

Hydrothermal synthesis and highly visible light-induced photocatalytic activity of acid functionalized MWCNTs as support for ZnS-photosensitized TiO₂ catalysts

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Nanoscale ZnS-photosensitized TiO₂ particles supported on acid functionalized multi-wall carbon nanotubes (MWCNTs) were prepared via a mild hydrothermal route. The new optical properties and porous structure of the as-prepared samples were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), BET surface area analysis, UV-vis DRS and X-ray diffraction (XRD). The photocatalytic activities of the composite catalysts were evaluated by the decomposition of an MB solution under visible light irradiation. The results indicate that the addition of an appropriate amount of MWCNTs as supports for TiO₂ and ZnS efficiently inhibit the agglomeration of ZnS/TiO₂ thus improving the dispersion of nanoparticles and the activity of visible photodegradation was remarkably improved.

Key words: ZnS, MWCNTs, TiO₂, Visible-light photocatalysis, Methylene blue.

Introduction

Modifying TiO₂ photocatalysts to enhance light absorption and photocatalytic activity under visible light irradiation becomes a main research direction in recent years. To improve the response of TiO₂ to visible light, transition metal [1] or non-metal atom [2] doped TiO₂ or metal complex [3] sensitized TiO₂ have been developed. Additionally, among various non-metal modified titania, carbon-containing composite titania has been reported as a type of promising photocatalyst. Kisch and co-workers [4-5] reported that carbon containing titania prepared by a modified sol-gel process using different alkoxide precursors was able to photo degrade *p*-chlorophenol under visible light ($\lambda > 400$ nm). Treschev et al. [6] found carbon-containing TiO₂ nanoparticles prepared under calcinations at 200 °C exhibited high photocatalytic activity for decoloring of methylene blue and the removal of nitrogen monoxide under visible light illumination. Kang et al. [7] synthesized C-doped TiO₂ powders by grinding TiO₂ in ethanol and heat treatment and this C-doped TiO₂ photocatalyst showed a good visible light activity for NO gas decomposition. Chen and co-workers [8] synthesized C-doped TiO₂ micronanospheres and nanotubes via a chemical vapor deposition method and they claimed that carbon doping led to lower band gap and higher photocurrent than TiO₂ P₂₅ under visible light irradiation.

On the other hand, an alternative approach for achieving this objective is to couple TiO₂ by using a narrow band gap semiconductor with a higher conduction band (CB) than that of TiO₂. It has been reported that the development of the coupled semiconductors with nanometre sizes is one of the effective approaches to prepare photocatalytic materials that can utilize the sunlight effectively. In addition, these coupled semiconductors including MS/TiO₂ (M = Pb, Zn, Cd) also exhibit fine optical properties (absorption and photoluminescence) compared with the corresponding bulk ones due to the quantum confinement effects [9]. ZnS is an important II-VI semiconductor and can be applied in cathode-ray tubes (CRTs) [10], luminescence materials [11], infrared windows [12], and photocatalysis [13-15]. In recent years, ZnS nanocrystals (NCs) have been extensively studied due to their unique properties and are reported to have potential as photocatalysts in environmental contaminant elimination, CO₂ reduction, and H₂ evolution [16-17]. For the sake of improving the photocatalytic efficiency of ZnS or TiO₂, nanoscale ZnS coupled TiO₂ photocatalyst has attracted a great deal of attention for potential applications such as purification of water or organic dyes [18-19]. However, as other powder photocatalysts, ZnS/TiO₂ nanoparticles have some disadvantages, such as being hard to collect, a low photocatalysis efficiency in the visible light region, a low utilization rate in practical applications owing to the fact that the generated electron/hole (e⁻/h⁺) pairs are easily recombined, meanwhile there are some dispersion problems due to this nanoparticles easily to cohere. Thus one way of improving these defects is choosing an appropriate catalyst support.

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Among the support materials, MWCNTs as a new class of nanomaterials, have drawn considerable attention for their applications as catalyst supports owing to their unique electrical properties, high chemical stability and high surface-to-volume ratio. Moreover, MWCNTs have a variety of electronic properties. They may also exhibit metallic conductivity as one of the many possible electronic structures. MWCNTs have a large electron-storage capacity (one electron for every 32 carbon atoms) [20], the ability of MWCNTs can promote the electron-transfer reactions at carbon nanotube modified materials.

On the basis of these studies, we have attempted to prepare a novel photocatalyst. This involves TiO₂ loading on the surface of MWCNTs modified by ZnS semiconductor, which, to the best of our knowledge, was not reported before. To explore the synergism induced after TiO₂ and ZnS nanoparticles are adsorbed on the MWCNTs surfaces, their structural characteristics were characterized by X-ray diffraction (XRD), UV-vis absorbance spectra, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and nitrogen adsorption Brunauer-Emmett-Teller (BET) specific surface area analyzer. Methylene blue (MB) was selected as the model reactant the photocatalytic activities of ZnS/TiO₂/MWCNTs irradiated by visible light were investigated, and the kinetics and mechanism of photocatalysis were also studied.

Experimental

Materials

MWCNTs (95.5%) powder with a diameter and length of 20 nm and 5 μm, respectively, was purchased from Carbon Nano-material Technology Co., Ltd, Korea. *m*-Chloroperbenzoic acid (MCPBA) as an oxidized reagent purchased from Acros Organics, New Jersey, USA was used to oxidize the MWCNTs surfaces. Benzene (99.5%) and ethyl alcohol were purchased as reagent-grade from Duksan Pure Chemical Co. (Korea) and Daejung Chemical Co. (Korea), and used as received. The titanium (IV) *n*-butoxide (TNB, C₁₆H₃₆O₄Ti) as a titanium source for the preparation of ZnS/TiO₂/MWCNTs composites was purchased from Kanto Chemical Company (TOKYO, Japan). Methylene blue (MB, C₁₆H₁₈N₃·Cl·3H₂O) was of analytical grade and purchased from Duksan Pure Chemical Co., Ltd. (Korea). Zinc chloride (ZnCl₂) and sodium sulfide 5-hydrate (Na₂S·5H₂O) were used for the preparation of ZnS supplied by Daejung Chemicals & Metals Co., Ltd, Korea and Yakuri Pure Chemicals Co., Ltd, Japan, respectively.

Synthesis of ZnS/TiO₂/MWCNTs photocatalyst

Functionalization of MWCNTs

A typical synthesis experiment was used to design the ZnS/CNT composites. MWCNTs present remarkable intrinsic properties, but, for many applications in which they have to interact with or to be integrated in a given

system, it is necessary to functionalize their surfaces to obtain a higher performance. In particular, even though no specific study has yet appeared on the subject, it has been shown that functionalization should be performed to produce well-dispersed supported catalysts [21]. The purpose of these oxidative treatments is (i) to improve MWCNT interaction with solvents and dispersion; (ii) to allow the grafting of nanoparticles; (iii) to modify MWCNT adsorption properties; (iv) to perform chemical treatments on MWCNT. On the basis of this knowledge, in this study 2 g of MCPBA was dissolved in 80 ml benzene, and 1 g of MWCNTs powder was added to the oxidizing agent solution, refluxed at 353 K for 6 h to form solid precipitates and dried at 393 K. Then the treated MWCNTs were milled and washed with distilled water and ethanol, and dried at 333 K in a vacuum.

Synthesis of ZnS/CNT composites

The detailed information of ZnS/CNT (Zn²⁺-S²⁻-refluxing) preparation is described as follows: 30 mg MWCNTs were dispersed in 50 ml of ZnCl₂ solution with continuous stirring for 30 minutes, and then a stoichiometric amount of 30 ml 2.59 mmol Na₂S solution was prepared separately and injected dropwise into the above mixture with continuous stirring for 3 h at 343 K. After that, the suspension obtained was heated and refluxed for another 4 h under stirring. The final products were filtered and washed repeatedly with distilled water and ethanol and then vacuum dried at 333 K.

Synthesis of ZnS/TiO₂/MWCNTs photocatalyst

To synthesize the ZnS/TiO₂/MWCNTs composites, the ZnS/CNT composites obtained was placed into a sol containing 4 ml TNB and 40 ml benzene, homogenized at 373 K for 10 h using a shaking water bath (Lab house, Korea) at a shaking rate of 120 rpm, and dried at 393 K and after a thermal treatment at 773 K for 1 h, the ZnS/TiO₂/MWCNTs photocatalyst was obtained.

For comparison, another two types of photocatalyst, named CNT/TiO₂, and ZnS/TiO₂ were prepared using similar procedures. The preparation conditions and code of samples are shown in Table 1. Also the functionalization and reaction mechanism of MWCNTs surface coated with ZnS and TiO₂ are schematically illustrated in Fig. 1.

Photodecolorization experiments

A 200 ml glass beaker was used as a photoreactor vessel. The visible light lamp (8 W, KLD-08L/P/N,

Table 1. Nomenclatures of ZnS/TiO₂, CNT/TiO₂ catalysts and ZnS/MWCNT/TiO₂ composites samples.

Preparation method	Nomenclatures
2.59 mmol Na ₂ S·5H ₂ O+ ZnCl ₂ +4 ml TNB	ZnT
0.3 g oxidized MWCNT+4 ml TNB	CT
0.3 g oxidized MWCNT+2.59 mmol Na ₂ S·5H ₂ O+ZnCl ₂ +4 ml TNB	ZnCT

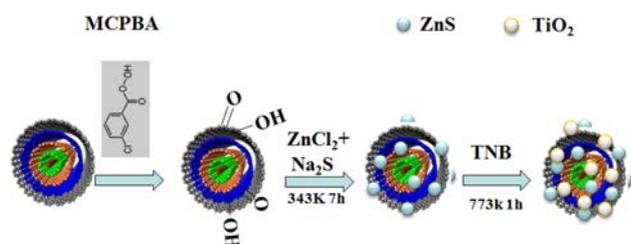


Fig. 1. Schematic of the functionalization of MWCNTs and reaction mechanism with ZnS and TNB.

Fawoo Technology) was placed 100 mm from the solution in a dark box. The initial MB concentration was chosen as 1.0×10^{-5} mol/l (c_0). 30 mg of pure MWCNT/ TiO_2 , ZnS/TiO_2 and $\text{ZnS}/\text{TiO}_2/\text{MWCNTs}$ composites were added into the reactor containing 100 ml aqueous solution of the methylene blue (MB) separately. After the photocatalysts were added into the aqueous solution under magnetic agitation for 30 minutes, the visible illumination was turned on. Air was supplied to the aqueous solution to ensure a constant supply of oxygen and promote a complete mixing of the solution and the photocatalyst, during the photoreaction. All the experiments were carried out at about 25 °C, controlled by water cooling. Three millilitres of solution were taken out using an injector and centrifuged for analysis by UV-vis spectroscopy, at different time intervals (30 minutes, 60 minutes, 90 minutes and 120 minutes). The UV-vis spectrum of the MB was recorded on a UV-vis spectrophotometer (Optizen POP, Mecasys Co., Ltd, Korea). The full spectrum (550-750 nm) of each sample was recorded and the characteristic absorption of MB at 665 nm was chosen as the monitored parameter for the photocatalytic degradation process.

Characterization of catalysts

The crystallographic structure of the inorganic constituent of the composites was examined by X-ray diffraction (XRD, Shimatz XD-D1, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda=0.154056$ nm) at room temperature. The EDX spectra were also used for elemental analysis of the samples. SEM (JSM-5200 JOEL, Japan) was used to observe the surface state and structure of the three photocatalyst composites. The Brunauer-Emett-Teller (BET) surface areas of these photocatalyst composites were determined by N_2 adsorption measured at 77 K using a BET analyzer (Monosorb, USA). Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to examine the size and distribution of the photocatalyst. The UV-VIS spectra for the MB solution degraded by CNT/TiO_2 , ZnS/TiO_2 and $\text{ZnS}/\text{TiO}_2/\text{MWCNTs}$ composites under visible light irradiation were recorded using a Genspec III (Optizen Pop Mecasys Co., Ltd., Korea) spectrometer. UV-vis diffused reflectance spectra (DRS) were obtained using an UV-vis spectrophotometer (Neosys-2000) by using BaSO_4 as a reference and were converted from reflection to absorbance by the Kubelka-Munk method.

Results and Discussion

Morphology and structure of prepared photocatalyst

The typical micro-surface structures and morphology of the ZnS/TiO_2 , CNT/TiO_2 and $\text{ZnS}/\text{TiO}_2/\text{MWCNTs}$ composites were characterized by SEM and TEM (Fig. 2). It can be observed from Fig. 2a that the ZnS/TiO_2 composite prepared mainly consists of shaped particles with smooth surfaces and has a high tendency to agglomerate. This can be attributed to that when the

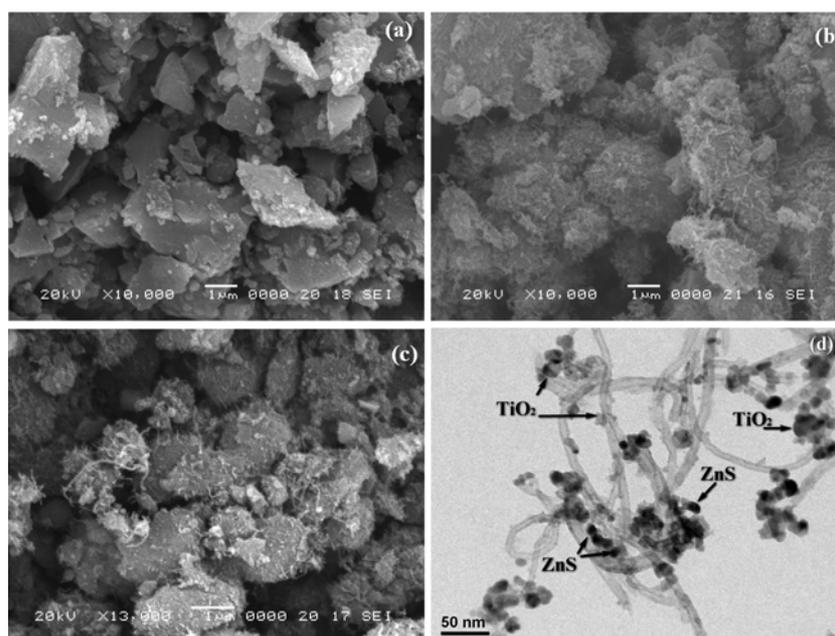


Fig. 2. SEM and TEM micrographs of ZnS/TiO_2 , CNT/TiO_2 catalysts and $\text{ZnS}/\text{TiO}_2/\text{MWCNTs}$ samples. (a) ZnS/TiO_2 , (b) CNT/TiO_2 , (c) $\text{ZnS}/\text{TiO}_2/\text{MWCNTs}$, (d) $\text{ZnS}/\text{TiO}_2/\text{MWCNTs}$.

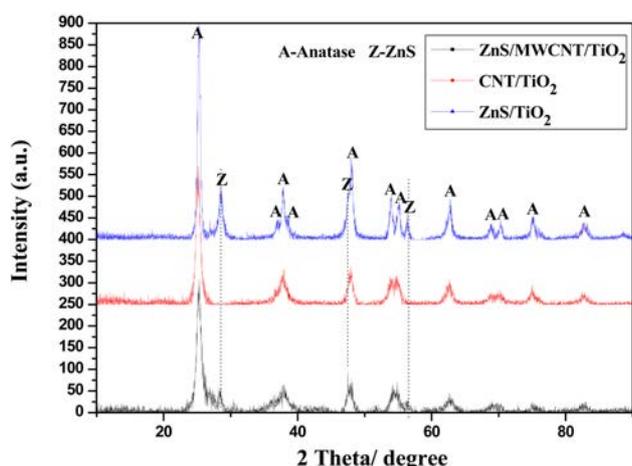


Fig. 3. XRD patterns of ZnS/TiO₂, CNT/TiO₂ catalysts and ZnS/TiO₂/MWCNTs composites.

crystal particle size is very small, it can easily agglomerate due to the weak forces of the surface. Fig. 2b shows us a good morphology of the CNT/TiO₂ composite. Most of the TiO₂ particles were uniformly enclosed or overlapped by the purified carbon nanotubes which have very smooth surfaces and are about 25 nm in diameter. Compared with the ZnS nanoparticles, an introduction of the MWCNTs can efficiently inhibit the agglomeration of TiO₂ catalyst particles. The-prepared ZnS/TiO₂/MWCNTs composites exhibit excellent properties of the in surface nanostructures which can be seen in Fig. 2c. The surface of carbon nanotubes was coated with uniformly dispersed TiO₂, ZnS particles and no aggregates were observed.

To obtain more detailed and higher magnification information, the surface nanostructures and particle sizes of ZnS/TiO₂/MWCNTs composites were studied by TEM. After treatment of MWCNTs with MCPBA under reflux, the nanosized tube networks were opened, oxidized and shortened, and exhibited a regular morphology. Fig. 2d, shows that TiO₂ particle are uniformly dispersed on the surface of MWCNTs with several ZnS particles among them, it can be clearly seen that the TiO₂ and ZnS particles of 10-20 nm size were regularly and individually distributed on the MWCNTs surfaces. This indicates that the presence of the MWCNTs can efficiently inhibit the agglomeration of ZnS/TiO₂ and improve the dispersion of nanoparticles.

The crystal phase structures of as-prepared ZnS/TiO₂, CNT/TiO₂ and ZnS/TiO₂/MWCNTs composites were characterized by X-ray diffraction measurements (Fig. 3). It can be confirmed that the TiO₂ in the three as-prepared photocatalysts is the anatase-phase, while the ZnS is a cubic-phase. The diffraction peaks corresponding to anatase are marked with 'A'; and the diffraction peaks corresponding to the ZnS phase are marked with 'Zn'. For these three samples, the (101), (004), (200), (105), (211), and (204) crystal planes originated from the anatase TiO₂ phase (JCPDS file, No. 21-1272), while the (111), (220), and (311) crystal planes are originated from the

Table 2. BET surface area of ZnS/TiO₂, CNT/TiO₂ catalysts and ZnS/MWCNT/TiO₂ composite samples.

Samples	S _{BET} (m ² /g)
Pristine MWCNT	232
ZnT	43
CT	109
ZnCT	72

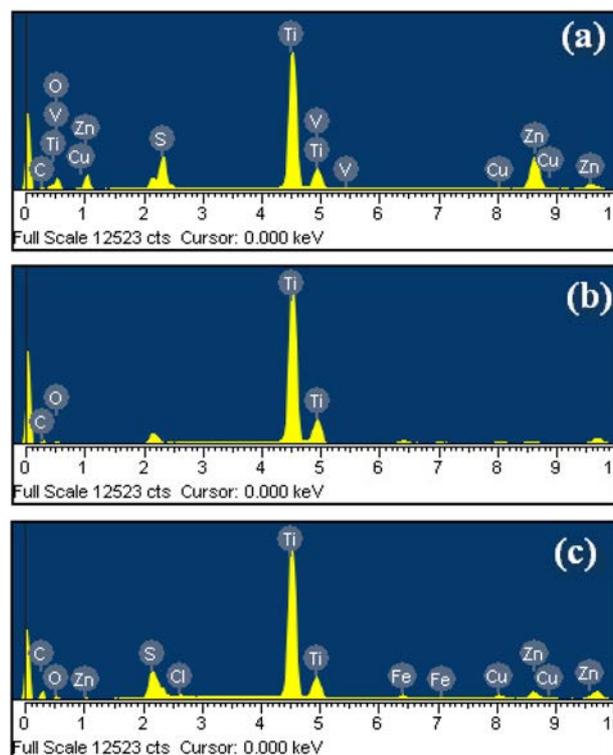


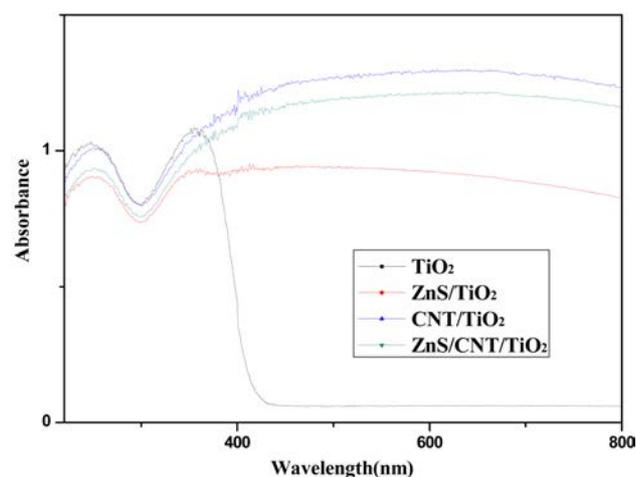
Fig. 4. EDX elemental microanalysis for ZnS/TiO₂, CNT/TiO₂ catalysts and ZnS/TiO₂/MWCNTs composites (a) ZnT, (b) CT, (c) ZnCT.

cubic ZnS phase (JCPDS files, No. 5-0566, 77-2100 and 02-0564). The broadening of the diffraction peaks indicates that the sizes of the TiO₂ and the ZnS/TiO₂ particles are very small, and the estimated particle sizes by the Scherrer equation are ca. 15 nm. However, the strong (002) diffraction from the hexagonal graphite at 2θ of about 25.88°, it is very difficult to see it in all of the composites due to strong overlapping by the TiO₂ diffraction peak. Therefore, it can be suggested that the as-prepared samples have a single and clear crystal structure of anatase.

Table 2 lists the BET surface areas of pristine MWCNT, ZnS/TiO₂, CNT/TiO₂ and ZnS/TiO₂/MWCNTs composites. The BET surface areas of MWCNTs, ZnT, CT and ZnCT were 232, 43, 109 and 72 m²/g, respectively. Agglomeration occurred easily in the process of ZnT preparation because of its higher surface energy. Also it has a smooth surface and a shaped structure which in against its adsorption properties. The

Table 3. EDX elemental microanalysis (wt%) of ZnS/TiO₂, CNT/TiO₂ catalysts and ZnS/TiO₂/MWCNTs samples.

Samples	Elements					
	C	O	Ti	Zn	S	Impurities
ZnT	3.02	12.94	38.76	39.46	4.67	1.15
CT	39.84	25.11	65.05	0	0	0
ZnCT	38.18	24.74	27.84	5.78	0.53	2.93

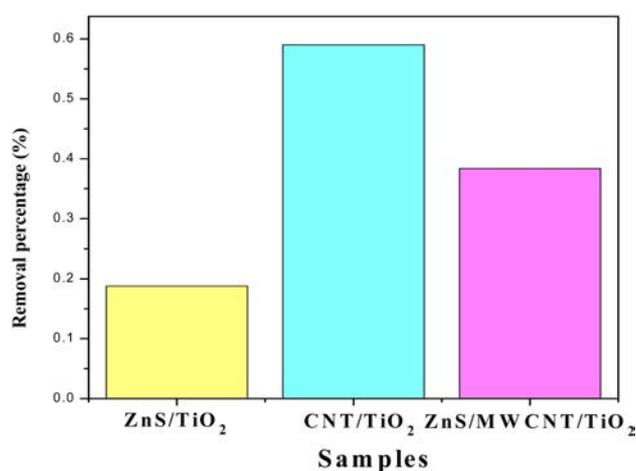
**Fig. 5.** UV-vis absorbance spectra of TiO₂ and the as-prepared samples.

addition of MWCNTs to the ZnT composite prevented the TiO₂ particles and ZnS particles from agglomerating, resulting in a large change in the micro-pore size distribution for the ZnCT composite compared to that of the ZnT. This suggests that the supported MWCNT is related directly to the adsorption ability of the photocatalyst composites.

The EDX spectra and elemental microanalysis (wt%) of ZnS/TiO₂, CNT/TiO₂ and ZnS/TiO₂/MWCNTs composites are shown in Fig. 4 and are listed in Table 3, respectively. In a comparison of the spectra between the ZnS/TiO₂ and ZnS/TiO₂/MWCNTs composites they have not only the peaks of S, Zn, Ti, and O, but also C. For the ZnS/TiO₂ sample, some impurity elements including C existed (which may be introduced from the TiO₂ heat treatment process) but it can be attested that the ZnS/TiO₂ composites were formed after being treated by TNB at 773 K. Compared with CNT/TiO₂ and ZnS/TiO₂/MWCNTs, when the cubic ZnS was introduced, the peaks of C, O and Ti were decreased a small extent.

UV-vis diffuse reflectance spectroscopy

The diffuse reflectance UV-vis absorption spectra of the different samples are presented in Fig. 5. As expected, we find that TiO₂, ZnS/TiO₂, CNT/TiO₂ and ZnS/TiO₂/MWCNTs composites absorb strangle in the ultraviolet region, TiO₂ shows a characteristic spectrum with its fundamental absorption sharp edge rising at 400 nm ($E_g = 3.2$ eV). On the other hand, ZnS/TiO₂,

**Fig. 6.** Adsorption abilities of the MB solution of different samples under magnetic stirring for 30 minutes.

CNT/TiO₂ and ZnS/TiO₂/MWCNTs composites are have good absorption in the visible region, this also means these composites have a greater photocatalytic activity under visible light irradiation. The ZnS nanoparticles can effectively absorb light and trap electrons in the conduction band, so ZnS/TiO₂ has good adsorption in the visible region. Compared with TiO₂ and ZnS/TiO₂, it is noticeable that there is an obvious correlation between the CNT/TiO₂, ZnS/TiO₂/MWCNTs composites and the UV-vis spectrum change. These observations might suggest an increase of surface electric charge of the oxides in the composite catalysts due to the introduction of MWCNTs, which may lead to modifications of the fundamental process of electron/hole pair formation when applying visible irradiation.

Adsorption ability

The adsorption ability of the ZnT, CT and ZnCT composites evaluated after stirring for 30 minutes in the dark is shown in Fig. 6. The degradation of MB on the CT composites was faster than that of any of the other photocatalysts. This was attributed to the high porosity of the CT surface due to the introduction of MWCNTs, which correlated with an increase in the adsorption ability. Compared with ZnT and ZnCT composites, by the introduction of MWCNTs the BET surface area of ZnCT was increased and the adsorption ability was also increased.

Photocatalytic studies

The photodegradation studies in aqueous suspensions containing ZnS/TiO₂, CNT/TiO₂ and ZnS/TiO₂/MWCNTs composite catalysts showed that the three types of tested samples could photocatalyze the degradation of MB. Fig. 7 shows the changes of the absorbance after a color removal process in the relative MB degradation concentration using these composites under visible light irradiation. The changes of the absorbance for the MB degradation with three types of photocatalysts

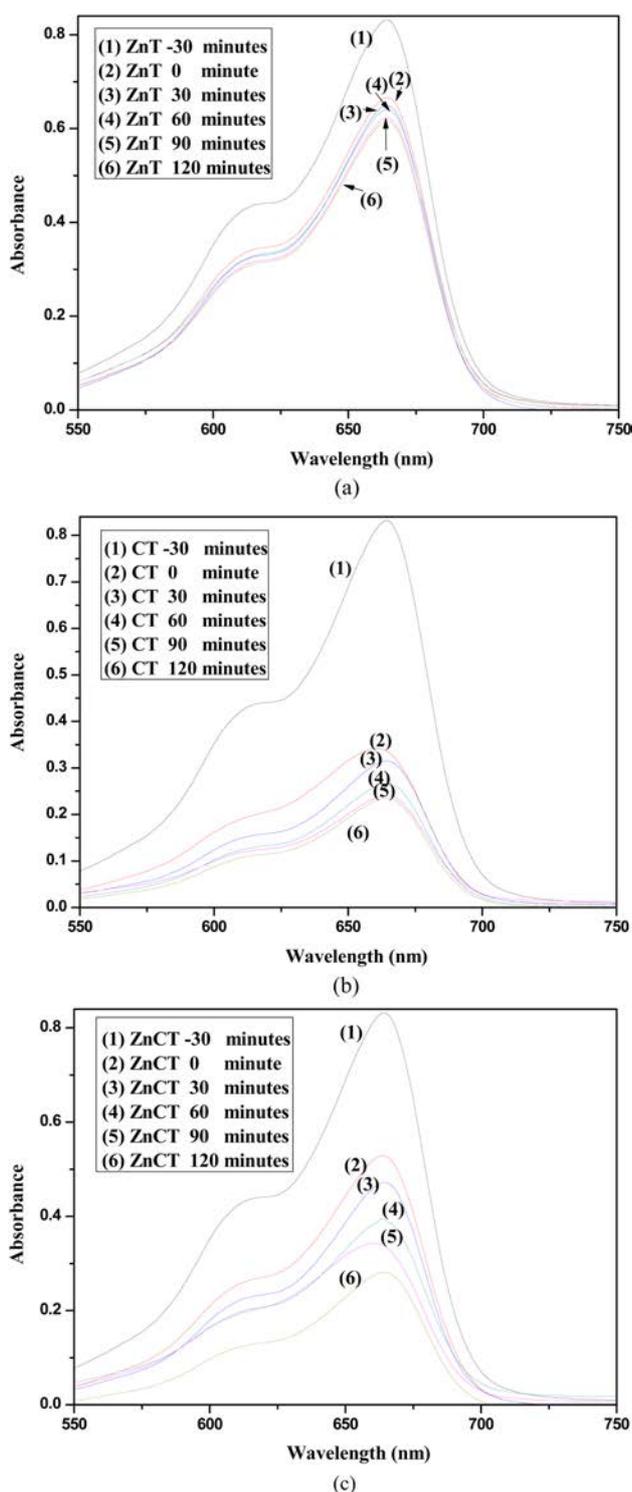


Fig. 7. UV-Vis spectra of MB concentration against the prepared composite catalysts under various irradiation time conditions; (a) ZnT, (b) CT, (c) ZnCT.

were used to measure the photolysis effect under visible light. The measurement of the absorbance maxima (λ_{\max}) value in the spectra with decomposed MB products was tried as a function of the degradation time against the ZnS/TiO₂, CNT/TiO₂ and ZnS/TiO₂/MWCNTs photocatalysts. It showed that the λ_{\max}

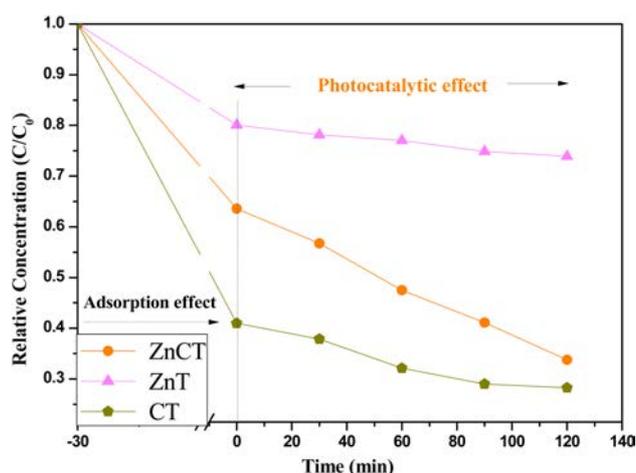


Fig. 8. MB solution on time of adsorption and visible light irradiation for different samples.

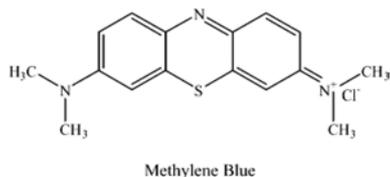
values moved to a lower absorbance region with an increase of the irradiation time. According to previous studies [22-23] it has been observed that the intensity of the λ_{\max} values measured as a function of the irradiation time depends on the concentration of organic dyes. The value of λ_{\max} was proportional to the concentration decrease of the transient formed after visible light excitation. The absorbance level defining the λ_{\max} values for the MB decomposed by the ZnCT sample was higher than that of the MB decomposed by the CT and ZnT samples. It is considered that the sharp decrease in the λ_{\max} values of absorbance can be attributed to a degradative reaction.

Photocatalytic activities of the samples were evaluated by measuring the degradation of MB in aqueous solutions under visible light irradiation. Temporal changes in the concentration of MB were monitored by examining the variations in maximal absorption in UV-vis spectra at 665 nm. Fig. 8 shows the results of the degradation of MB in the presence of different samples. In the presence of ZnS/TiO₂, degradation of MB was observed but it showed a low photocatalytic efficiency. It can be considered that when the particle size was small and agglomeration appeared after heat treatment the probability of electron-hole recombination was increased which results in its photocatalytic efficiency being reduced. However, in the presence of CNT/TiO₂ samples, it exhibited a higher visible light photocatalytic activity than ZnS/TiO₂. This could be attributed to the effects of the porous carbon materials, with the introduction of CNT to the TiO₂ samples its dispersion problem was improved and the degradation efficiency was also enhanced due to the photo-generated electron (e^-) which was easily transferred to the conduction band of TiO₂, similar results have also been observed by Oh et al. [24]. Among the three samples, sample ZnCT exhibited the highest visible light photocatalytic activity after irradiation for 120 minutes. Also, the ZnS here enhances the photogenerated electron transfer. Consequently, the

photocatalytic degradation of MB using the ZnS/TiO₂/MWCNTs composite is better than that of the ZnS non-treated CNT/TiO₂ composite.

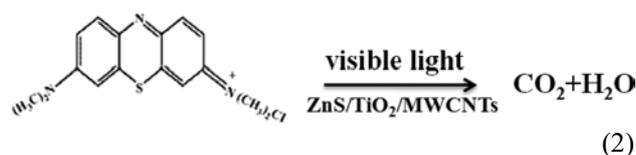
Mechanism proposal

In the degradation of methylene blue, OH⁻ radicals are supposed to attack the C-S⁺=C functional group, which is in a direct Coulombic interaction with the titania surface. Therefore, the first step is the cleavage of C-S⁺=C functional group bonds, which induces the opening of the central aromatic ring containing both heteroatoms, S and N. Second and third attacks by the OH radical lead to the dissociation of two benzene rings and finally the formation of sulfonic acid (R-C₆H₄-SO₃H). Now the sulfur has reached its final stable and maximum oxidation degree of +6. The fourth attack by OH radical leads to the release of SO₄²⁻ ions and R-C₆H₄ radicals, which can further react with either OH giving a phenolic compound or with H radicals. Similar attacks at the N-C site leads to the formation of NH₄⁺ or NO₃⁻ ions and a photo-kolbe process is responsible for generation of CO₂:



(1)

The significantly enhanced photodegradation of MB in the presence of ZnS/TiO₂/MWCNTs composites under visible light irradiation may be ascribed to the cooperative effect of ZnS and nanocarbon dopants. The interparticle electron transfer between porous MWCNTs and a TiO₂ semiconductor system has been investigated [25]. The excited electrons from the MWCNTs under visible light irradiation are quickly transferred to the conduction band of TiO₂ and the electrons of the valence band (VB) of TiO₂ transferred to MWCNTs simultaneously. In other words, the injected electrons migrating from the MWCNTs to TiO₂ could catch the O₂ adsorbed on the surface of TiO₂ to yield very active radicals, superoxide radical ions, and the positive charged hole could catch OH⁻ to yield hydroxyl radicals. Both superoxide radical ions and hydroxyl radicals were responsible for the degradation of phenol. The total reaction is shown in Eq. (2):



On the other hand, under visible light irradiation, the

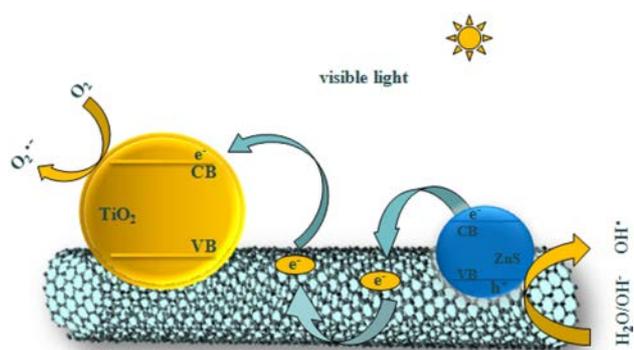


Fig. 9. Schematic representation of electron capture of ZnS/TiO₂/MWCNTs composites.

ZnS nanoparticles which coupled on the surface of TiO₂ can effectively adsorb the visible light, meanwhile the excited photoelectrons could migrate to TiO₂ thus the photocatalytic degradation efficiency for organic materials is enhanced [26]. Compared with ZnS/TiO₂, the photocatalytic degradation efficiency of ZnS/TiO₂/MWCNTs was enhanced due to the typical properties of porous carbon materials. A simple schematic mechanism of the photocatalytic activity of ZnS/TiO₂/MWCNTs composites is shown in Fig. 9.

Conclusions

This paper presents a new method for the preparation of the efficient photocatalytic materials ZnS/TiO₂/MWCNTs nano-composites. XRD determination results show that the ZnS in the composites is a cubic-phase, while the TiO₂ is the anatase-phase. The porous structure and the TiO₂ particles coated on the ZnS coated MWCNTs composite can be observed from SEM image analysis. The composites show efficient visible-light photocatalytic activity to degrade aqueous methylene blue, which is higher than that of a ZnS coupled TiO₂ photocatalyst. This efficient photocatalytic activity is attributed to (i) the synergetic effect resulting from the combination of the cubic ZnS and anatase TiO₂ that the excited e⁻ of ZnS, can migrate the TiO₂ which resulting the ZnS/TiO₂ composites exhibiting visible-light absorption behaviors (ii) porous MWCNTs as supports were introduced in the ZnS/TiO₂/MWCNTs system, this indicates that the presence of the MWCNTs can not only efficiently inhibit the agglomeration of ZnS/TiO₂ and improve the dispersion of nanoparticles, but also remarkably improve the efficiency of the photocatalytic reaction because the recombination of e⁻/h⁺ pairs is retarded.

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