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## **Fabrication of TiO<sub>2</sub>/Ag<sub>2</sub>S nano-composites via a new method for photocatalytic degradation of p-xylene & chlorophenol**

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### **ABSTRACT**

*TiO<sub>2</sub>/Ag<sub>2</sub>S nano-composites were successfully prepared in different temperature for p-xylene and chlorophenol Photodegradation. Transmission electron microscope (TEM), powder X-ray diffraction (XRD) were used to characterize the microstructure and morphology of the products obtained at various temperatures. The results of the photocatalytic degradation of p-xylene and chlorophenol aqueous solution by TiO<sub>2</sub>/Ag<sub>2</sub>S nano-composites is considerably faster when compared with the use of TiO<sub>2</sub>. The p-xylene & chlorophenol degradation increased as the size of Ag<sub>2</sub>S nanoparticles decreased.*

**Key Words:** TiO<sub>2</sub>/Ag<sub>2</sub>S; nanocomposite; Thioacetamide; p-xylene, photocatalyst; morphology;

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### **INTRODUCTION**

Among various oxide semiconductor photocatalysts, TiO<sub>2</sub> is one of the most promising photocatalysts because of its non-toxicity, chemical stability, relatively low price, and capability of photooxidative destruction of most organic pollutants [1].

So far, a variety of methods such as sol-gel [2], pulsed laser deposition (PLD) [3], metal organic chemical vapor deposition (MOCVD) [4] and reactive magnetron sputtering [5] have been developed to prepare TiO<sub>2</sub> materials. However, its wide band gap (3.2 eV) allows it to absorb only the UV light ( $\lambda < 388$  nm) which account for merely 4–5% of the solar energy, thereby hampering its wide application [6].

To lower the threshold energy for photoexcitation, a great deal of research has focused on doping TiO<sub>2</sub> with transition metals or non-metal ions. It has been reported earlier that many investigators could improve the visible light absorption of TiO<sub>2</sub> nanocrystals by incorporation of substitutional atoms into the lattice, including both non-metal and metal atoms [7].

Some efforts have been made on the sensitization of TiO<sub>2</sub> photoelectrodes with narrow band gap semiconductors [8]. Semiconductors such as CdS, CdSe, CdTe, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuInS<sub>2</sub>, and so on, which absorb light in the visible, can serve as sensitizers because they are able to transfer electrons to large band gap semiconductors such as TiO<sub>2</sub> or ZnO [9-12].

In the present work, TiO<sub>2</sub>/Ag<sub>2</sub>S nanoparticles were synthesized in different preparing temperatures and The catalytic activity of the prepared nanocomposites were evaluated by photocatalytic degradation of p-xylene & chlorophenol..

## EXPERIMENTAL SECTION

### 2.1. Materials

The chemical materials all were of analytical grade reagents and were used as the starting ingredients without any purification.

### 2.2. Materials synthesis.

silver thiobenzoate (Ag(SCOPh)) precursor crystals were found to decompose in amine at room temperature to give Ag<sub>2</sub>S nanoparticles The nanocomposite particles were prepared by adding drop-wise a solution of the precursor dissolved in trioctylphosphine (TOP) under nitrogen to a warm mixture of hexadecylamine (HDA) and 0.2 g of the TiO<sub>2</sub> (anatase) particles at 60,80, 100 and 120°C and stirred for 2 h . The suspension formed was then refluxed with stirring. The grey solids were collected for distinct reaction times and isolated by centrifugation and finally washed thoroughly with acetone. and then dried at 100 °C overnight.

### 2.3. Characterization

The morphology and structure of the Ag<sub>2</sub>S nano-sized powders were further investigated by transmission electron microscope (TEM), TEM (Philips EM208) were operated at 100 kV. The Powder X-ray diffraction (XRD) pattern was recorded on a Seisert Argon 3003 PTC using nickel-filtered XD-3a CuK $\alpha$  radiations ( $\lambda=0.1542$  nm). The average primary particle size was also estimated from the XRD pattern using the X-ray line broadening analysis.

### 2.4. Photocatalytic activity

Photodegradation experiments were performed with a photocatalytic reactor system surrounded by a circulation water jacket to control the temperature during reaction. This bench-scale system consisted of a cylindrical Pyrex-glass cell with 12-cm inside diameter and 15 cm height. A 100-W mercury lamp was placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stopper. The lamp and the tube were then immersed in the photoreactor cell with a light path of 3.5 cm.

Suspensions have been prepared by adding 50mg of the nanocomposite powder into a 100mL of 0.2mM p-xylene aqueous solution. Prior to the photoreaction, the colloid solution/powder

suspension was magnetically stirred in the dark for 15 min to establish adsorption/ desorption equilibrium. During the photoreaction, the colloid solution or suspension was irradiated by UV-visible light for 90 minutes with air blowing and magnetically stirring. At the given time intervals, the samples were taken from the colloid solution or suspension and stored in the dark before analysis. The suspensions were filtered and analyzed for the residual concentrations of p-xylene and chlorophenol by Gas chromatography.

## RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of powders that were crystallized by using different temperatures from 60 to 120°C. The XRD peaks at  $2\Theta = 25.28^\circ$  (1 0 1) and  $2\Theta=27.4^\circ$  (1 1 0) are often taken as the characteristic peaks of anatase and rutile crystal phase, respectively. According to the XRD patterns, five distinctive TiO<sub>2</sub> peaks at 25.38°, 37.98°, 48.08°, 54.68° and 62.88°, corresponding to anatase (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 0 4) crystal planes (JCPDS 21-1272) shows that the pure TiO<sub>2</sub> sample constituted pure anatase phase. Silver sulfide is known to exist in two main polymorphic modifications, the monoclinic  $\alpha$ -Ag<sub>2</sub>S (achantite) and the body centred cubic  $\beta$ -Ag<sub>2</sub>S (argentite). The distinction of these two phases by powder XRD is not straightforward though the XRD patterns in Fig. 1 are consistent with the presence of essentially  $\alpha$ -Ag<sub>2</sub>S. As the synthesize temperature Increased, the size of the Ag<sub>2</sub>S nanoparticles were decreased too.

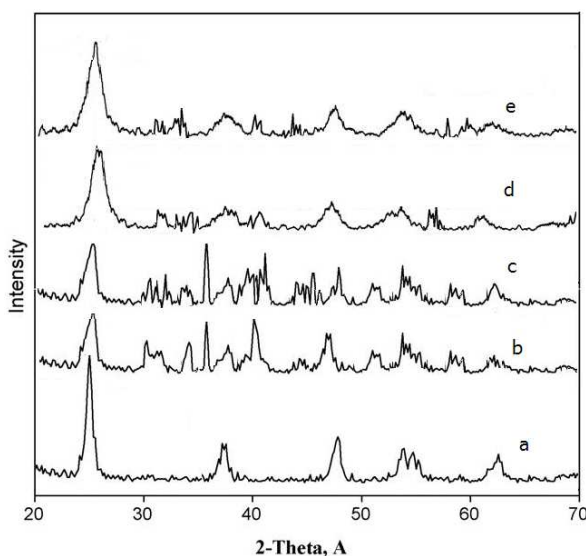


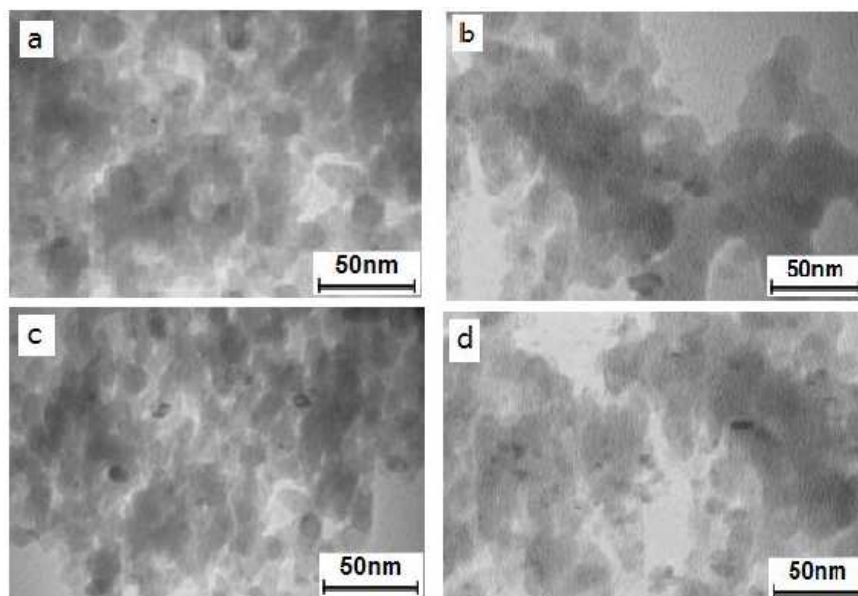
Figure 1. X-ray diffraction patterns of : a) TiO<sub>2</sub> and TiO<sub>2</sub>/ Ag<sub>2</sub>S samples with different preparing temperature ; b) 60°C ; c) 80°C ; d) 100°C ; e) 120 °C

The average grain sizes ( $D$ ) of the products prepared in different temperatures are shown in Table 1, which is calculated from the width of the lines in the XRD spectrum with the aid of the Scherrer formula :  $D = k\lambda / (\beta\cos\Theta)$ , where  $\lambda$  is the wavelength of X-ray used (Cu K $\alpha$  radiation  $\lambda = 0.1541$  nm),  $\beta$  the width of the line at the half maximum intensity and  $K\alpha$  constant, 0.89. From Table 1, it can be seen that the average particle size decrease with increasing preparing temperature, which is in a good agreement with the result of TEM analysis.

**Table 1: The average grain size of products obtained in different temperatures**

Preparing temperature (°C)	Preparing time (h)	<i>D</i> (nm)
60	2	26.35
80	2	22.72
100	2	16.43
120	2	13.65

Fig. 2 a-d shows the TEM images of the TiO<sub>2</sub>/ Ag<sub>2</sub>S photocatalyst. Silver sulfide is presented as nanoparticles dispersed in the Titania network. Silver sulfide nanoparticles were surrounded by Titania which paved the way for the photocatalyst to have a large specific surface area. The resistance to mass transfer of photocatalytic reaction is low and the reactant easily gets in contact with the catalytic active site.

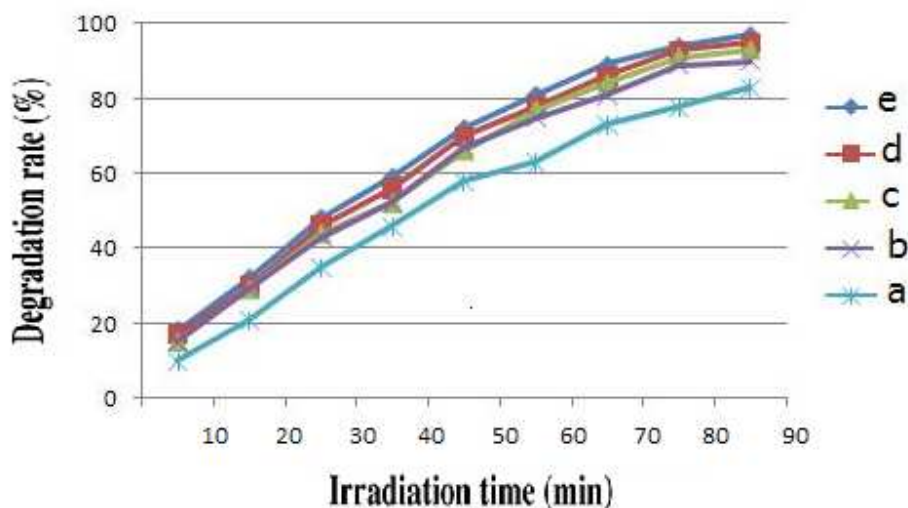


**Figure 2.** TEM micrographs of samples of TiO<sub>2</sub>/ Ag<sub>2</sub>S prepared in different temperatures : a) 60°C , b) 80°C , c) 100°C and d) 120°C

### 3.1. photocatalytic activity

Figs.3&4 show effect of TiO<sub>2</sub>/ Ag<sub>2</sub>S preparing temperature on p-xylene & chlorophenol degradation. Samples of pure TiO<sub>2</sub>, and TiO<sub>2</sub>/ Ag<sub>2</sub>S ratios were studied. The p-xylene & chlorophenol degradation increased with decreasing the size of Ag<sub>2</sub>S nanoparticles because of

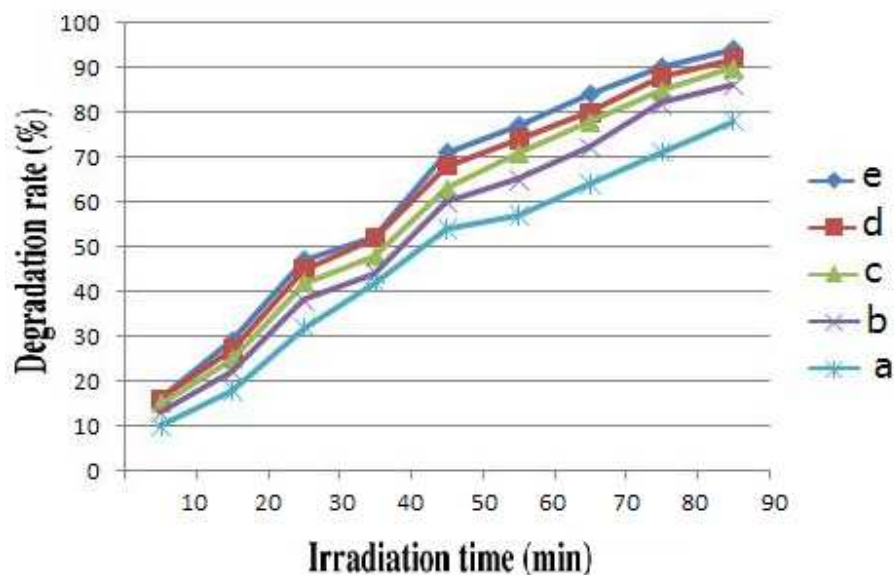
increasing the surface area. for all the used samples TiO<sub>2</sub> showed the lowest degradation efficiency.



**Fig. 3.** Photocatalyzed degradation of p-xylene in the presence of a) pure TiO<sub>2</sub> and b-e) a series of TiO<sub>2</sub>/ Ag<sub>2</sub>S under UV-vis illumination.

The degradation increased with decreasing Ag<sub>2</sub>S nanoparticles size reaching a maximum efficiency value of 94% for p-xylene. This can be explained as follows; TiO<sub>2</sub> is well known established as an effective photocatalyst that producing electrons and positive holes with UV-irradiation. The concept of the photocatalytic process is that TiO<sub>2</sub> semiconductor acts as a photocatalytic oxidation agent and a reductant. In a photocatalytic process, electron-hole pairs are generated which must be trapped in order to avoid recombination.

Under UV-vis illumination, electrons can be excited from the valence band (VB) to the conduction band (CB) of the anatase when a photon with higher energy is absorbed, creating a charge vacancy in the VB. In the absence of the Ag<sub>2</sub>S, most of these charges quickly recombine without any valuable utilization. It has been reported that the CB position of anatase is about-4.21 eV using vacuum level (AVS) as a reference, with a band gap of about 3.2 eV.



**Fig. 4.** Photocatalyzed degradation of chlorophenol in the presence of a) pure  $\text{TiO}_2$  and b-e) a series of  $\text{TiO}_2/\text{Ag}_2\text{S}$  under UV-vis illumination

when  $\text{Ag}_2\text{S}$  nanoparticles are attached to the surface of the  $\text{TiO}_2$  the relative position of the  $\text{Ag}_2\text{S}$  nanoparticles CB edge permits the transfer of electrons from the  $\text{TiO}_2$  surface allowing charge separation, stabilization, and hindered recombination. At the same time,  $\text{Ag}_2\text{S}$  can also absorb photons with lower energy and excite photoelectron from VB to CB. And the electrons from last two means can be shuttled freely along the oriented  $\text{TiO}_2$  leading to enhance photochemical performances of the composite  $\text{Ag}_2\text{S}/\text{TiO}_2$ .

Based on the presented results, it can be concluded that the proposed fabrication of  $\text{TiO}_2/\text{Ag}_2\text{S}$  nanocomposite, can be a successful and generic strategy to develop highly active photocatalysts under visible light.

## CONCLUSION

$\text{Ag}_2\text{S}$  nanoparticles synthesized in this work are in contact with the surface of bulky  $\text{TiO}_2$ . The effect of heat treatment of  $\text{Ag}_2\text{S}$  has been discussed. the formation of  $\text{TiO}_2/\text{Ag}_2\text{S}$  nanocomposite photocatalyst is more effective strategy than single  $\text{TiO}_2$  photocatalyst to acquire an active photocatalyst. The photocatalytic activity increased when the  $\text{Ag}_2\text{S}$  nanoparticles decreased gradually.

The photocatalytic activity of synthesized  $\text{TiO}_2/\text{Ag}_2\text{S}$  is tested by decomposition of p-xylene & chlorophenol. The results demonstrate that the  $\text{Ag}_2\text{S}$  nanoparticles are successfully incorporated into the framework of  $\text{TiO}_2$ . The highest photoactivity of  $\text{TiO}_2/\text{Ag}_2\text{S}$  is obtained when the size of  $\text{Ag}_2\text{S}$  nanoparticles are about 14 nm.

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## REFERENCES

- [1] X Quan; N Lu; JY Li ; S Chen; HT Yu; GH Chen, *J. Phys. Chem. C*, **2007**, 111, 11836–11842.
- [2] T Watanabe; A Nakajima; R Wang; T Minabe; S Koizumi; A Fujishima; K Hashimoto; *Thin Solid Films*, **1999**, 351, 260–263.
- [3] Y Choi; S Yamamoto; T Umebayashi; M Yoshikawa; *Solid State Ionics* , **2004**, 172, 105–108.
- [4] MK Lee; YM Hung ; JJ Huang; *Jpn. J.Appl.Phys.* **2001**,40 ,6543–6546.
- [5] S Tanaka; S Suzuki; H Okada; H Hosono; *Thin Solid Films* , **2001**, 392, 338–344.
- [6] R Molinari; R Amadelli; A Maldotti; P Battioni; D Mansuy; *J. Mol. Catal. A* , **2000** , 158 , 521–531.
- [7] T Tachikawa; S Tojo; K Kawai; M Endo; M Fujitsuka; T Ohno; K Nishijima; Z Miyamoto; T Majima; *J. Phys. Chem. B*, **2004** , 108 , 19299.
- [8] F Gracia; JP Holgado; A Caballero; AR Gonzalez-Elipe; *J. Phys. Chem. B*, **2004**, 108 ,17466.
- [9] H Gerischer; M Lubke; *J. Electroanal. Chem.* **1986**, 204 ,225.
- [10] HM Jia; Y Hu; YW Tang; LZ Zhang, *Electrochem. Commun.* **2006** , 8 ,1381.
- [11] S Das; SK Datta; H ; *Phys. Stat. Sol. A*, **1993**, 136, 251.
- [12] J Tousek; D Kindl; J Tousek, *Phys. Stat. Sol. A*, **1994** , 142 ,539.