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Sol-Gel Fabrication and Photocatalytic Properties of Indium Oxide-CNT Composite

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Abstract

Carbon nanotube-In_2O_3 nanocomposites were synthesized by sol-gel method with the help of ultrasonic radiation. The samples were characterized by X-ray diffractometer, transmission electron microscopy and energy dispersive spectrometer. The UV absorbing properties were detected by the UV spectrophotometer. Photo degradation of methylene blue in aqueous solution was investigated by using CNT/In_2O_3 nanocomposite as photocatalyst. The results showed that nanocomposites were composed of carbon nanotubes coated evenly by In_2O_3, with diameter of 50-60 nm. UV-visible spectrum indicated that the as-prepared CNT/In_2O_3 nanocomposite had absorption of visible light as well as ultraviolet light. 40 % carbon nanotube (molar radio of carbon nanotube to $InCl_3 \cdot 4H_2O$) nanocomposite had the highest degradation rate for methylene blue under the sunlight irradiation.

Keyword: Carbon nanotube-In_2O_3 nanocomposites, Sol-gel method, Photocatalytic property

1. Introduction

Azo dyes are the most widely used synthetic dyes and typically are major pollutants in dye waste waters [1,2]. Owing to their toxicity and slow degradation, they are categorized as environmentally hazardous materials. Photocatalytic oxidation is an alternative means of completely degrading azo dyes. Semiconductive indium oxide (In_2O_3) with a wide bandgap (direct bandgap around 3.6 eV at room temperature) has attracted much attention in recent years, owing to its potential applications in solar cell [3], lithium-ion battery [4], biosensor [5], gas sensor optoelectronics [6] and photocatalysis [7]. Used as photocatalytic degradation materials, In_2O_3 can only work under UV irradiation because of its wide band gap and can only absorb UV light. Thus treatment cost is large, explaining the need to develop more efficient and economic methods, which consume less chemical and energy. Therefore In_2O_3 based materials capable of visible light photocatalysis are required. Due to their unique physical and chemical properties, carbon nanotubes have broad applications in nanoelectronics [8], catalysis [9], sensors [10], etc. Carbon nanotube based nanocomposite has aroused researchers' great interest because of its potential application in many areas. With large specific surface area and hollow structure, carbon nanotubes can absorb organic substance strongly. Thus, combining In_2O_3 nanoparticles with carbon nanotubes is expected to produce a new kind of material which can be used as photocatalysis under visible light irradiation. In this paper, using carbon nanotube as temperate, carbon nanotube/In_2O_3 nanocomposite was prepared by sol-gel method. Photo degradation of the methylene blue in aqueous

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solution under visible light was investigated by using carbon nanotube/In_2O_3 nanocomposite as photocatalyst.

2. Experimental

2.1 Preparation of sample

Carbon nanotube was synthesized by the catalytic decomposition of acetylene using Co-Mo mixtures supported on zeolite as catalysts. It was purified by refluxing 6 h in mix acid (mole ratio of H2SO4 and HNO3 was 1:3), followed to be filtrated and thoroughly washed with deionized water until pH = 7. Carbon nanotube/In_2O_3 nanocomposite was prepared by sol-gel method. All the chemicals used were analytical grade reagents. Firstly, 0.2 mmol InC_{13}.4H2O, 2 mg polyethylene glycol (PEG) 2000 were dissolved in 50 mL mixture solution (volume ratio of water to alcohol was 1:1) under vigorous stirring, then 0 mg, 0.24 mg, 0.48 mg, 0.72 mg, 0.96 mg, 1.2 mg carbon nanotube (corresponding to molar radio of carbon nanotube to $InCl_3.4H_2O$ being 0 %, 10 %, 20 %, 30 %, 40 %, 50 %) were respectively added. After dispersed for 0.5 h under ultrasonic radiation, aqueous ammonia was added dropwise to maintain pH = 8. Carbon nanotube/In_2O_3 sol had been obtained. Set for 8 h, the sol changed into gel. Dried the gel for 10 h in vacuum, then calcined 4 h at 500 ºC. A series of CNT/In_2O_3 nanocomposites named as the sample 0#-5# (corresponding to molar radio of Carbon nanotube to InC_{13}.4H2O being 0 %, 10 %, 20 %, 30 %, 40 %, 50 %) had been obtained. The phase of products was determined by D5005 X-ray diffractometer, with CuK_a radiation. The size and morphology of products was determined by HitachiH-7500 transmission electron microscopy. The kind of element was determined by XFORD INCA25 energy dispersive spectrometer. The UV-visible absorption spectroscopy was studied by UV-2100 spectrophotometer.

2.2 Degradation for methylene blue:

Added CNT/In_2O_3 nanocomposite to 30 mL aqueous solution of methylene blue. After stirred for 10 min, the mixture solution was placed outside the room and irradiated for 0.5 h by sunlight. Separating the solid by centrifugalization, the absorbance of the resulting solution was determined by UV-2100 spectrophotometer. The degradation rate of methylene blue was calculated according to the formula:

$$R\ (\%) = (A_0 - A)/A_0 \times 100\ \%$$

where A0 and A respectively referred to the absorbance of methylene blue before and after irradiated.

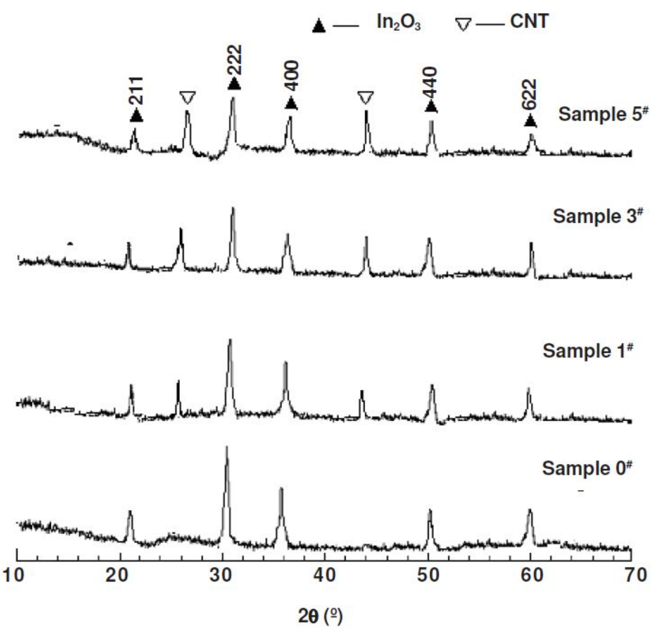

Figure 1. XRD patterns of the samples

3. Result and Discussion

The XRD patterns of products are shown in figure 1. Curve 1 shows the characteristic peaks of the cubic structure In_2O_3 (JCPDS card No. 74-1990©). Curve 2-4 shows the peaks of In_2O_3 and carbon nanotube. These peaks are similar except the peak intensity of carbon nanotube. TEM images of carbon nanotube, sample 0#, sample 3# and sample 5# are respectively shown in figure 2. The diameter of carbon nanotube is about 20-30 nm and the wall is smooth. Sample 0# was prepared without carbon nanotube in the synthesis system, being pure In_2O_3, with the size of 40-50 nm. When carbon nanotube was added to the synthesis system, In_2O_3 disposed on the wall of carbon nanotube, therefore the wall became coarser and wider, with diameter about 50-60 nm. Optical property was studied by using UV-visible absorption spectroscopy. The room temperature UV-visible absorbance spectra of the samples, which were ultrasonically dispersed in absolute ethanol (figure 4).

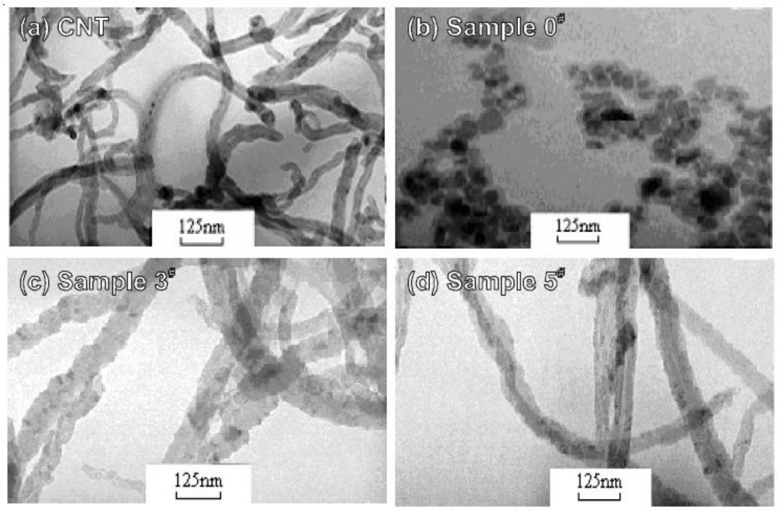

Figure 2. TEM images of the samples

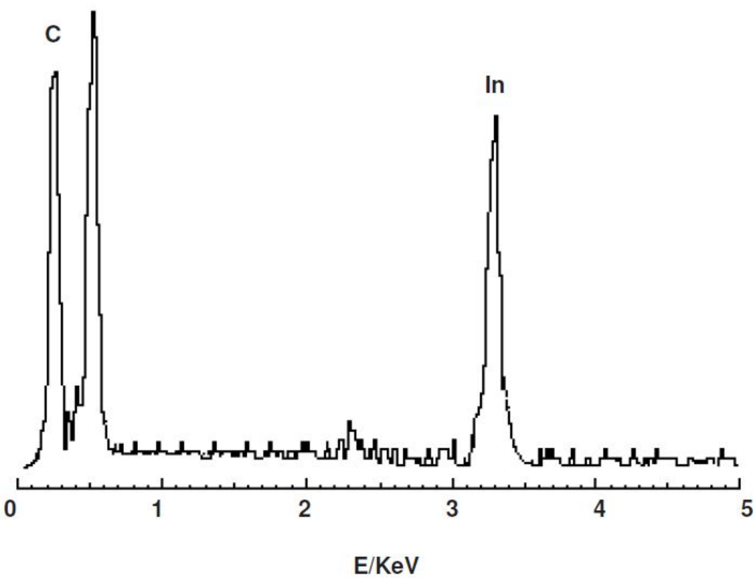

Figure 3. EDS of the sample 3.

These spectra were corrected for the solvent contribution. Figure 4 shows that these samples have absorption almost in the whole violet light and visible light region. With carbon nanotube content increasing, peaks have blue shift from 365 to 330 nm and also its intensity increased, due to the absorption of carbon nanotube. Blue shift of the peak means that there are more electron and hole pairs when light illuminates samples. So CNT/In_2O_3 nanocomposite has stronger oxidation reduction potential and stronger photocatalysis activity. figure 5 showed the degradation rate curves of methylene blue using sample 0#-5# as photocatalyst, concentration of methylene blue being 20 mg/L, dosage of catalyst being 10 mg. figure 5 shows that the degradation rate of methylene blue is highest when the content of carbon nanotube is 40 %. The reason why In_2O_3 has photocatalytic property is that In_2O_3 can produce electron and hole pairs (e−/h pairs) under light irradiation. When In_2O_3 attaches to carbon nanotube, due to the strong interfacial connection between In_2O_3 and carbon nanotube, the excited e− of the conduction band of In_2O_3 can migrate to carbon nanotube, which is relatively good electron acceptors. So the recombination of the e−/h pairs is retarded, which results in the promotion of photocatalytic activity in CNT/In_2O_3 nanocomposite. Meanwhile, carbon nanotube has larger surface area, so O2 can easily be adsorbed on the surface of carbon nanotube and accepts e- to form more OH, which is very reactive to eliminate organic molecules. So when the content of carbon nanotube is less than 40 %, the degradation rate of methylene blue increases with the content of carbon nanotube increasing.

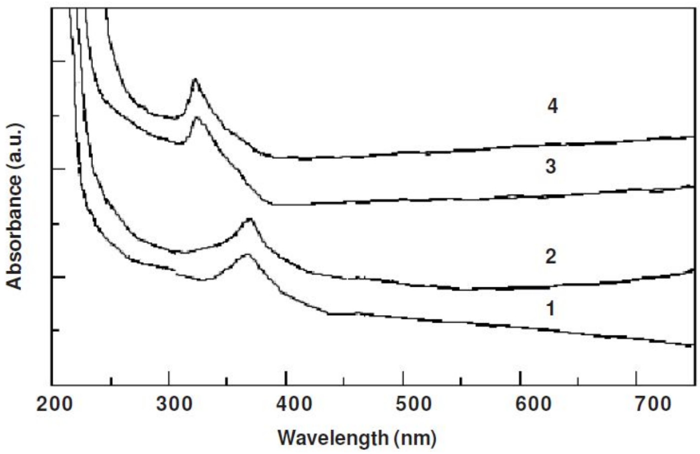

Figure 4. UV-visible absorption spectra of samples

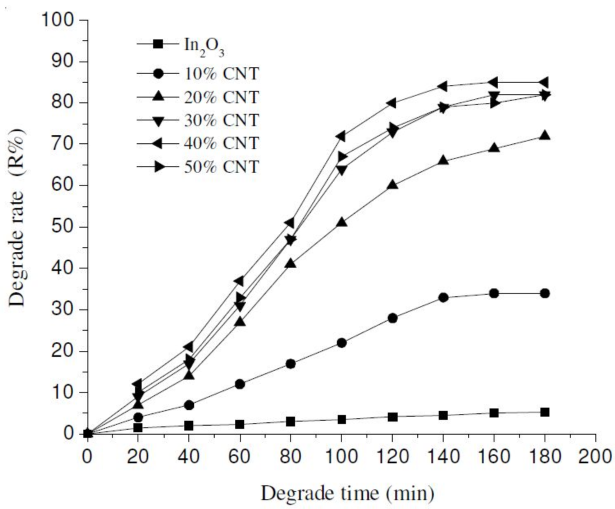

Figure 5. Degradation rate curves of CNT/In2O3 for methylene blue

When the content of carbon nanotube is larger than 40 %, carbon nanotube twists each other, which enhances the chance that electrons collided each other and benefit for e−/h pairs to recombine. So the degradation rate of methylene blue decreases. Conclusion using carbon nanotube as a template, CNT/In_2O_3 nanocomposite was synthesized by a sol-gel method. Nanocomposite is composed of carbon nanotubes coated evenly by In_2O_3 particles. UV-visible spectra indicates that CNT/In_2O_3 nanocomposite has absorption of visible light as well as ultraviolet light. With carbon nanotube content increasing, the peak has blue shift and its intensity increases. There is best degradation effect for methylene blue under sunlight irradiation using 40 % CNT/In_2O_3 nanocomposite as catalyst.

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