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Comparison of optical properties and photocatalytic behavior of TiO2/MWCNT, CdS/MWCNT and TiO2/CdS/MWCNT nanocomposites



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ABSTRACT

In this paper CdS nanoparticles has been synthesized by hydrothermal method, TiO₂ nanoparticles by sol-gel and TiO₂/MWCNT, CdS/TiO₂/MWCNT and CdS/MWCNT composites were synthesized in two steps for controlling the size of nanoparticles. The first one has involved the synthesis of CdS and TiO₂ nanoparticles then the addition of carbon nano tube to them in the second step. XRD and FTIR analyses were done for structure study and SEM used for nanocomposite morphology investigation. EDAX element analyses confirmed the success of nanocomposite synthesize. Optical properties of MWCNT were enhanced by adding CdS and TiO₂ that PL and UV-vis analyses confirm it. These composites Also have good photocatalytic characteristics.

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1. Introduction

Based on recent examinations water pollution is a global issue [1]. Nowadays environment and cleaning it converted to an important issue for human due to the industrialization of countries and the proliferation of pollution caused from wastewater of factories and vehicles metropolises etc [2,3]. So far many steps have been taken for cleaning the environment around the world. One of the newest methods is the use of materials that are activated by sunlight and ultraviolet rays, called photocatalysts [4].

In addition to flexibility in eliminating various kind of bacteria and another contamination photocatalyst usage also compared to another method economically [5,6]. It is also necessary to purification microbial contaminate drinking water. Utilizing photocatalytic materials based on nano catalyst is a very promising way for perfect elimination of water pollution [7–10]. Many different suitable photocatalysts have been proposed in various researches. Some of them, alone and some composites have the good photocatalytic characteristic [11–14]. Titanium oxide and cadmium sulfide can be mentioned as nanoparticles that most commonly used for photocatalytic application [15–17]. Nanoparticles are much more effective than large molecules are there in photocatalysts. On the other hand, a new category of materials is nonorganic- carbon nanotube-hybrid that have attracted a lot of attention because of their excellent optical, mechanical, electrical and thermal properties in recent years [18]. Therefore the purpose of this study was to synthesize TiO₂/CdS/MWCNT composite and comparison the

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photocatalytic application of this composite with $TiO_2/MWCNT$ and CdS/MWCNT composites. TiO_2 and CdS are chemically stable with high ability to break down the bonds in the molecule [19]. Also, these materials are not rare and expensive. So there are a lot of fast and inexpensive different methods for synthesizing the nanoparticles of these materials. Ultra violet ray has required to activation TiO_2 and CdS [20,21]. The results of the recent research are shown that various contaminants can be destroyed by nanoparticles of TiO_2 and CdS successfully [22,23]. The results also compare the mechanism of TiO_2 and CdS in nano and micro scale and show that photocatalytic characterization has been greatly enhanced by using nanoparticles. In this research nanoparticle of TiO_2 and CdS was synthesized by hydrothermal method and in second step this product has been added into carbon nanotube by using stirrer. Although this synthesize was possible in one step but these composites were synthesized in two steps to control the size of nanoparticles.

In addition of enhancement in photocatalytic properties of carbon nanotube, the optical properties of these composites have improved by adding TiO₂ and CdS nanoparticles because these nanoparticles have good optical properties.

2. Experimental

2.1. Materials and instruments

In this study, 3CdSO4.8H2O, Na2S.6H2O, thioglycolic acid (TGA), titanium isopropoxide (C12H28O4Ti) and acetic acid were purchased from Merck and MWCNT was purchased from sigma Aldrich. All of the materials were used without additional purification. Deionized water was used as a solvent. The PW1800 Philips Netherlands was used for determination of crystallite structural. FTIR spectroscopy was done with Bruker Tensor 27 set in the range 4000 400 nm. The EDX and UV Vis analysis was done by Hitachi su3500 and Cary 300 version 9.00 set, respectively.

2.2. Photocatalytic experiment

Methylene blue photo degradation was done under UV radiation. The source of UV light was UV-Philips $96 \, \text{W}$, $2500 \, \text{cm}^{-1}$. To determine the photocatalytic property of these samples, $20 \, \text{mL}$ solution of $10 \, \text{ppm}$ Mb has been prepared in $25 \, \text{mL}$ glass at first. Then $0.01 \, \text{g}$ of the composite was added to this solution. This mixture was stirred by a magnetic stirrer in dark for $40 \, \text{min}$ until achievement the adsorption-desorption dye equilibrium on the surface. Then this solution should rest under ultraviolet ray for $30 \, \text{min}$ again. The reactions took place in room temperature by uniform stirring. The solution was analyzed by UV-vis spectrophotometer in all steps. Dye concentration determined in solution by this method. Therefore there are three spectra for each sample. The first one is related to Methylene blue absorption, the second is absorption in dark and the third is related to photocatalytic degradation that it's percentage expressed by the following equation. C_0 is Mb primary concentration after equilibrium achievement in dark and C is dye concentration after the period that the sample was exposed to ultraviolet light.

$$E\% = \frac{C}{C_0}$$

$$E\% = \frac{C_0 - C_c}{C_0}$$

2.3. Synthesis of nanoparticles and nanocomposites

2.3.1. Synthesis of CdS nanoparticles

 $50\,\mu\text{L}$ TGA was added to 0.01 M CdSO4 aqueous solution and stirred for 10 min. Then 0.01 M Na2S.6H2O aqueous solution was added drop by drop and stirred for 10 min. The final aqueous solution was transferred to stainless steel batch reactor and was placed under hydrothermal reaction at $140\,^{\circ}\text{C}$ for 30 min. In the final stage, the obtained precipitate was separated by centrifuge technique and washed with deionized water and ethanol for 3 times and dried at $60\,^{\circ}\text{C}$ for 6 h.

2.3.2. Synthesis of TiO2 nanoparticles

TiO2 nanoparticles are synthesized by sol-gel method. First, $20\,\text{mL}$ titanium isopropoxide is added to $40\,\text{mL}$ acetic acid and is stirred on a magnetic stirrer for $15\,\text{min}$ for obtaining a homogeneous solution. Then $120\,\text{mL}$ deionized water is added to solution drop by drop and stirred for $2\,\text{h}$. A gel is formed when the solution is placed in the oven at $90\,^\circ\text{C}$ for $12\,\text{h}$. Yellow powder is obtained by drying the gel at $200\,^\circ\text{C}$ for $2\,\text{h}$. Then powder is pulverized in a porcelain mortar and is done calcination operation at $400\,^\circ\text{C}$ for $4\,\text{h}$.

2.3.3. Synthesis of TiO2/MWCNT nanocomposite

First 20 mL deionized water is added to 0.01 gr MWCNT and is placed under ultrasound waves for 30 min 0.04 gr TiO2 nanoparticles are added to 20 mL deionized water and stirred by using magnetic stirrer for 15 min then is added to MWCNT blue solution and is sonicated for 15 min. Finally, the mixture is stirred by a magnetic stirrer for 18 h then is done centrifuge and the precipitation is dried in oven at $50\,^{\circ}$ C for 2 h.

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