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Synthesis and Performance for Hydrogen Production of Carbon Nanotubes-ZnTHPP-TiO_2 Nanocomposite Catalyst†

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Using carbon nanotubes (CNTs) as temperate, CNTs-ZnTHPP-TiO_2 nanocomposite was prepared by sol-gel method. Its structure was characterized by XRD, TEM and EDS. The UV absorbing property was detected by the UV spectrophotometer. The results showed that nanocomposite was composed of carbon nanotube coated evenly by ZnTHPP-TiO_2 particles, with diameter of 50-60 nm. ZnTHPP increases the visible light absorbable range of TiO_2 significantly. As photocatalyst, CNTs-ZnTHPP-TiO_2 nanocomposite has better performance for hydrogen production under irradiation of visible light and the rate of hydrogen production is the highest when the content of carbon nanotube is 40 %.

Key Words: Carbon nanotubes-ZnTHPP-TiO_2 nanocomposite, Sol-gel method, Hydrogen production.

INTRODUCTION

Hydrogen has attracted much attention as a kind of promising energy due to its clean, renewable and non-polluting nature. Photocatalysis hydrogen production using titanium dioxide (TiO_2) as catalyst is a kind of highly promising technology[1,2]. However, TiO_2 can be activated only by UV light because of its large band gap (3.2 eV) and only the small UV fraction of solar light, about 2-3 %, can be utilized, which limits its effective application of solar energy[3,4]. Zinc porphyrin (ZnTHPP) has better stability for light and heat. It has strong absorption for sunlight. Therefore the synthesis of TiO_2 nanoparticles doped with ZnTHPP has aroused researchers' great interest[5,6].

With large specific surface area and hollow structure, carbon nanotubes (CNTs) can absorb organic substance strongly. So combining ZnTHPP-TiO_2 nanoparticles with CNTs is expected to produce a new kind of material which can be used as photocatalyst under visible light irradiation.

In this paper, using CNTs as temperate, ZnTHPP-TiO_2 nanocomposite was prepared by sol-gel method. The performance for hydrogen production under irradiation of visible light was investigated using CNTs-ZnTHPP-TiO_2 nanocomposite as photocatalyst.

EXPERIMENTAL

Preparation and Purification of carbon nanotubes: Carbon nanotubes was synthesized by the catalytic decomposition of acetylene using Co-Mo mixtures supported on zeolite as catalysts[7]. Then purified by mixing acid (H_2SO_4 and HNO_3 was 3:1), refluxing 6 h, following by filtration and thoroughly washing with deionized water until pH = 7.

Preparation of CNTs-ZnTHPP-TiO_2 nanocomposite: CNTs-ZnTHPP-TiO_2 nanocomposite was prepared by sol-gel method. Firstly, 1.4 mL pyrrole, 2 mL benzaldehyde, 75 mL propanoic acid and CNTs with different ratio were mixed. After dispersing for 0.5 h by ultrasonic, $Zn(OAc)_2{\cdot}2H_2O$ with appropriate ratio was added. The resulting mixture being stirred 20 min, 34 mL tetra-butyl titanate ($Ti(OBu)_4$) was added and formed sol. Set for 5d, the sol became gel. Dried the gel 12 h under vacuum, then calcined 4 h under 400 ºC. The CNTs-ZnTHPP-TiO_2 nanocomposites named sample $0^{\#}$-$5^{\#}$ according to content of CNTs had been got (the mole ratio of CNTs and $Ti(OBu)_4$ is 0, 20, 40, 60, 80 and 100 %, respectively).

Determination of photocatalytic activity: Photocatalytic decomposition of water was carried out in an inner irradiation closed gas circulating flask-shaped Pyrex reaction cell system. With the solution being stirred, 0.05 g catalyst was dispersed

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in 60 mL mixture of 1.25 g Na_2S and 0.25 g Na_2SO_3. A 300W xenon lamp was used to give visible light. Argon was used to remove traces of oxygen and moistures. Irradiation started after the suspension had been mixed. Every hour, the hydrogen and the oxygen evolved were collected in a Tedlar bag and analyzed with a gas chromatograph (HP 6890C).

RESULTS AND DISCUSSION

The XRD patterns of products are shown in Fig. 1. Curve 1 is the XRD patterns of sample 0# showing the characteristic peaks of ZnTHPP and TiO_2. Curve 2-3 are the XRD patterns of CNTs-ZnTHPP-TiO_2 and also shows the peaks of ZnTHPP and TiO_2. Because the peaks of CNTs and of TiO_2 are overlapped, so there no peaks of CNTs in curve 2-3. The peaks of ZnTHPP and TiO_2 become weaker from curve 1 to curve 3, because of the content of CNTs increasing and the content of ZnTHPP and TiO_2 accordingly decreasing.

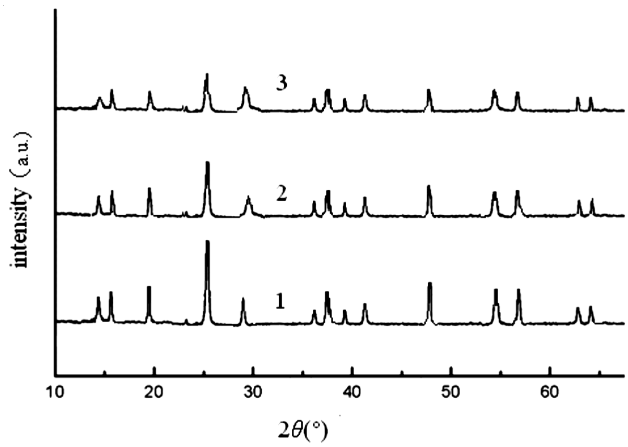
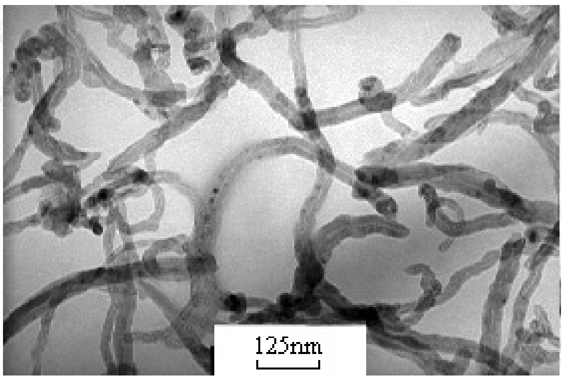
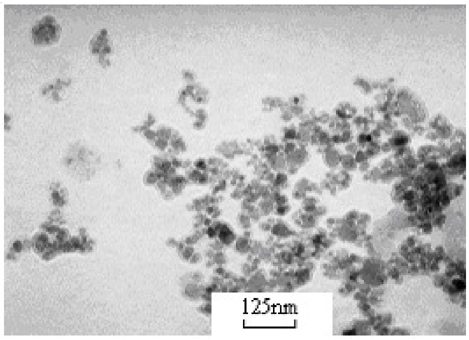


Fig. 1. XRD pattern of samples. 1-sample 0# (0 % CNTs) 2-sample 2# (40 % CNTs) 3- sample 5# (100 % CNTs)

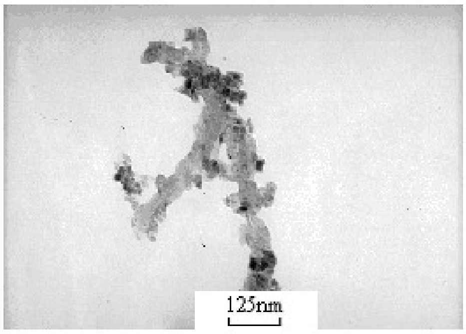
TEM images of carbon nanotube, sample 0#, sample 3# and sample 5# are, respectively shown in Fig. 2. The diameter of carbon nanotube is about 20-30 nm and the wall is smooth. Sample 0# is ZnTHPP-TiO_2 with the size of 20-30 nm. When CNTs was added to the synthesis system, ZnTHPP-TiO_2 disposed on the wall of CNTs, thus the wall of CNTs became coarser and wider, with diameter about 50-60 nm. With the content of CNTs increasing, the content of ZnTHPP-TiO_2 decrease, so the particles disposed on the wall of CNTs decrease, just as shown in the TEM of sample 5#.



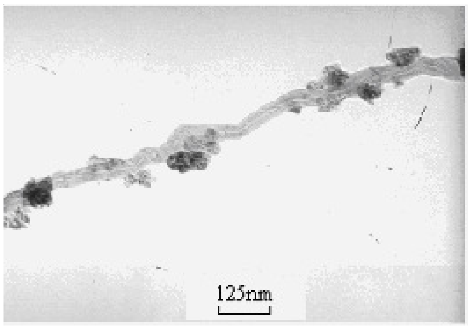
CNTs



0#



2#



5#

Fig. 2. TEM images of the samples. 0#- ZnTHPP-TiO_2, 2#-40 % CNTs-ZnTHPP-TiO_2, 5#- 100 % CNTs-ZnTHPP-TiO_2

Fig. 3 is EDS spectrum of sample 3. It shows that the sample is composed of C, Ti, O. Because the content of ZnTHPP is too low (the mole ratio of ZnTHPP and TiO_2 is 1 %), there is no peak of N and H in Fig. 3.

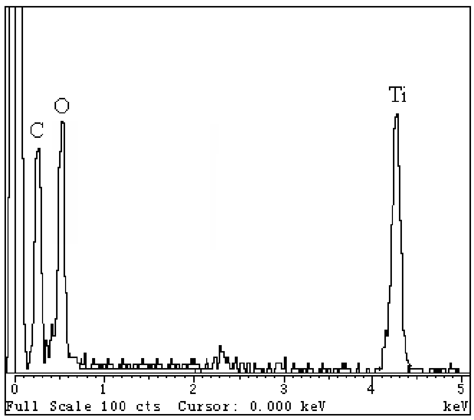


Fig. 3. EDS of the sample 3#

UV-VIS absorbance spectra of the samples are given in Fig. 4. It shows that these samples have absorption peaks in 420 nm, which is the absorption peak of B band in ZnTHPP and also have absorption peaks in 564 and 615 nm, which are the absorption peaks of Q(1, 0), Q(0, 0) in ZnHTPP. Compared with ZnTHPP-TiO_2, 40 % CNTs-ZnTHPP-TiO_2 has more absorption in visible light. Therefore CNTs-ZnTHPP-TiO_2 nanocomposite has stronger photocatalysis activity for visible light than ZnTHPP-TiO_2.

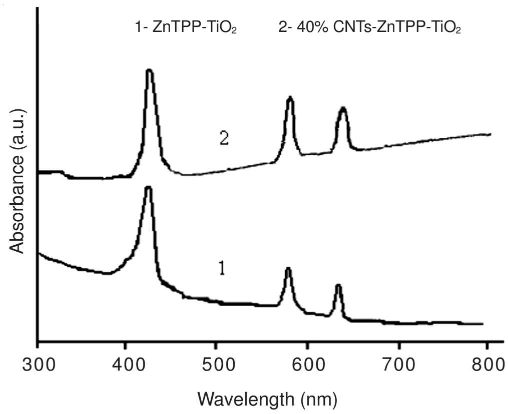


Fig. 4. UV-VIS spectrum of samples

Fig. 5 is the hydrogen production curve using sample 0#-5# as photocatalyst. Fig. 5 shows that it almost doesn't produce hydrogen under the irradiation of visible light when using P25 as catalyst. When doped with ZnTHPP, catalyst has some photocatalysis activity for visible light, it can produce hydrogen under the irradiation of visible light when using 0# (ZnTPP-TiO_2 composite) as catalyst. When added CNTs, the catalyst has higher photocatalysis activity for visible light. The rate of hydrogen production is the highest when the content of CNTs is 40 % (Fig. 5).

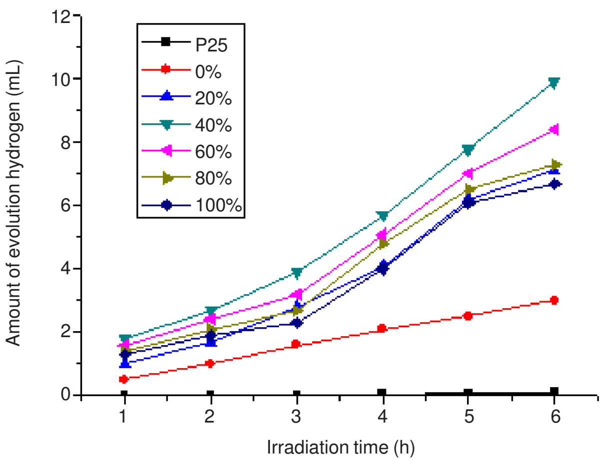


Fig. 5. Hydrogen production curves under visible light irradiation

Carbon nanotubes has larger surface area and hollow structures. Using CNTs as temperate, ZnTHPP-TiO_2 particles deposits on the CNTs surface. TiO_2 produce electron and hole pairs (e^-/h pairs) under light irradiation. When TiO_2 attaches to CNTs, due to the strong interfacial connection between TiO_2 and CNTs, the excited e^- of the conduction band of TiO_2 can migrate to CNTs. Thus the recombination of the e^-/h pairs is retarded. Meanwhile, CNTs has larger surface area, therefore ZnTHPP can easily be adsorbed on the surface of CNTs. When the content of CNTs is less than 40 %, the rate of hydrogen production increases with the content of CNTs increasing. When the content of CNTs is more than 40 %, CNTs twists each other, which enhances the chance that electrons collided each other and benefit for e^-/h pairs to recombine. At the same time, with the content of CNTs increasing, the content of ZnTHPP-TiO_2 accordingly decreases. Therefore the rate of hydrogen production decreases.

Conclusion

Using CNTs as temperate, CNTs-ZnTHPP-TiO_2 nanocomposite was prepared by sol-gel method. Nanocomposite is composed of carbon nanotubes coated evenly by ZnTHPP-TiO_2 particles, with a diameter of 50-60 nm. UV-VIS spectra indicates that as-prepared nanocomposite has absorption of visible light. There is the highest rate of hydrogen production using 40 % CNTs-ZnTHPP-TiO_2 nanocomposite as catalyst.

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