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Study about the morphology effect on the photo-efficiency of WO_3

Dávidné Nagy[1], Imre Miklós Szilágyi[2,3], Tamás Firkala[2], Xianfeng Fan[1]*

[1]University of Edinburgh, The King's Buildings, Mayfield Road, Edinburgh, EH9 3JL,UK; [2]Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry, Szent Gellért tér 4., Budapest, H-1111, Hungary; [3]Technical Analytical Research Group of the Hungarian Academy of Sciences, Szent Gellért tér 4., Budapest, H-1111, Hungary

Abstract

The photocatalytic activity of hexagonal (h-) WO_3 nanoparticles (NPs) and nanowires (NWs) was investigated and compared with the performance of monoclinic (m-) WO_3 nanoparticles in the aqueous photo-bleaching reaction of methyl orange (MO) under UV irradiation. It has been known that the m-WO_3 is better photocatalyst than the h-WO_3, but due to the advantageous morphology we investigated whether the h-WO_3 NWs can reach the photo-efficiency of the m-WO_3 NPs. The h-WO_3 was successfully synthesized in NW and NP morphology using a microwave (MW) assisted hydrothermal procedure starting from Na_2WO_4 and thermal annealing of hexagonal ammonium tungsten bronze, $(NH_4)_{0.33-x}WO_3$, respectively. We found that the h-WO_3 NWs exhibited almost three times higher photoactivity than the h-WO_3 NPs. The improved performance of the NWs can be attributed to the enlarged surface area and the good charge carrier ability of the nanowire morphology. The catalytic tests also confirmed that the morphological effect could lead to as high photoactivity in the case of h-WO_3 NWs as exhibited by the m-WO_3 NPs.

Kewords: photocatalysis, WO_3, hydrothermal, annealing, synthesis, morphology

1. Background and objectives

In the last few decades much attention has been attracted to alternative energy resources including renewable and nuclear fusion energy due to the limitation of fossil fuel availability on the Earth. Exploring solar light is one of the highly studied possibilities for future energy as it can provide environmental friendly and renewable source of energy. Photocatalysts are able to convert solar energy into chemical energy which can be used for numerous purposes like generation of hydrogen fuel through water splitting; purification of different aqueous media; green synthesis of various chemicals. [1]

* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
E-mail address: author@institute.xxx .

TiO_2 was historically the first photocatalyst and still remained one of the most efficient photocatalysts under UV light. However, the large band gap energy of TiO_2 makes its application in solar photocatalysis insufficient. An option to develop solar sensitive photocatalyst is to couple TiO_2 with other semiconductors, which absorb in the Vis range. As a beneficial consequence of making composites with TiO_2, delayed recombination of the photo-generated charges can be provided. The electrons and holes can be effectively separated in the different semiconductor layers resulting in higher photo-efficiency. Narrow band gap semiconductors like WO_3, V_2O_5, Bi_2O_3 are usually considered to form a heterojunction with TiO_2. [2-4]

WO_3 attracted much attention recently, owing to its broad application prospective and advantageous chemical and electrical properties. [4, 5] WO_3 is a good candidate for the fabrication of solar response photocatalyst with TiO_2 as it has absorption in the Vis range. [6] The photocatalytic activity depends on many factors, and numerous attempts were made in order to control the size distribution and the dimensionality of the nanocatalysts, because these are considered key parameters in affecting their photocatalytic performance. [7-10] Various morphologies were already achieved including nanotrees, nanorods, nanospheres etc. [9, 11, 12] Unexpectedly, it was recently reported that despite their high specific surface area in some cases certain WO_3 particles showed lower photo-efficiency. [13] The peculiar finding was accounted for the facilitated charge recombination which surpassed the positive effect of the enlarged surface area. It is also known that the crystalline phase and the composition of WO_3 play an important role in the photo-efficiency. It was revealed that usually m-WO_3 possesses better photocatalytic ability than h-WO_3. [14]

Considering these factors in this study we aimed to investigate the overall effect of the morphology on the photocatalytic performance of different polymorphs of WO_3, with the pronounced future objective to fabricate solar active nanocomposites by coupling WO_3 polymorphs with TiO_2.

2. Experimental

H-WO_3 NPs were prepared by thermal annealing of hexagonal ammonium tungsten bronze, $(NH_4)_{0.33-x}WO_3$ at 470 ºC in air. [15] H-WO_3 NWs were obtained in a microwave assisted hydrothermal synthesis at 160 ºC. [5] The reaction mixture was prepared from sodium tungstate dihydrate ($Na_2WO_4·2H_2O$), ammonium sulphate ($(NH_4)_2SO_4$), HCl and distilled water followed by the MW process in a Synthos 3000 Anton Paar reactor. After the synthesis the nanocrystals were centrifuged, washed with water and ethanol and finally dried at 80 ºC for 24 h. For the preparation of the m-WO_3 NPs, $(NH_4)_{0.33-x}WO_3$ was annealed at 600 ºC in air. [15]

The morphology of the as-prepared catalysts was investigated by TEM, and the images were collected by a FEI Morgagni 268D instrument. The determination of the crystalline phase of the WO_3 photocatalysts was performed by recording Raman spectra. A Jobin-Yvon Labram type Raman spectrometer coupled with an Olympus BX-41 microscope was used. Nd-YAG laser with a wavelength of 532 nm was applied as a light source in the Raman spectrometer. The specific surface area was determined by applying the BET model based on the absorption isotherm of nitrogen at 77 K using a NOVA 2000E equipment (Quantachrome, USA).

The photocatalytic activity was measured in aqueous methyl orange (MO) (10 mg/350 ml) solution under UV irradiation. In a typical test 100 mg catalyst powder was suspended in the MO solution. The photo-reactor was a cylindrical glass reactor equipped with a Heraeus TQ 150 mercury immersion lamp. The solution was stirred and oxygen bubbling was provided. Room temperature was maintained by circulating cold water in the jacket of the photo-reactor. The concentration of MO was followed by a Jasco V-550 type UV-Vis spectrophotometer at 465 nm.

3. Results and discussion

The morphology of the nanostructures was confirmed by TEM (see in Fig. 1.). The images revealed that the h-WO_3 NWs had diameters between 5 and 10 nm and were several hundred nm long. The h-WO_3 NPs consisted of 50-70 nm particles, while the m-WO_3 NPs were made up by 60-90 nm particles.

The BET specific surface area of the h-WO_3 NP and NW was found to be 11 m^2g^{-1} and 101 m^2g^{-1}, respectively. The nanowire morphology resulted in one order of magnitude higher specific surface area, compared to that of the nanoparticle. [14]

The Raman spectra were in good agreement with the literature data and confirmed the hexagonal and monoclinic crystalline phase of the certain WO_3 nanostructures. [14]

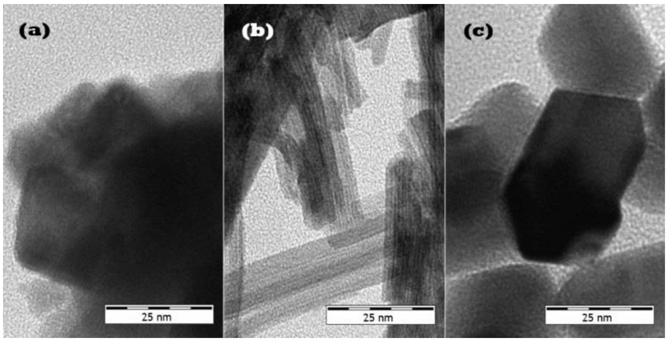

Fig. 1. TEM images of (a) h-WO_3 NPs; (b) h-WO_3 NWs; (c) m-WO_3 NPs

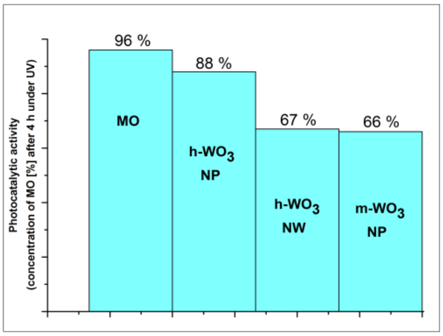

Fig. 2. MO concentrations given in percentage after 4 hour UV irradiation in the photocatalytic test reaction

In the photocatalytic test we found that the h-WO_3 NWs were almost three times more effective in the degradation of MO than h-WO_3 NPs (see Fig. 2.). By the end of the 4 hour UV irradiation 12 % of the initial MO was decomposed by the h-WO_3 NPs, while the h-WO_3 NWs photo-bleached 33% of the original concentration of MO. The remarkable improvement in the photocatalytic activity could be attributed to the beneficial morphology of the h-WO_3 NWs. The findings also confirmed how important the precise control is over the morphology. The nanowire structure can provide better carrier transport to the separated charges and possess higher specific surface area leading to triple efficiency. The performance of h-WO_3 NWs was compared with the activity of m-WO_3 NPs as well. It was concluded that by the end of the photocatalytic test the h-WO_3 NWs were even more efficient (34 % MO decomposed) than the nanoparticles of the inherently better photocatalyst m-WO_3 (33 % MO decomposed). This finding revealed that the h-WO_3, which attracted much interest due to its unique open-tunnel structure, can also achieve similarly high photon efficiency as m-WO_3.

4. Conclusions

In this study we successfully synthesized h-WO_3 both with NW and NP morphology along with m-WO_3 with NP nanostructure, either by a MW assisted hydrothermal synthesis route or by annealing $(NH_4)_{0.33-x}WO_3$. The crystal phase of the nanostructures was confirmed by Raman spectroscopy while the microstructures were investigated by TEM. The morphological effect on the photo-efficiency of the as-prepared h- and m-WO_3 nanostructures was elucidated. The photoactivity of the h-WO_3 NWs was higher almost three times higher compared to the performance of the h-WO_3 NPs. The significant improvement in the photo-efficiency clearly indicated the positive effect of the high aspect ratio of the NWs, which could provide more enhanced carrier transport in the photocatalytic reaction than the NP nanostructure. It was also studied whether the h-WO_3 NWs can exhibit as high photoactivity as the m-WO_3 NPs, which have been otherwise considered to be better photocatalysts. It was found that by the end of the degradation test the h-WO_3 NWs surpassed even the performance of m-WO_3 NPs to some extent.

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