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The effect of platinisation on the photocatalytic activity of Bi_2WO_6

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ABSTRACT

Bi_2WO_6 obtained by hydrothermal method, the Bi_2WO_6 doped with platinum ($PtBi_2WO_6$) were prepared by adding Chloroplatinic acid H_2PtCl_6, 6 H_2O (0, 5 Pt) to pure Bi_2WO_6 and their photocatalytic activity to degrade methyl orange (MO) under UV irradiation were studied. In the present study $PtBi_2WO_6$ sample demonstrate much higher photocatalytic efficiency to degrade MO than pure Bi_2WO_6.

Keywords: Photocatalyst, Bi_2WO_6, Platinisation, Methyl orange oxidation, $PtBi_2WO_6$

INTRODUCTION

The increase of the industrials activities has become a serious problem that leads to an increasing contamination of air, water and soil. To phase this problem the scientific community works to find new methods to undo the pollution. Various methods have been used for the degradation of pollutants [1], among them Advanced Oxidation Process (AOPs) that is considered to have a big potential. Those techniques are very appealing alternatives for the degradation of organic pollutants because they permit a partial or complete mineralization of pollutants. It is based on the production of the very reactive and nonselective entities (particularly the radical hydroxyls OH^-) having a higher oxidizing capacity than traditional oxidants (O_2, Cl_2, ClO_2, H_2O_2, O_3…) [2-4].

The development of new photocatalysts is attracting vast interest. Among them the Bismuth tungstate (Bi_2WO_6) is a typical n-type direct band gap semiconductor with a band gap of 2.75 eV and has prospective applications in electrode materials [5], solar energy conversion [6] and catalysis [7–9]. Bi_2WO_6 exhibit possible catalytic ability to numerous organic chemicals and it is mostly synthesized by hydrothermal or solvothermal method.

In order to enhance catalytic efficiency, Bi_2WO_6 catalyst could be doped with metal or metal oxide which might trap the photogenerated electrons and restrain the recombination of hole-electron pair [10-12].Among noble metals, platinum has been one of the most used metals for semi-conductor surface modification [10]. The effect of platinisation on the photocatalytic activity has been a controversial subject in the literature.

The role of platinum in photocatalysis is still not totally understood and the degree of enhancement of the activity of Bi_2WO_6 by platinisation seems to depend highly on the substrate to be degraded [13, 14].In general it is accepted that in platinised Bi_2WO_6 a better separation of charge carriers (electrons and holes) is observed. Additionally, it is assumed that some of the photogenerated electrons would interact with platinum state and be spatially separated from holes.

In the present work, hydrothermal prepared Bi_2WO_6 was platinised with the intention of obtaining improved photocatalysts leading to an improvement of the photocatalytic activity.

Methyl orange (MO) is used to imitate no biodegradable, toxic organic compounds. The photocatalytic activity of Bi_2WO_6 and $PtBi_2WO_6$ for photooxydation reaction of MO is evaluated.

MATERIALS AND METHODS

2. 1 Catalysts preparation

The Bi_2WO_6 was prepared by dissolving 4, 85 g of Bi $(NO_3)_3.5H_2O$ in 10 mL of glacial acetic acid, and 1, 7 g of Na_2WO_4, $2H_2O$ in 90 mL of distilled water, then those two solutions were mixed forming a white suspension (pH≈2), which was kept under stirring for 1h. The white suspension was transferred into a Teflon recipient inside stainless steel autoclave.

The hydrothermal treatment was done at 140°C for 20h, and then the precipitate was filtered, washed and dried overnight at 120°C, finally the sample was submitted to a calcination treatment at 300°C for 4h.

The Bi_2WO_6 doped with platinum were prepared by dissolving 0, 04 g of Chloroplatinic acid H_2PtCl_6, 6 H_2O (0, 5 Pt) in 23 mL of isopropanol+ 977 mL of water. For 2g of the catalyst we added 450 mL of the solution, and then the mixture was irradiated under UV light with stirring for 2 hours, finally the precipitate was filtered, washed and dried overnight at 120°C.

2. 2 Characterization

X-ray diffraction (XRD) was carried on a simens D-501 diffractometer using Cu Kα radiation, the scanning rang was from 10° to 80°.

Brunauer- Emmett- Teller (BET) surface area measurements were performed on a Micrometrics 2010 instrument, the nitrogen adsorption and desorption isotherms were measured at 77 K.

Diffuse reflection spectra (DRS) were measured with a Cary 100 (Varian) spectrometer at the range of 250-600 nm. For the measurements, the samples were mixture with $BaSO_4$ that does not absorb in the UV-vis radiation range.

The morphologies and microstructures of the photocatalyst were analyzed by scanning electron microscope (SEM) (S-4800 Hitachi). The samples were dispersed in ethanol.

2. 3 Photocatalytic experiments

Photocatalytic activity of the catalysts was evaluated by photocatalytic degradation of methyl orange (MO) using an Orsam ultra-vitalaux lamp (300 W) with sunlike radiation spectrum. A concentration of 1g/L of photocatalyst was used; the initial concentration of MO was 20 ppm. The intensity of the incident UVA light on the solution was measured with a PMA 2200 UVA photometer: 90 W/m^2.

Before the experiment, the mixed solution (catalyst+ MO) was magnetically stirred in dark for 20 min to ensure the establishment of an adsorption-desorption equilibrium between the catalyst and ph or MO. At given times, a definite volume of the suspension was sampled and filtered using a filter. The MO in the suspension was measured by cary UV-vis spectrophotometer at λ= 460 nm.

RESULTS AND DISCUSSION

3.1. Characterization

XRD patterns are shown in fig 1. The Bi_2WO_6 presented russellite phase (JCPDS 39-0256). None of the XRD patterns of the platinised samples exhibited Pt peaks, since metal sites are estimated to be lower than the detection limit of X-ray analysis.

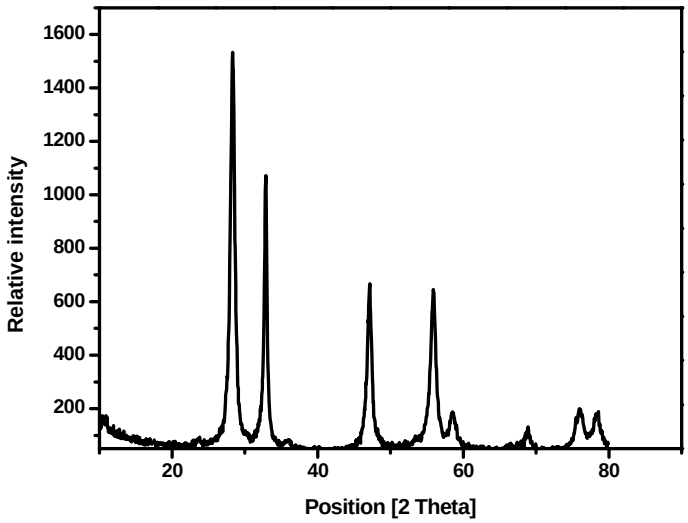

Figure 1 : The XRD patterns of the Bi_2WO_6

The UV-vis diffuse reflectance spectra (DRS) are shown in Fig.2. The pure Bi_2WO_6 absorbed in the near UV region at $\lambda \leq 450$ nm. Comparison between the diffuse reflectance spectra of platinised and non platinised samples showed no differences in the UV range.

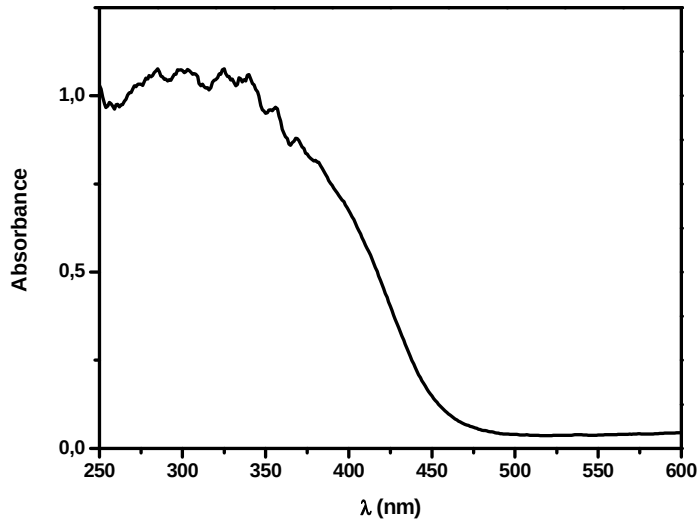

Figure 2: UV-vis diffuse reflectance spectra of Bi_2WO_6

The band gap energy was calculated by plotting Kubelka-Munk function $(F(R\infty).h\gamma)^{1/2}$ against $h\gamma$ [15]. Platinised and non platinised samples presented similar band gap around 2, 8 eV.

The S_{BET} of pure Bi_2WO_6 was about 24.4465 m^2/g. The BET surface area values were not affected by the platinisation process.

SEM pictures of Bi2WO6 produced are shown in Fig.3. Bi_2WO_6 showed (Fig.4) a flower-like spherical superstructure as it was found in other studies [16]. Wang and coworkers have proposed that the flower- like microstructures were constructed from nanoplates with single crystal structure. The formation of this flower-like structure was proposed to follow a three-step process: self aggregation, Ostwald ripening and self-organization.

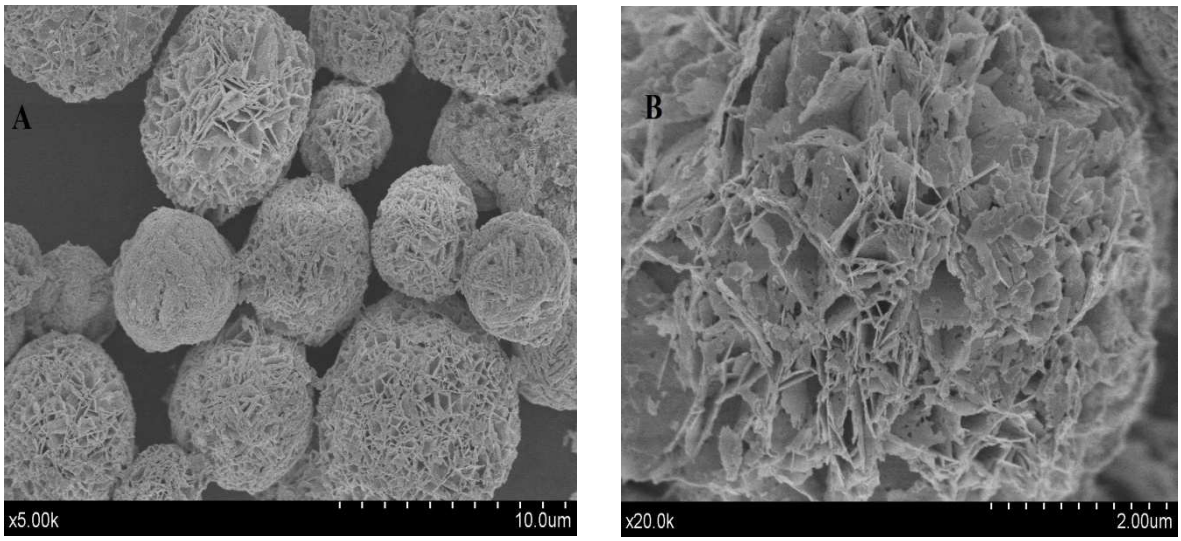

Figure 3: SEM images of Bi_2WO_6. (A): x5K; (B): x20K

3.2. Photocatalytic performance

The photocatalytic activity of the samples was tested in the reaction of photooxydation of MO. Platinised samples showed significantly higher photocatalytic activity than non-modified Bi_2WO_6.

The photocatalytic efficiency of Bi_2WO_6 and $PtBi_2WO_6$to degrade MO is shown in figure 4.

The pure Bi_2WO_6 displayed negligible degradation efficiency (only 8%); however the PtBi2WO6 presented a 95% removal of MO.

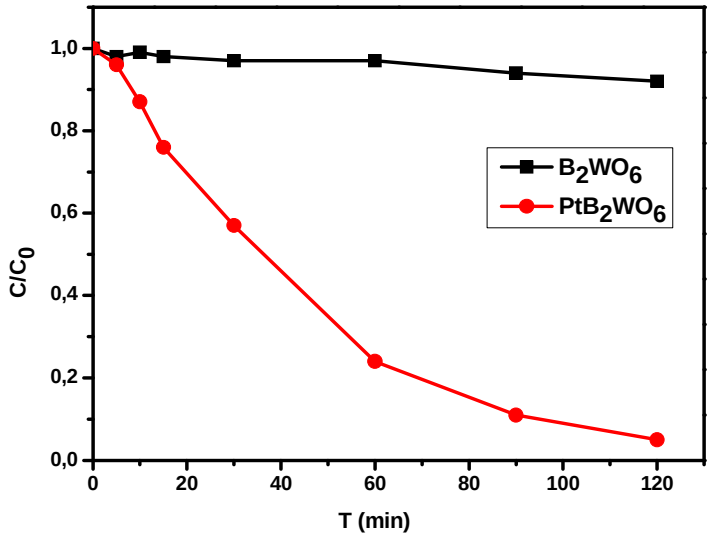

Figure 4: Photocatalytic removal of MO with Bi_2WO_6 and $PtBi_2WO_6$

It is established that noble metal nanoparticles as platinum deposited on the semi-conductor surface are effective traps for photogenerated electrons due to the formation of a Schottky barrier at the metal–semiconductor contact. These electrons can improve the rate of reduction of oxygen (cathodic half-reaction in the photocatalytic process) and reduce the probability of electron–hole recombination as shown in fig.5 [10, 12]. In agreement with the results obtained, the photocatalytic efficiency of Bi_2WO_6 was improved due to platinum deposits as electron traps.

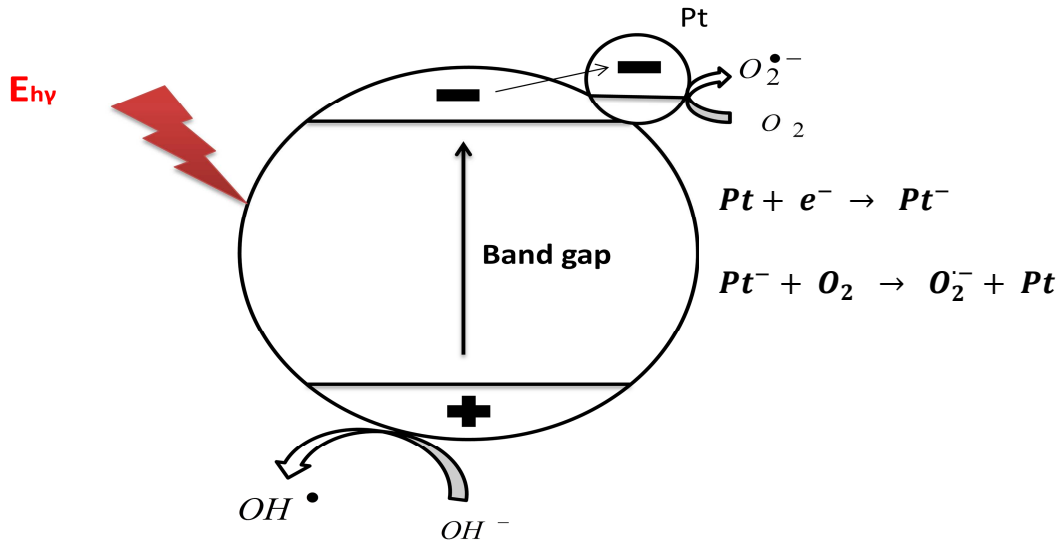

Figure 5: Schematic illustration of charge transfer process

To quantify the increase of the photoactivity for Bi_2WO_6 doped with platinum the "Enhancement Factor" is calculated.

$$E_f = \frac{velocity\ of\ the\ reaction\ with\ doped\ catalyst}{velocity\ of\ the\ reaction\ without\ doped\ catalyst}$$

Sample	V Pt (mol /L/s)	V wtht Pt (mol /L/s)	E_f
Bi_2WO_6	1,4 x 10^{-4}	9,5 10^{-6}	14,73

The $PtBi_2WO_6$ sample is significantly more active than pure Bi_2WO_6. The samples platinised obtained a remarkable improvement of the photocatalytic activity for MO degradation.

CONCLUSION

During the present study, we established that doping Bi_2WO_6 with platinum improved the photocatalytic capacity to degrade Methyl orange under UV illumination. This improvement was explained by platinum deposits as electron traps for photogenerated electrons improving the rate of reduction of oxygen (cathodic half-reaction in the photocatalytic process) and reducing the probability of electron–hole.

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