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Der Pharma Chemica, 2013, 5(6):208-212 (*http://derpharmachemica.com/archive.html*)



ISSN 0975-413X CODEN (USA): PCHHAX

Visible light active novelWO3 nanospheres formethylene blue degradation

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ABSTRACT

In this work, size and morphology controllednovel tungsten oxide nanosphereshave been synthesized via ureaassisted solution combustion method. Ureaplayed the role of a fuel in the combustion process. The prepared WO_3 nanospheres were characterized by different methods. X-ray diffraction analysis indicated that the particles were fine crystallised in the nanorange with amonoclinic phase purecrystalline structure. The field emission scanning electron microscopy images confirmed the nanospheres like morphology of WO_3 particles with high agglomeration tendency. Grain size of the nanospheres was noted to be almost same (10-20 nm) when the preparation was done with urea, whereas the size control is found to be diminished in the absence of urea. Adsorption and photodegradation of methylene blue was investigated over the WO_3 nanospheres under visible light, indicating the potential role of WO_3 nanospheres for the permanent removal of dyes from waste water.

Keywords:WO₃ nanospheres, Visible light, Adsorption, Photodegradation, Methylene blue.

INTRODUCTION

Nanocrystalline semiconductor metal oxides have been caught much special attention in the materials research and more concentrated research is now on-going in the field of synthesis, characterization and applications of nanoparticles. Tungsten oxide nanoparticles have been getting much more attention compared to other metal oxides in recent years in accordance with their remarkable electrical,optical and surface properties [1,2]. Tungsten oxide is the widely used n-type semiconductor with a variety of applications, especiallyin the field of photocatalysis [3], photoluminescent materials [4], sensors [5,6],electrochromic devices[7] etc.Recently several methods have been investigated for the synthesis of WO₃nanomaterials, which includes sol gelmethod [8, 9], acidification method [10], chemical vapour deposition [11], hydrothermal [12], electrodeposition[13], thermal evaporation [14], electro spinning [15], pulsed laser deposition [16]etc.However the rapid synthesis of WO₃ nanoparticles with high yield is an area of current interest in the research.

In this article we report the synthesis, characterization, adsorption and photocatalytic activity of the size controlled tungsten oxide nanospheres, obtained via the solution combustion method using urea as the fuel/surfactant. The enhanced photocatalytic activity of the tungsten oxide nanoparticles was evaluated using the methylene blue degradation under visible light illumination.

MATERIALS AND METHODS

2.1. Synthesis and characterization of WO₃ nanospheres

Fuel assisted solution combustion method was applied for the material synthesis. Equal amounts of (wt %) ammonium tungsten oxide pentahydrate (Alfa Aesar, Ward Hill) and urea (J.T. Baker, USA) were ground in a mortar and dissolved in minimum amount of water in a small beaker followed by heating at 60°C for 1 hour in an

oven. Finally, the material was transferred to a crucible, aged and calcined 400° Cfor 4 hours to obtain the orangeyellow coloured WO₃nanocrystals.Fig. 1 shows the schematic representation of the synthesis route. For the comparison purpose, we prepared sample without urea.

The as-prepared WO₃ nanomaterials were characterized for structure, phase and morphology identification. Fourier transform infrared spectra (FT-IR) were recorded in transmission mode with a thermo scientific NICOLET 6700 apparatus in the 400-4000 cm⁻¹ region. Powder X-ray diffraction (XRD) analysis was performed using a Bruker D8 Focus powder diffractometer with Cu K α radiation at a wavelength of 0.15406 nm. The samples were scanned from 3 to 80° with a step size of 0.025° and the mean crystalline size for each sample was determined using the Scherrer's equation. Field emission scanning electron microscopy (FESEM) images were taken using a Zeiss SUPRA 55 scanning electron microscope with an operating voltage of 10 kV. Transmission electron microscopy (TEM) images were taken using a Philips CM-12 TEM instrument operated at 100 kV.Absorbance of the dye solution after the adsorption and photodegradation experiments was monitored using a UV-visible spectrophotometer (Perkin Elmer Lambda-35).



Fig. 1 Schematic representation of the synthesis

2.2.Photodegradation of methylene blue

In the typical experiment, 0.10g tungsten oxide was added to 50 mL of methylene blue (2.5 mg/L)solution taken in a glass tube and continuous air bubbling was provided with the aid of an aerator for the proper dispersion of WO_3 nanospheres in the dye solution. After 30 minutes duration of adsorption, the solution was irradiated under visible light in a photoreactor(Rayonet type Photoreactor, Associate Technica, India) with 16, 8Watt visible lamps for 4 h to check thedegradation. The decreased dye concentration was measured and percentage of degradation was calculated using the equation,

Efficiency (%) = $((Ao - A)/Ao) \times 100(1)$

Where Ao represents the initial absorbance of the dye solution and A represents the absorbance after the reaction.

RESULTS AND DISCUSSION

In the present work, novel WO_3 nanospheres were synthesized via the urea assisted solution combustion method. Ureaplayed animportant role in material development, contributing to the enhancement of surface activity of

WO₃nanoparticles [17, 18].Fig.2 represents the FT-IR spectra of the as-prepared samples. The well resolved wide band centered at around 750 cm⁻¹ was attributed to stretching vibration of W–O–W bonds [19, 20]. The weak broad band present ataround 3500 cm⁻¹ regioncorresponds to the stretching vibration of O-H group, which is due to the adsorbed water molecules. No other surface adsorbed impurities of urea were present in the urea assisted sample.



Fig. 2- FT-IR spectra of the prepared samples(a) without urea (b) with urea

Fig. 3(a) and (b) depicts the XRD patterns of the products prepared with and without the assistance of urea. All the diffraction patterns were directly indexed to the monoclinic phase pure structure of WO₃ with the lattice parameters a = 0.7301 nm, b = 0.7538 nm, c = 0.7689 nm and P21/n (14) space group (JCPDS no: 01-083-0951). No other peaks were identified in the XRD plot, indicating the phase purity of the as-prepared samples. High crystallinity was observed for both samples as evident from the high intensity of the diffraction peaks. The calculated crystalline size was found to be 29.2 nm for the sample without urea. By the assistance of urea, the crystalline size of WO₃ was significantly reduced to 14.8 nm.



Fig. 3- XRD patterns of the products (a) without urea (b) with urea

FESEM images of the WO₃nanoparticles were shown in Fig4. Fig. 4(a) shows the morphology of tungsten oxide synthesized without the assistance of urea. It can be seen that there is a collection of irregular particles and which were agglomerated randomly. Size of the particles in this sample was found to be very large. But the urea assisted sample showed the existence of more spherical particles with some tiny alterations. Many of the particle sizewere falling in the size range of 10-20 nm, which is in high correlation with XRD data. TEM images of the samples validate this observation as shown in Fig. 5. A porous network was clearly observed Fig. 5(b), due to the inter agglomeration of spherical nanoparticles [21].



Fig. 4- FESEM images of the WO3 prepared (a) alone, (b) with urea



Fig. 5- TEM images of the WO₃ nanoparticles prepared (a) alone (b) with urea

Photodegradation was done to illustrate the catalytic activity of the synthesized systems [22, 23]. Anionic dye pollutant methylene blue (MB) was selected to monitor the adsorption and photodegradation capacity of tungsten oxide nanospheres. Under visible light illumination and in the absence of photocatalysts, there is no appreciable change in the concentration of methylene blue, indicating the lack of self-degradation of dye molecules. On mixing with the as-prepared WO₃nanocatalysts, significant adsorption was noted. Then we investigated the adsorption of methylene blue over the as-synthesized WO₃ nanoparticles with time. For this study we selected 50 ml of dye solution with 2.5 mg/L concentration and 100 mg of WO₃tungsten oxide catalysts. It can be seen that the 99% adsorption was noted in the urea assisted sample within the first 5 minutes of aeration. This can be attributed due to the small size of the tungsten oxide crystals [24]. Whereas the samplesprepared without the aid of urea have alow

adsorption capacity. Only 43% adsorption was achievedunder the same experimental conditionseven for 10 minutes duration of aeration. After that no appreciable change was observed for the sample. The significant change in the adsorption performance of the WO₃ nanoparticles is mainly due to the difference in the dangling-bond density and surface area/porosity of the samples, as reported by Hidayat et al. [25]. By the assistance with urea, the dangling-bond density gets increased due to its reduced particle size [26], resulting the fast adsorption of dye molecules. Since adsorption using a catalytic material is not a fully satisfied method for the destruction of aquatic dye pollutants, we investigated the degradation of adsorbed dye molecules by the illumination with visible light. For the photodegradation, the samples leftafter the adsorption process were irradiated under visible light for 4 hours with continuous air bubblingto check the possibility for adsorbed dye molecules. The dispersed green color solutionobtained after the adsorption of methylene blue by the urea aided catalyst was finally converted to a clear solution, indicating the complete degradation of the adsorbed dye molecules. But the sample prepared without urea showed a mild degradation rate and only 16% degradation were achieved within 4 hours, which additionally explores the role of urea in the activity.

CONCLUSION

Monoclinic phase pure WO_3 nanoparticles with spherical morphology have been successfully fabricated via a urea assisted solution combustion method. The size and morphology of the nanospheres werecontrolled when the preparation was done with urea. Enhanced adsorption and photodegradation was observed for the urea aided sample due to the controlled size and morphology than the WO_3 prepared without urea.

Acknowledgements

We acknowledgeUKM DIP-2012-04, UniversitiKebangsaan Malaysia for the financial support. FST and CRIM are acknowledged for the materials analysis.

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