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Fabrication of nano silver sulfide doped titanium oxidein poly vinyl alcohol PVA matrice for photocatalytic degradation of ethanol

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ABSTRACT

This study investigated the applicability of TiO_2/Ag_2S nanocomposite in poly vinyl alcohol PVA matrice,for ethanol Photodegradation. Transmission electron microscope (TEM), powder X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) were used to characterize the microstructure and morphology of the products.The results showed that the overall photocatalytic activity of TiO_2/Ag_2S nanocomposite in PVA under UV –Visible for ethanol degredation was significantly higher than pure TiO_2. The results indicate that PVA can be a suitable inert matrice for photocatalysts.

Key Words: TiO2/Ag_2S; nanocomposite; ethanol;photocatalyst; morphology; X-ray diffraction.

INTRODUCTION

Among various oxide semiconductor photocatalysts, TiO_2 is one of the most promising photocatalysts ,because of its non-toxicity, chemical stability, relatively low price, and capability of photo-oxidative destruction of most organic pollutants. During this process, the highly active hydroxyl radicals (•OH) non-selectively attack the organic substrates to yield desired inorganic minerals[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_2 particles. However, its wide band gap (3.2 eV) allows it to absorb only the UV light (< 388 nm) ,which account for merely 4–5% of the solar energy, thereby hampering its wide application[6].

It has been reported earlier that many investigators could improve the visible light absorption of TiO_2 nanocrystals by incorporation of semiconductors[7]. Coupled semiconductors photocatalysts exhibit a very high photocatalytic activity for both gas and liquid phase reactions[8]. Semiconductors such as CdS, CdSe, CdTe, PbS, Bi_2S_3, $CuInS_2$, and so on, which absorb light in the visible, can serve as sensitizers. They are able to transfer electrons to large band gap semiconductors such as TiO_2[9-17].

Accordingly, herein we extend the previous study by preparing Ag_2S nanoparticles doped into the TiO_2 lattice in PVA matrice to evaluate its role on photocatalytical activity. The photocatalytic activity of the prepared nanocomposites were evaluated by photodegradation of ethanol by UV –Visible.

EXPERIMENTAL SECTION

2.1. Materials

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

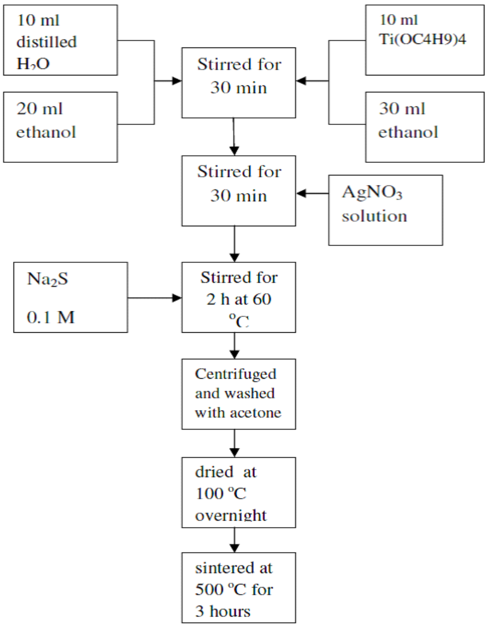

Fig. 1. Sol–gel process to prepare nano TiO2/Ag_2S nanocomposites

2.2. Materials synthesis.

2.2.1 Synthesis of TiO2/Ag_2S nanocomposite in PVA matrice

To synthesis TiO2/Ag_2S nanocomposite in PVA matrice, In a typical preparation process, 5mlTi(OC4H9)4 ,1.5 mmol of AgNO3 and 15 ml ethanol was dissolved into a 10% (by weight) homogeneous PVAdistilled aqueous solution. An aqueous solution of Na_2S 0.1 M was added dropwise at 60 ^{o}C and stirred for 2 h. The resulting viscous solution was cast on the glass plates and dried at room temperature for 12 h, and then dried at 80°C for 12 h for the complete removal of water. The films with thickness about 30 mm were peeled off from the plates.

2.2.2 Synthesis of TiO2/Ag$_2$S nanocomposite

The TiO_2/ Ag_2S nanocomposite was prepared by sol–gel method as shown in Fig-1. A mixture of 10 ml distilled H_2O/20 ml ethanol was added at room temperature to a mixture of 10 ml $Ti(OC_4H_9)_4$ /30 ml ethanol and stirred for 30 min.

The TiO_2/Ag_2Snanocomposite was prepared by adding solution of 1.5mmol of the $AgNO_3$ to the mixture at room temperature under magnetic stirring. After 30 min an aqueous solution of Na_2S 0.1 M was added dropwise at 60 ^oC and stirred for 2 h. The suspension formed was then refluxed with stirring. The grey solids were collected and isolated by centrifugation. They were washed thoroughly with acetone ,dried at 100 ^oC over night and finally sintered at 500 ^oC for 3 hours.

2.3. Characterization

The morphology and structure of the TiO_2/ Ag_2Snanoparticles were further investigated by transmission electron microscope (TEM (Philips EM208) was operated at 100 kV). The Powder X-ray diffraction (XRD) pattern was recorded on a Seisert Argon 3003 PTC using nickel-filtered XD-3a CuKα radiations (λ=0.1542 nm). The average primary particle size was also estimated from the XRD pattern using the X-ray linebroadening analysis. The Brunauer–Emmett–Teller (BET) surface area of the photocatalyst was obtained from nitrogen adsorption–desorption data (Quanta chrome Autosorb-1 system).

2.4. Photocatalytic activity

Photodegradation experiments were performed with a photocatalytic reactor system surrounded by a circulation water jacket to control the temperature at 25 ^oC,duringthe 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 diameterquartz tube with one end tightly sealed by a Teflon stopper. The lamp and the tube were then immersed in the photo-reactor cell with a light path of 3 cm.

Suspensions have been prepared by adding 50mg of the nanocomposite powder into a 100mL of 0.2mMethanol 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 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 suspension and stored in the dark before analysis. the suspensions were filtered and analyzed for the residual concentrations of ethanol by GC-Chromatography.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD patterns of TiO_2 ,TiO2/ Ag_2S nanocomposite and TiO2/ Ag_2S in poly vinyl alcohol PVA matrice. 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. According tothe XRD patterns, five distinctive TiO2 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_2 sample constituted pure anatase phase.Silver sulfide is known to exist in two main polymorphic modifications, the monoclinic α-Ag_2S(achantite) and the body centredcubic β-Ag_2S (argentite). The XRD patterns in fig.2b and 2c are consistent with the presence of essentially α -Ag_2S.

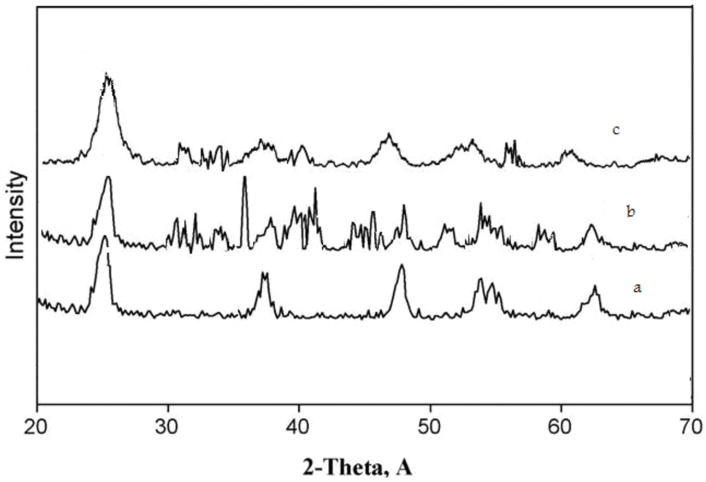

Figure 2. X-ray diffraction patterns of : a) TiO2 , b)TiO2/Ag2S and TiO2/Ag2S in PVA matrice.

The average size (D) of the Ag_2S nanoparticlesare shown in Table 1. They were calculated with the aid of Scherrer formula : $D = k\lambda/ (\beta\cos\Theta)$, where λ is the wavelength of X-ray used (Cu Kα radiation $\lambda = 0.1541$ nm), β the width of the line at the half maximum intensity and $K\alpha$ constant, 0.89. It can be seen that Ag_2S nanoparticles in PVA are smaller because of the role of the matrice on particle size.

The measured Brunauer-Emmett-Teller (BET) surface areas (table -1) shows that photocatalyst type b-TiO_2/ Ag_2S has the largest surface area of 112.58 m2/g while the pure TiO_2 particles have only 38.42 m2/g.

Table -1: The average size of Ag_2S nanoparticles and surface area of products obtained with different types of TiO2/ Ag2S

Nanocomposite type	Surface area ($m^2\ g^{-1}$)	average size of Ag_2S nanoparticles D (nm)
a- TiO2	38.42	-
b- TiO2/ Ag2S	112.58	23
c- TiO2/ Ag2S/PVA	98.16	21

Fig. 3 shows TEM imagesof all photocatalysts. It is evident that b-TiO_2/ Ag_2S consisted of 20-25 nm hexagonal Ag_2S nanoparticles , which is consistent with the grain size estimated from the XRD result.

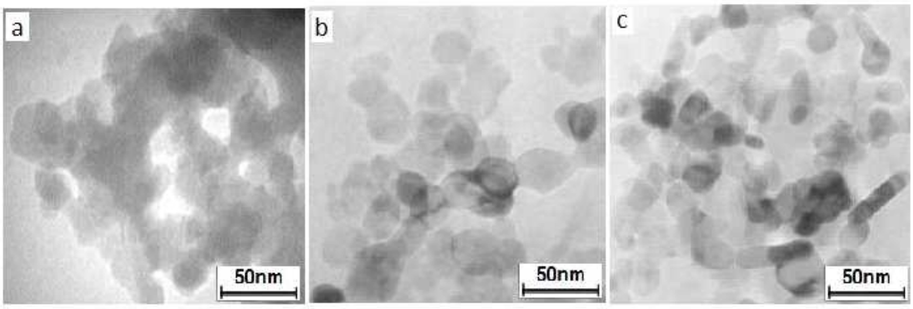

Figure3. TEM micrographs of : a) TiO2 , b)TiO2/Ag2S and TiO2/Ag2S in PVA matrice.

3.1. photocatalytic activity

The photocatalytic degradation of ethanol was investigated by determining the remaining concentration ofethanol at various time intervals. Fig.4 shows the photocatalytic activity of TiO_2/Ag_2S nanocomposites for ethanol degredation by 100-W mercury lamp. The ethanol degradation increased as the surface area increased too. It is remarkable that doping ,a small percent of Ag_2S nanoparticles results such a significant improvement in photocatalytical activity. As can be seen from the fig.5 , the degredation rate was decreased for TiO_2/Ag_2S nanocomposite when it was performed in PVA matrice. It can be mentioned that as PVA matrice reduces surface area for nanocomposite, photocatalytical activity would hamper.

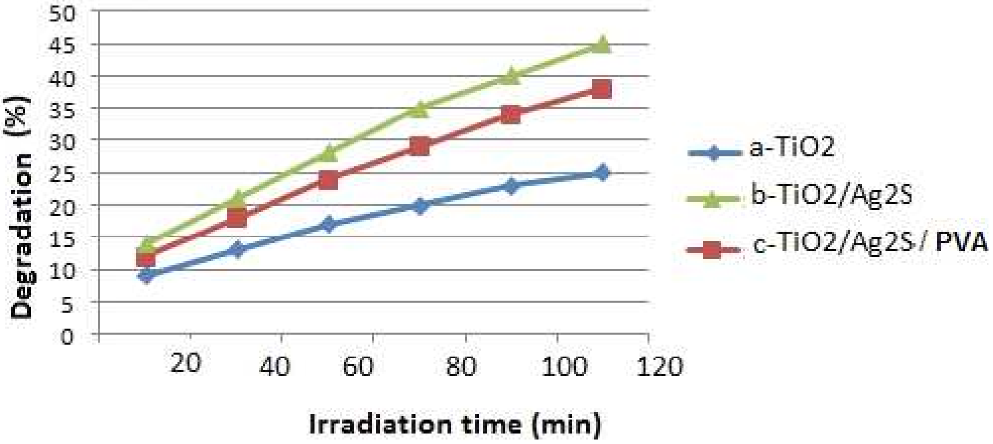

Fig. 4.Photocatalyzed degradation of ethanol in the presence of a) TiO2 , b)TiO2/Ag2S and TiO2/Ag2S in PVA matrice.

TiO_2 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_2 semiconductor acts as an oxidation agent and a reductant. In a photocatalytic process, electron–hole pairs are generated ,which must be trapped in order to avoid recombination.

$TiO_2 \qquad e^- + h^+$

$h^+ + H_2O \qquad H^+ + OH^0$

$h^+ + OH^- \qquad OH^0$

$e^- + h^+ \qquad N + \text{energy}$

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, creates a charge vacancy in the VB. In the absence of the Ag_2S, 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 [18].

When Ag_2S nanoparticles are attached to the surface of the TiO2 , the relative position of Ag_2S nanoparticles CB edge, permits the transfer of electrons from the TiO2 surface ,which allows charge separation, stabilization, and hindered recombination. At the same time, Ag_2S nanoparticles can also absorb photons with lower energy and excite electrons from VB to CB ,that enhance ,the photo chemical performances of TiO_2/Ag2S nanocomposites.

Based on the presented results, it can be concluded that the proposed fabrication of TiO_2/ Ag2S nanocomposite in PVA matrice, can be a successful and generic strategy to develop highly active photocatalysts .

CONCLUSION

TiO_2/Ag_2S nanocomposite in PVA matrice, produced by hybrid sol–gel method demonstrate efficient photocatalysis activity. TiO_2/Ag_2S nanocomposite in PVA matrice was prepared and its photocatalytical activity was compared with pure TiO_2 and TiO_2/ Ag_2S nanocomposite. The studies showed that PVA could be a proper binder or matrice for photochemical activity because of its inertness ,low cost and non-toxicity. The formation of TiO_2/Ag_2S nanocomposite photocatalyst is more effective strategy than single TiO_2 photocatalyst to acquire an active photocatalyst. The photocatalytic activity increased when surface area of the Ag_2S nanoparticles increased gradually.

The photocatalytic activity of synthesized TiO_2/Ag_2S is tested by decomposition of ethanol by 100-W mercury lamp. The results demonstrate that the Ag_2S nanoparticles are successfully coupled with framework of TiO_2 and PVA has little effect on photocatalytical activity of TiO_2/ Ag_2S nanocomposite.

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