

Photocatalytic properties of single crystalline MoV_2O_8 nanowires

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In this study, we synthesized high quality single crystalline MoV_2O_8 nanowires using spin coating technology and subsequent thermal annealing process. Structural investigations showed the successful preparation of 1D nanostructure of MoV_2O_8 in wires morphology owning average diameter less than 100 nm, and lengths ranging from 1-5 μm . Furthermore, the TEM analysis identified $\langle 001 \rangle$, the most prominent growth direction of MoV_2O_8 nanowires. The nanowires have also proven to be a potential photocatalyst for the degradation of toluidine blue O dye under ultraviolet irradiation. Therefore, we expect that MoV_2O_8 nanowires will be useful as material for future photocatalyst.

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1. Introduction

In the last few decades, one-dimensional (1D) nanostructures have been enormously prepared in diverse morphologies (nanowires, nanotubes, nanofibres and nanorods) and these tiny structures have promising properties for use in next generation applications [1, 3]. Amongst other 1D nanostructures, nanostructures of metal oxides with layered structures are attracted for applications in the field of electronics, actuators, energy storages devices and sensitizers for photolysis of water [4-6]. In this context, the nanostructures of metal vanadates are important functional materials and have different properties depending on their structures and composition. Literature shows that different vanadates molybdenum vanadate (MoV_2O_8) in the form of thin film and bulk powder has gained considerable interest due to its excellent catalytic, electrical, and magnetic properties [7-10]. Furthermore, the photocatalytic activity of the different metal oxide catalysts such as TiO_2 , WO_3 , $\text{Bi}_{12}\text{TiO}_{20}$, NaNbO_3 , and $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$ [9-13] has also been investigated under UV/visible light. In this regard, we we have recently prepared a new photocatalyst which have shown significant efficiency in both UV and visible region. [give reference] It is well known that the MoV_2O_8 nanostructures in wire morphology (absorption of UV/Vis light) is susceptible to photoactivation with wavelengths less than 400 nm thus it can be used, as a semiconductor-type photocatalyst, for the photooxidation of organic pollutant in the liquid phase and the photocatalytic degradation of water pollutants. Based on this fact, it is suggested that the MoV_2O_8 may be an effective catalyst for the photocatalytic degradation of organic pollutants. It is well known that shape, size, and crystal structure of

complex metal oxides can significantly influence the energy density, cycling life, and performance of photocatalytic and electrochemical energy devices [12-14].

In the present work we synthesized high-quality single-crystalline MoV_2O_8 nanowires by spin coating the solution directly on a substrate followed by thermal decomposition process without dangerous reagents, harmful solvents, and surfactants. Our results indicate that by controlling the structural morphology, MoV_2O_8 showed excellent photocatalytic performance which significantly enhanced as compared to bulk which, in turn, makes them promising candidates for the fabrication of photocatalytic devices.

2. Experimental

Material and synthesis

All chemicals used in this experiment which includes, Ammonium metavanadate (NH_4VO_3) molybdenum water and hydrochloric acid (HCl) were of analytical grade and purchased from Sigma Aldrich. They were used without further purification. In a typical synthesis of MoV_2O_8 nanowires ammonium metavanadate (0.1 mmol) was dissolved in 2 ml of molybdenum water (Mo-water) with continuous stirring. Concentrated HCl (1ml) was added drop wise for complete dissolution of NH_4VO_3 . The resultant yellow solution was used for further experimentation. The precursor solution was spin coated on SiO_2 substrates at 2000 rpm for 30 seconds which have been ultrasonically cleaned in acetone, alcohol and IPA prior to the deposition. The spin coated substrates were placed into the oven at 550 °C for 2 hours.

Bulk MoV₂O₈ powder was also synthesized by annealing the dried powder of ammonium metavanadate (NH₄VO₃), molybdenum water and hydrochloric acid (HCl) solution at 550°C for 2 hours for the comparison of photocatalytic degradation of toluidine blue O (TBO) dye.

3. Results and discussion

The FE-SEM analysis (JEOL JSM – 7401F) of the synthesized MoV₂O₈ nanowires was carried out and the results are presented in the Fig. 1(a). The results show that the nanowires having an average diameter 100 nm and length up to tens of micrometers. X-ray diffraction patterns of the MoV₂O₈ nanowires shown in Fig. 1(b). It is in good agreement with the standard peaks for the orthorhombic phase of MoV₂O₈ (JCPDS card 74-0050). The nanowires were further characterized by TEM and HR-TEM analysis. The TEM image of the single nanowire is shown in Fig. 2(a). HR-TEM image of a nanowire is shown in Fig. 2(b) in which the lattice fringes are clearly visible. The distance between the neighboring fringes was found to be 4.1 Å which is consistent with the (201) plane of orthorhombic MoV₂O₈. The selective area electron diffraction (SAED) pattern Fig. 2(c) confirms the single crystalline nature of nanowire. TEM analysis indicates that the growth direction of nanowires is along <001>, resulting in an angle of 60° between the zone axes and nanowires. The chemical composition of the nanowires was characterized by energy-dispersive x-ray spectra (EDS). The EDX spectra and compositions shown in the Fig. 2 (d), feature peaks corresponding to elements Mo, V, and O peaks (the Cu peaks come from the Cu TEM grid), which show the characteristic composition of a nanowire. Moreover, EDX measurement for the nanowires (Fig. 2 (d)) shows that the dominant component of nanowires is vanadium 38.50%, while the molybdenum amount is 3.12% have been detected.

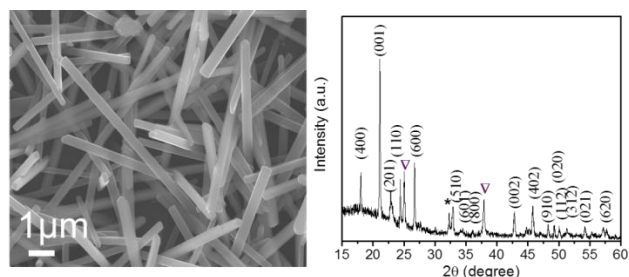


Fig. 1. (a) FE-SEM image of the MoV₂O₈ nanowires synthesized at 500°C for 2 hours. The FE-SEM analysis shows that the average diameter of the nanowires was about 120 nm, with lengths in the micrometer range, (b) Powder X-ray diffraction patterns of MoV₂O₈ nanowires (where the labeled peaks (Δ) represent MoO₃ and (*) represent the Si substrate). XRD patterns were recorded on an MX Labo powder diffractometer using Cu K α radiation = 1.54 Å (40 kV, 20 mA), at the rate of 2 °C min⁻¹ over the range 15–60.

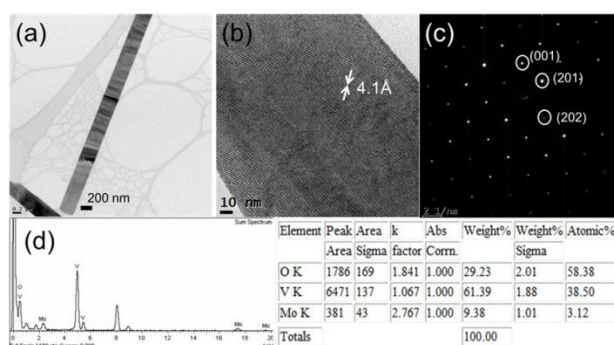


Fig. 2. (a) Low magnification TEM image of MoV₂O₈ nanowire, (b) HR-TEM of nanowire showing high crystallinity with a d200 spacing of 0.41 nm, (c) corresponding SAED pattern of individual nanowire recorded along [010] zone axis. (d) EDS spectrum of MoV₂O₈ nanowire. The characteristic Cu X-ray peaks are due to scattering from the TEM support grid.

3.1. Photocatalytic performance

Before examining the photocatalytic activity it is important to study the optical absorption of the as-prepared nanowires because the UV-Vis absorption edge is relevant to the energy band of the semiconductor catalyst [19-20]. The UV-Vis spectra of MoV₂O₈ nanowires in Fig 3 (a) show an edge in 370 nm UV region. The photocatalytic activity of the samples was measured using a TBO in aqueous medium. The reaction mixture was prepared by adding MoV₂O₈ nanowires to a TBO with an initial concentration of 0.5 mmol. The solution was stirred continuously in the dark for 30 mins to equilibrate the adsorption-desorption process of TBO. After the adsorption-desorption process, 3 ml of the solution was used for analysis of the TBO concentration using a UV-VIS spectrophotometer (UV-3600 Shimadzu). A sample of TBO (3 ml) solution was removed after regular intervals and centrifuged at 6000 rpm for 2 min to separate the catalyst particles from the solution. The 98% of dye solution is decolorized in less than 40 mins under UV light as shown in Fig. 3(b). The TBO without nanowires as a catalyst under UV light is stable and only 2% of TBO decolorizes after 90 mins. For the comparison we also study the photocatalytic behavior of commercially available TiO₂ and bulk MoV₂O₈ with present sample are shown in Fig. 4(a).

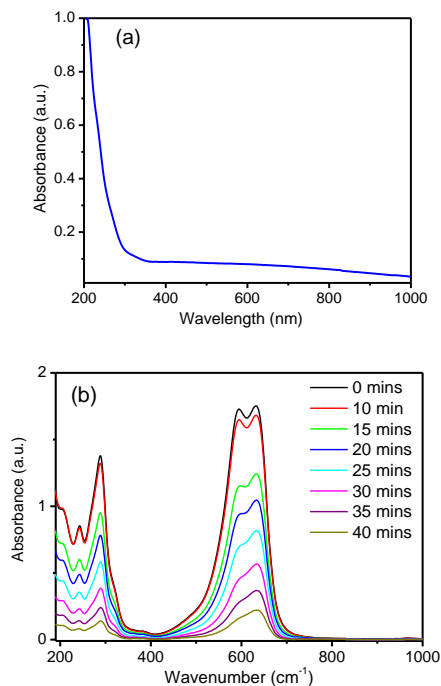


Fig. 3. (a) Optical absorption of MoV_2O_8 nanowires, (b) Absorption spectra of the TBO solution at different photocatalytic degradation times under UV-vis light irradiation.

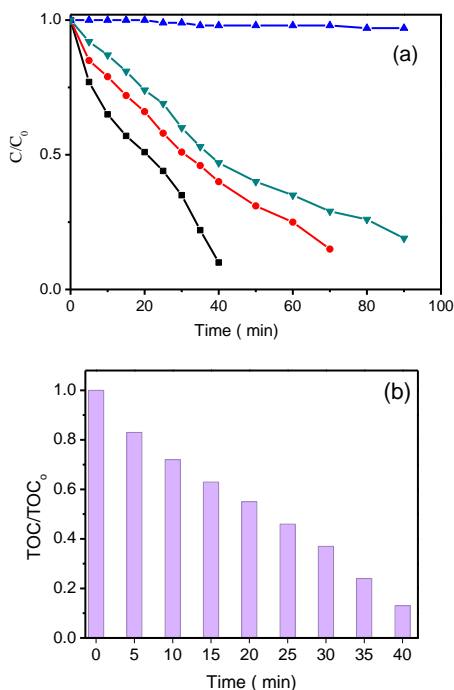
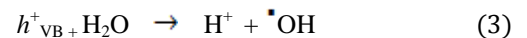
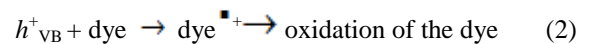
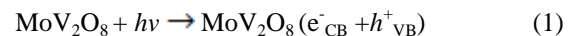


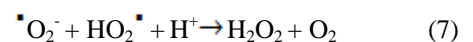
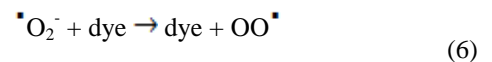
Fig. 4. (a) Photocatalytic degradation profile of TBO under UV-vis light irradiation. (I) MoV_2O_8 , (II) TiO_2 , (III) bulk MoV_2O_8 , (IV) only TBO without catalyst. (b) The mineralization rate of contaminant was determined by measuring the disappearance of total organic carbon (TOC) during the photocatalytic degradation of TBO by photocatalysis with MoV_2O_8 nanowires under UV-visible light irradiation.

The degradation of TBO solution has also been proved by total organic carbon (TOC) analysis. From Fig. 4(b), the degree of mineralization of TBO was estimated by the determination of the decrease in the TOC in the reaction solution [21]. In Fig. 4(b), it is clearly shown that the degree of mineralization for MoV_2O_8 under UV light is 90% after 40 min. Thus, we are further convinced that most of the TOC was completely mineralized.

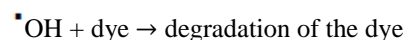
It has been established that the photocatalysed degradation of organic matter in solution is initiated by photo excitation of the semiconductor, followed by the formation of an electron-hole pair on the surface of catalyst (Equation. (1)). The high oxidative potential of the hole (h^+_{VB}) in the catalyst permits the direct oxidation of organic matter (dye) to reactive intermediates (Equation. (2)). Very reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. (3)) or by the reaction of the hole with OH^- (Equation. (4)). The hydroxyl radical is an extremely strong, non-selective oxidant ($E_0 = +3.06$ V) which leads to the partial or complete mineralization of several organic chemicals.



Electron in the conduction band (e^-_{CB}) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (5)). This radical, in the presence of organic scavengers, may form organic peroxides (Eq. (6)) or hydrogen peroxide (Eq. (7)).



Electrons in the conduction band are also responsible for the production of hydroxyl radicals, species which have been indicated as the primary cause of organic matter mineralization [15–17].



The faster charge transfer of MoV_2O_8 compared to TiO_2 was confirmed by electrochemical impedance spectra (EIS). The Nyquist plots of the MoV_2O_8 and TiO_2 electrodes are shown in Fig. 5(a). The EIS analysis indicates that the semicircle in the plot became shorter for MoV_2O_8 as compared to TiO_2 , which clearly indicates a

decrease in solid state interface layer resistance and the charge transfer resistance on the surface. Hence, MoV₂O₈ nanowires effectively suppressed the charge recombination process and leaving more charge carriers to form reactive species to promote the degradation of TBO dye during the photocatalytic reaction.

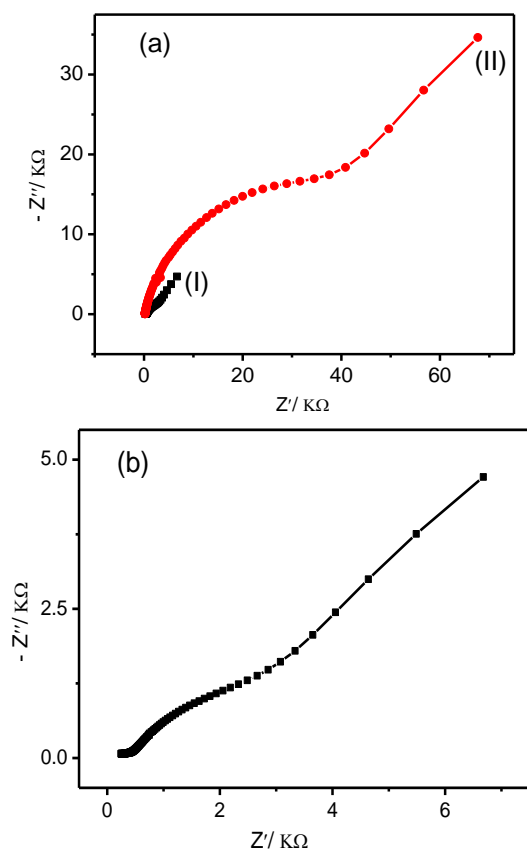


Fig. 5. (a) Impedance analysis of MoV₂O₈ nanowires (I) and TiO₂ powder (II) in the presence of a 2.5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture as a redox probe in 0.1 M KCl aqueous solutions, Z': real impedance. Z'': imaginary impedance (b) shows an enlarged scale.

4. Conclusion

In summary, we have synthesized MoV₂O₈ nanowires by spin coated chemical solution deposition method and their photocatalytic properties were investigated. The photocatalytic measurements show MoV₂O₈ nanowires under UV light can be efficiently used for the photocatalytic degradation of TBO. We believe that the concepts presented in this study provide a general route for designing nanostructured photocatalyst application

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