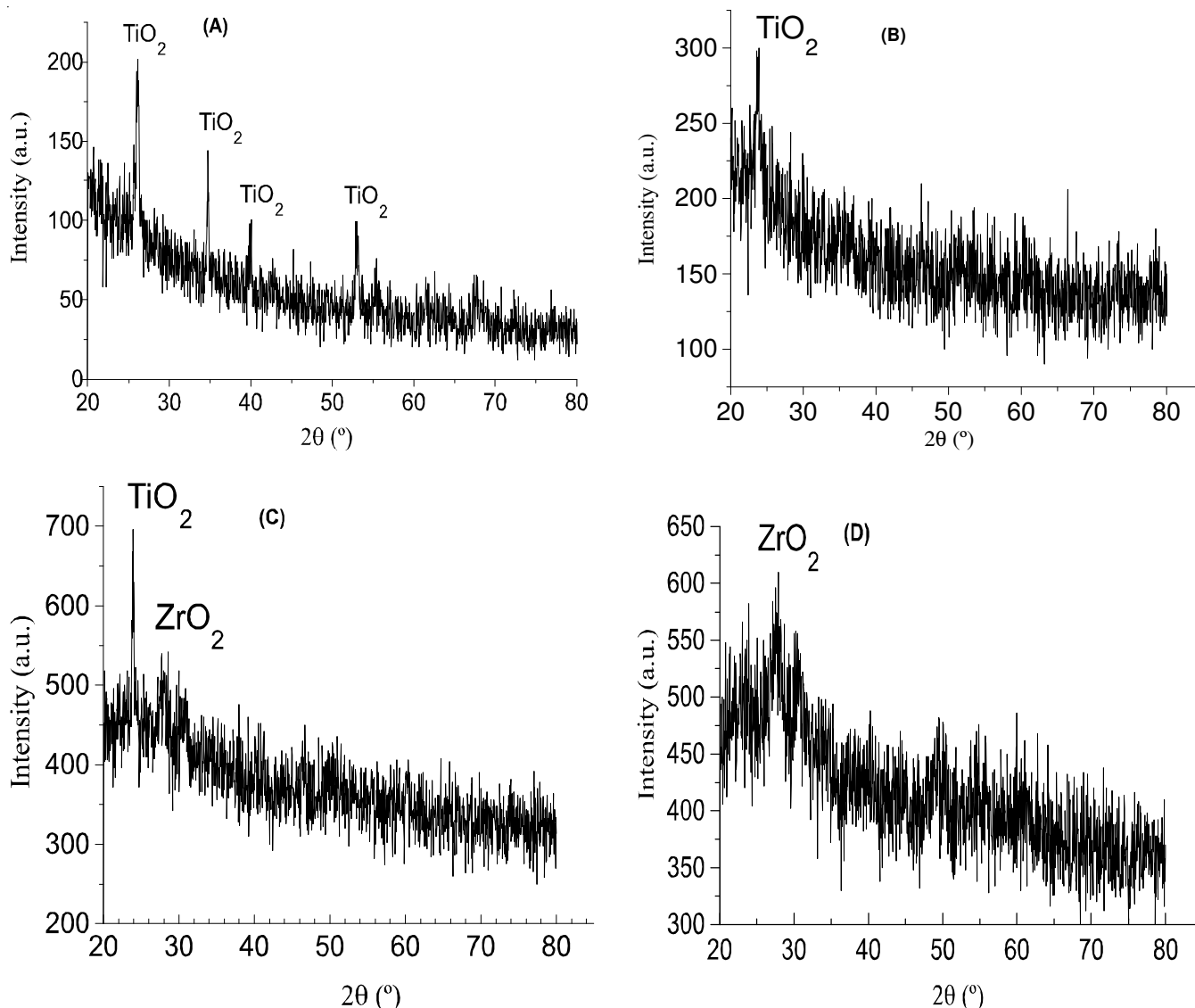
Fig. 4.   XRD patterns of ZrO₂/TiO₂-CNTs nanoparticle complexes of different composition, n(ZrO₂):n(TiO₂) = (A) 1:100-1:1000, (B) 1:5-1:10, (C) 1:1 and (D) 4:1

tically dark colour, whereas ZrO₂-CNTs complexes have white tubular structures, presumably caused by ZrO₂ adsorption upon carbon nanotubes' surface (Fig. 5B). ZrO₂/TiO₂-CNTs complexes doped with 0.1 % ZrO₂, on the other hand, have dark coloured and agglomerated columnar grains, which is typical morphology of rutile TiO₂ crystallites (Fig. 5C). In contrast, when ZrO₂/TiO₂-CNTs complexes are doped with 10 % ZrO₂, carbon nanotubes are coated homogeneous with globular ZrO₂/TiO₂ nanoparticles on the surface (Fig. 5D), characteristics of anatase TiO₂ crystallites. Collectively, our TEM results are consistent with our XRD data where TiO₂ is in the rutile phase when doping ratio n(ZrO₂) : n(TiO₂) is less than 1:10 (Fig. 4A), while TiO₂ 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 TiO₂ 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 TiO₂[8-10], yet in this study our data have revealed that doping content of ZrO₂ is playing a major role under

moderate temperatures like 200 °C. When doping ratio (nZrO₂:nTiO₂, hereafter) is less than 1:10, ZrO₂ dopes into TiO₂ lattice, forming stable TiO₂ solid solution. As ZrO₂ content drops, phase transition occurs from anatase TiO₂ (Fig. 4B) to rutile TiO₂ (Fig. 4A). This is probably because Zr⁴⁺ has similar radius (79 pm) to that of Ti⁴⁺ (68 pm). As proposed previously, doping cations have easier access to lattice gaps or have higher tendency to replace Ti⁴⁺ when they have similar radius as Ti⁴⁺, giving rise to homogeneous distribution in TiO₂ crystallites. Lower content of doping Zr⁴⁺ defuses among TiO₂ 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 TiO₂ to initiate phase transition.

When doping ratio is 1:1, diffraction peaks unique to monoclinic ZrO₂ and anatase TiO₂ can be observed, suggesting the possibility that equal amount of ZrO₂ and TiO₂ form solid solution and mixed crystallites (Fig. 4C).

When doping ratio is larger than 1:1, excess ZrO₂ renders Ti⁴⁺ to be the doping cation, which enters into ZrO₂ lattice and
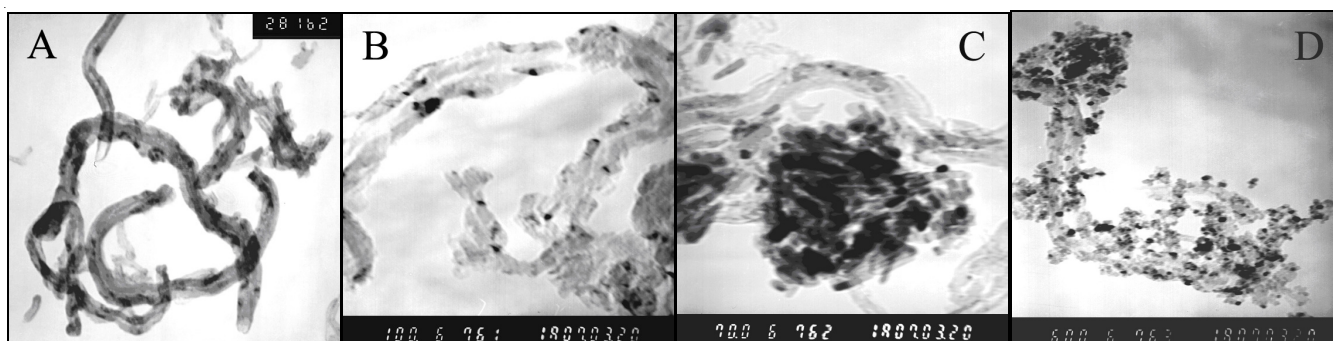
Fig. 5. TEM images of ZrO₂/TiO₂-CNTs nanoparticle complexes of different composition, (A) carbon nanotubes alone (50000X), (B) ZrO₂-CNTs (100000X), (C) ZrO₂/TiO₂-CNTs complexes doped with 0.1 % ZrO₂ (70000X), (D) ZrO₂/TiO₂-CNTs complexes doped with 10 % ZrO₂ (60000X)

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 ZrO_2/TiO_2-CNTs nanoparticle complexes with hydrothermal synthesis under 200 ºC. When $n(ZrO_2) : n(TiO_2) > 1:1$, only the diffraction peaks of ZrO_2 can be observed; When $n(ZrO_2) : n(TiO_2) = 1:1-1:10$, ZrO_2 can inhibit the phase transition of TiO_2, giving rise to globular anatase TiO_2, which makes it easier for ZrO_2/TiO_2 complex to be adsorbed to carbon nanotubes; When $n(ZrO_2) : n(TiO_2) = 1:100-1:1000$, phase transition of TiO_2 occurs under 200 ºC, from anatase to rutile TiO_2, making the ZrO_2/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 ZrO_2/TiO_2 nanoparticle complexes upon the surface of carbon nanotubes.

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