

Improved Photocatalytic and Electrochemical Performance of Hydrothermally Synthesized Mg_2SnO_4 Nanocubes and their Effect on Loading with Activated Carbon

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Abstract

Highly crystalline Mg_2SnO_4 nanocubes were successfully synthesized using a facile hydrothermal method. Further activated carbon was loaded with Mg_2SnO_4 nanoparticles in order to enhance the photocatalytic performance. Photocatalytic performance of Mg_2SnO_4 nanocubes and activated carbon loaded Mg_2SnO_4 nanocomposites were examined by methyl green and methylene blue dye degradation under the exposure of UV light. However, results suggest that activated carbon loaded Mg_2SnO_4 nanocomposites has significantly enhanced the photocatalytic performance over Mg_2SnO_4 nanocubes. It is assumed that better photocatalytic activity is caused by the higher specific surface area of activated carbon loaded Mg_2SnO_4 nanocomposites. Furthermore, cyclic voltammetry was used to analyze the electrochemical properties of the samples. Results indicate that activated carbon significantly enhanced the electrochemical properties of Mg_2SnO_4 nanoparticles. Copyright © VBRI Press.

Keywords: Photocatalysis, hydrothermal synthesis, Mg_2SnO_4 , activated carbon.

Introduction

Ternary metal stannates A_2SnO_4 (A=Zn, Mg, Cd, Co, Ni) are one class of metal oxides with interesting properties towards various applications. Mg_2SnO_4 (MTO) is one of the A_2SnO_4 compounds having cubic spinel structure with space group $Fd\bar{3}m$. Most of the research on MTO was mainly focused on its application as phosphor and as lithium-ion battery anodes [1, 2]. Recently, Yuan Quin et al. explored the photocatalytic property of MTO/ SnO_2 nanostructures using degradation of methylene blue (MB) dye under UV light irradiation. They found that MTO/ SnO_2 polyhedral nanocomposites exhibited an excellent photocatalytic activity against MB dye [3]. However, reports on MTO in photocatalytic applications are scarce. Activated carbon with its rapid adsorption kinetics, huge adsorption capacity, and luxury of regeneration, is mostly utilized in industries as a support meant for heterogeneous catalysis. [4]. In this work, MTO nanoparticles and activated carbon loaded MTO nanocubes (AC/MTO) have been successfully synthesized via simple hydrothermal method.

Photocatalytic performance of the samples was analyzed through degradation of methylene blue and methyl green dyes. Additionally, electrochemical characteristics of the synthesized powders were examined. To our knowledge best, this is the first attempt on analyzing the photocatalytic and electrochemical performance of AC/MTO nanoparticles.

Experimental

Chemicals of analytic grade were used in this work without any additional purification. Here, 50 ml of deionized water was added with 0.06M of magnesium chloride hexahydrate and 0.03M of tin chloride pentahydrate and stirred continuously, later slowly 2M of KOH solution was added dropwise leads to the formation of a white colored solution. This mixed solution then moved into a Teflon coated stainless steel autoclave and kept at 180 °C for 12 hours in a hot air oven. Then, the resultant product was filtered and washed by deionized water and absolute ethanol repeatedly. Lastly, the product was dried at 80 °C for

three hours and calcined at 550 °C, 750 °C and 950 °C. For preparing the MTO/activated carbon nanocomposites same procedure was followed in addition commercially purchased activated carbon was added into the solution with the weight ratio of 1:2. X-ray diffraction (XRD), FESEM and HR-TEM was used to characterize the prepared samples. Optical properties were examined by a UV-vis spectrometer. Surface area measurements were analyzed by Brunauer – Emmett – Teller (BET) analysis. Cyclic voltammetry analysis was done by an electrochemical work station whereas photocatalytic degradation reactions were carried out under ambient temperature (303 K) using a multi-lamp photoreactor with UV lamp (365 nm).

Results and discussion

The crystal structure and the corresponding phases of the samples were investigated using XRD method. **Fig. 1(a-e)** illustrates the XRD patterns of as-synthesized, calcined (at 550 °C, 750 °C and 950 °C) MTO and MTO/AC samples. XRD pattern of the precursor $\text{MgSn}(\text{OH})_6$ is shown in **Fig. 1a**, observed diffraction peaks matched with the pure cubic phase of $\text{MgSn}(\text{OH})_6$ (JCPDS #20-0727) [5]. Diffraction patterns of samples calcined at 550 °C and 750 °C were showed in **Fig. 1 (b and c)**. However, both the samples exhibited amorphous like broad peaks corresponding to SnO_2 . Further XRD pattern of sample calcined at 950 °C (**Fig. 1d**) showed a drastic change, all the diffraction peaks of the samples were in consistent with the standard JCPDS #24-0723 of cubic spinel MTO. This sample was optimized as the activated carbon loaded MTO nanoparticles. **Fig. 1e** illustrates the XRD pattern of AC/MTO nanocomposites, it is evident from **Fig. 1e** that all the peaks were in well agreement with the JCPDS #24-0723. However, the intensity of the peaks was reduced and the peaks were broadened which results in reduced crystallite size this might be the effect of activated carbon. For convenience synthesized MTO nanoparticles (annealed at 950 °C) and MTO/activated carbon nanocomposites were denoted as MTO and MTO/AC. The average crystallite size of the MTO and MTO/AC samples was estimated as 29.97 and 16.85nm, respectively using Scherrer's formula.

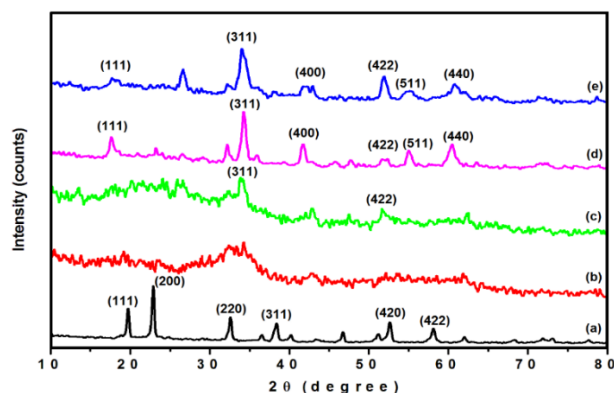


Fig. 1. XRD patterns of as-synthesized (a), calcined (at 550°C, 750°C and 950 °C) MTO (b-d) and MTO/AC samples (e).

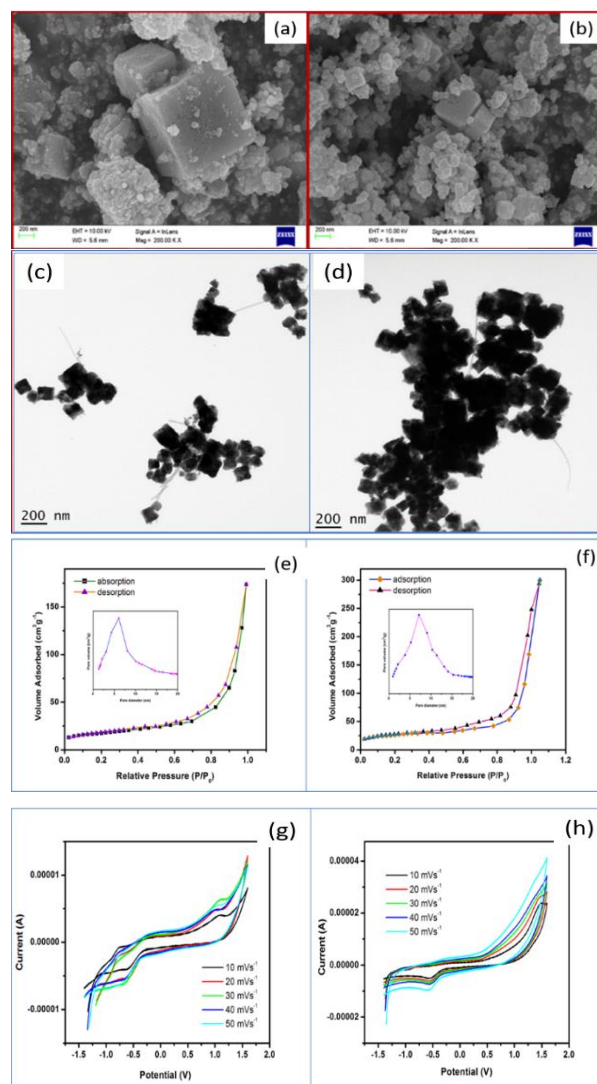


Fig. 2. FESEM images of MTO (a) and MTO/AC (b) samples, HR-TEM images of MTO (c) and MTO/AC (d) samples, N_2 adsorption – desorption isotherms of MTO (e) and MTO/AC (f) samples, Cyclic voltograms of MTO (g) and MTO/AC (h) samples at different scan rates.

Results of FESEM reveals that MTO sample (**Fig. 2a & b**) possess cubic like morphology whereas MTO/AC sample (**Fig. 2c & d**) showed irregular cubic with some spherical shaped morphology. **Fig. 2 (e and f)** exemplifies the N_2 adsorption – desorption isotherms of MTO and MTO/AC samples, while inset shows the pore size distribution, respectively. It is widely accepted that increased surface area would lead to the enhanced photocatalytic behavior of nano-photocatalysts. It is apparent from the results that type IV isotherm with the hysteresis range of 0.4 - 1.0 P/P_0 exhibited by both the samples which infers the mesoporous nature of the prepared samples [6]. The calculated average pore size of the MTO is 6.18 nm and for MTO/AC is 7.21 nm, which can be attributed to the mesoporous nature. BET was used to determine the specific surface area of the samples and the value is estimated as $23 \text{ m}^2 \text{ g}^{-1}$ for MTO sample and $97 \text{ m}^2 \text{ g}^{-1}$ for MTO/AC sample.

Hence, loading of activated carbon into MTO nanoparticles enhances the specific surface area considerably which perhaps result in enhanced photocatalytic activity. **Fig. 2 (g and h)** divulges the CV curves of MTO and MTO/AC at 10, 20, 30, 40 and 50 mVs^{-1} scan rates in -1.5 V and +1.6 V potential window. From the figures it is clear that shape of the curves of both the samples was not rectangle hence the samples doesn't possess conventional electric double layer capacitance (EDLC). This variation in the curves from rectangular profile is because of the pseudo capacitive characteristics of the samples. Pseudo capacitance with its high transfer of energy during the faradaic reaction tips to have improved storage compared to conventional EDLC's [7]. Calculated specific capacitance values of MTO sample at 10, 20, 30, 40 and 50 mVs^{-1} are 31, 23, 17, 12, 7 Fg^{-1} similarly for MTO/AC sample the values are 103, 71, 48, 29, 18 Fg^{-1} . Results suggesting that activated carbon played a substantial role in enhancing the electrochemical properties of the MTO nanoparticles. Furthermore, high specific capacitance value was obtained at 10 mVs^{-1} with the increase of scan rate specific capacitance value of both the samples gets decreased this can be attributed to the low faradaic reaction process. However, higher specific surface area of the MTO/AC sample than the MTO sample could also be the reason for the enhanced electrochemical performance, which is evident from the BET analysis.

Photocatalytic activity

Fig. 3 represents the degradation absorption spectra of MG (a & b) and MB (c & d) dyes in the presence of MTO and MTO/AC as photocatalysts, respectively. Degradation of dyes without the addition of prepared photocatalysts was negligible. When the dye solution is added with prepared samples and kept in dark, it is observed that the solution remained stable which indicates degradation of dyes were due to the prepared photocatalysts and also with the UV light irradiation. It is well-known that, when the surface of the catalyst irradiates by the photon of UV-light, electrons present in the conduction band could get excited to the valence band which generates the same number of holes in the valence band. These holes will interact with the surface of the catalyst, to generate the active oxygen species (OH^{\cdot} , HO_2^{\cdot} and $\text{O}_2^{\cdot-}$ radicals), which leads to dye degradation [3]. From results, it is evident that MTO/AC nanocomposite exhibited better photocatalytic activity than the MTO photocatalyst, MTO/AC nanocomposite exhibited 93 and 92 % for MG and MB dyes whereas, MTO photocatalyst attained 82 and 78 % of degradation, respectively. Enhanced photocatalytic performance of MTO/AC nanocomposites could be ascribed to the superior specific surface area and greater pore size. Present investigation showed boosted photocatalytic activity for degradation of MB dye with MTO as photocatalyst under UV – light irradiation.

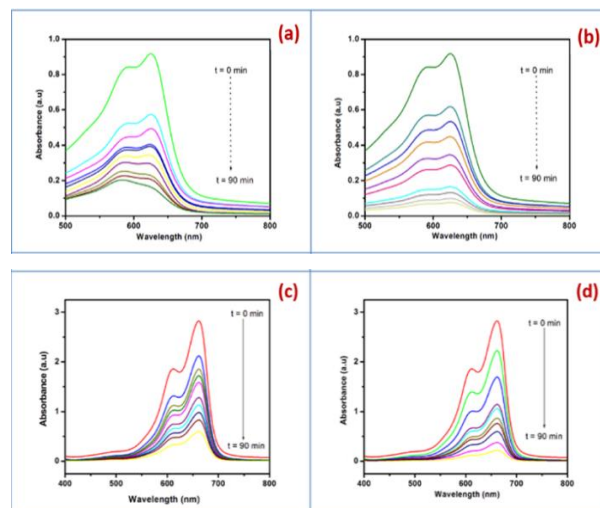


Fig. 3. UV-Vis absorption spectra of MG (a and b) and MB (c and d) dye solution at various times with MTO and MTO/AC samples as photocatalyst.

Conclusion

In summary, cubic spinel MTO nanocubes and activated carbon loaded MTO nanocomposites have been successfully synthesized via facile hydrothermal method by calcining the sample at 950 °C. FESEM and HRTEM results revealed the cubical morphology of the synthesized samples. Further, MTO/AC sample exhibited better photocatalytic activity over MTO sample on degradation of MG and MB dyes upon exposure of UV light over a time period of 90 min. Electrochemical results showed that MTO obtained 31 Fg^{-1} and MTO/AC attained 103 Fg^{-1} specific capacitance at 10 mVs^{-1} scan rate. The enhanced photocatalytic activity and electrochemical performance of the MTO/AC sample is accredited to its higher specific surface area than the MTO sample. Hence, MTO/AC nanocomposites could be useful in photocatalytic and electrochemical applications. Further, the role of activated carbon in the present study portrays its effectiveness in enhancing the properties of nanomaterials. Moreover, this result paves the way for new class of electrode materials for supercapacitor applications.

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