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Facile Preparation and Characterization of Copper Molybdate Nanostructures for Photocatalysis via Novel Microwave Combustion Technique

A. Shameem, V. Siva, A. Murugan, Shamima Hussain, S. Asath Bahadur

Abstract*: Spherical copper molybdate ($Cu_3Mo_2O_9$) nanoparticles (NPs) have been prepared via the microwave combustion technique. The structural, morphological and elemental characterizations have been investigated by PXRD, SEM and EDS studies. It was found that the as-prepared sample possesses nanoplate morphology and particles size was found to be around 18 nm. The as-prepared sample was inspected in the disintegration of Methylene Blue (MB) dye envisioned using UV-Visible spectroscopy. It was found that the prepared nanocatalyst could serve as an active photocatalyst for MB under direct sun light.

Keywords:* microwave combustion, copper molybdate, methylene blue, sun light.

I. INTRODUCTION

Copper based materials are widely utilized for the locale of catalysts for example, ion exchange, intercalation science and photochemistry [1]. Amid, copper molybdate ($Cu_3Mo_2O_9$) nanocatalyst is the ongoing consideration one, in view of their positive application in various fields [2]-[5]. Henceforth, the advancement of apparent path for the development of nano-$Cu_3Mo_2O_9$ catalyst with a complicated surface morphology having plenteous noteworthiness for the forthcoming investigations of both physical and chemical properties. At atmospheric pressure $Cu_3Mo_2O_9$ shows two polymorphs, 1) stable α structure with molybdenum situated in a tetrahedral domain and 2) metastable γ structure with molybdenum situated in an octahedral situation. The oxide shows up a genuine buzzer of various significant properties: thermochromic, trisochromic, tribochromic, piezochromic and photoelectrochemical properties, subsequently display phase transition related to the shading variation from green to dark coloured [6], [7]. The first order transition was progressed by solid difference in volume and anisotropic splitting of grains, happens as indicated by dominocascade kinetics. Besides, temperatures or pressures for transition were flexible by synthetic doping. As a result, pristine material was discovered in enormous applications like catalyst, sensor, supercapacitor, etc. The multifaceted nature of $Cu_3Mo_2O_9$ legitimizes the various investigations on this oxide [2]-[5], [8], [9]. Copper molybdate is one of the significant inorganic transition metal oxides that possess high potential application in different fields such as catalysis, laser hosts, optical fibers, microwave, humidity and gas sensors applications. Recently, numerous investigations have been accounted for the synthesis of copper molybdate like precipitation [10], hydrothermal [11], flame spray strategy [12] sonochemical [13], micro-emulsion [14], etc. In many cases, these techniques more often require post high temperature calcination, time consuming, larger solution usage, complicated steps requirements, etc. resulting a great challenge for industrial applications. This problem may be solved by using simple and low-cost microwave combustion method. This method is superior to other synthetic approach better purity product, elevated reaction response and energy saving [15]. This paper deals with the preparation of a fine powder of $Cu_3Mo_2O_9$ by a facile microwave combustion method and it embellishes to solve environmental issues.

II. EXPERIMENTAL

A. Synthesis of Copper molybdate

Copper molybdate compound was synthesized using $Na_2MoO_4.2H_2O$ and $Cu(NO_3)_2.3H_2O$ as precursors (A.R grade) and urea ($CO(NH_2)_2$) as a fuel by facile microwave combustion method as described earlier by our group [15].

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* Correspondence Author (s)
A. Shameem, Department of Physics, School of Advanced Sciences & Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil, Tamil Nadu, India – 626126 . Email: shameemirfu@gmail.com
V. Siva, Department of Physics, School of Advanced Sciences & Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil, Tamil Nadu, India – 626126. Email: vsiva33.physics@gmail.com
A. Murugan, Department of Physics, School of Advanced Sciences& Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil, Tamil Nadu, India – 626126. Email: murugan027@gmail.com
Shamima Hussain, UGC-DAE CSR Kalpakkam Node, Kokilamedu, Kalpakkam, Tamil Nadu, India- 603104. Email: sh@csr.res.in
S. Asath Bahadur*, Department of Physics, School of Advanced Sciences & Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil, Tamil Nadu, India – 626126. Email: s_a_bahadur@yahoo.co.in

ZAqueous solution of precursor and fuel salts were mixed together in double distilled (DD) water under vigorous stirring until it becomes a homogeneous solution. Then, the mixture in crucible was moved to microwave oven and irradiated for 7 min. and allowed for combustion. Later, the precipitate underwent washing with DD water followed by ethanol and dried overnight. A domestic IFB-20PG3S microwave has been utilized for the preparation having 1000 W with vitality 2.45 GHz.

III. RESULT AND DISCUSSION

A. Structural and morphological studies:

The phase purity, crystal structure and crystallinity of the prepared copper molybdate sample were characterized using powder XRD analysis. Bruker D8 advance ECO XRD systems were used for analysis. It holds SSD160 1D Detector X-ray diffractometer with Cu-Kα1 and Kα2 having wavelength of 1.5406 and 1.54439 Å respectively. Figure 1 shows powder XRD pattern of $Cu_3Mo_2O_9$ and the XRD measurement matched with the JCPDS card number #70-2493. It belongs to the orthorhombic crystal structure with primitive lattice. The PXRD peak confirms that the prepared sample is of $Cu_3Mo_2O_9$ and their hkl values are represented in the Fig. 1. The average crystalline size was around 18 nm which was calculated using Debye-Scherrer formula [2], [15].

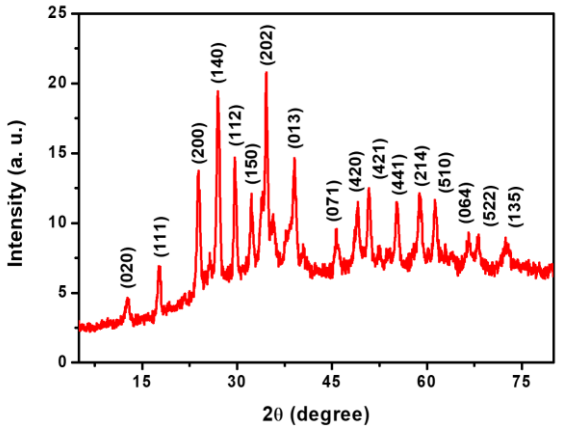

Fig. 1. Powder XRD pattern of copper molybdate nanocatalyst.

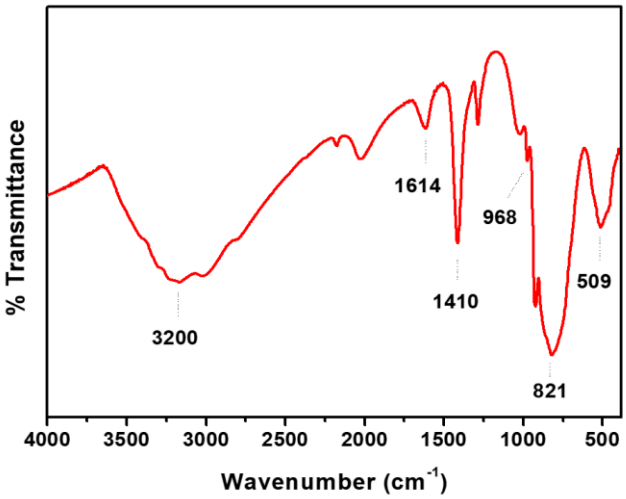

Fig. 2. FT-IR spectrum of as-prepared copper molybdate NPs.

The Fourier transform infrared spectrum (FT-IR) of the powder sample has been determined by Shimadzu (IR Tracer-100) spectrophotometer. Fig. 2. represents FT-IR spectrum of prepared sample detected between 400 and 4000 cm^{-1} by means of KBr pellet method. A very broad band appeared around 3200 cm^{-1} is the stretching vibrations of absorption of H_2O and a peak at 1410 and 1614 cm^{-1} is symmetric and asymmetric metal bonded stretching vibration of C-O groups [16], [17]. The characteristic peak assigned at 968 cm^{-1} may be because of Mo=O bond, indicating υ vibration of a distorted MoO_6. The peak observed between 600 and 1050 cm^{-1} was dispensed to vibration of the Mo-O-Mo. A strong absorption peaks observed in the range of 390–650 cm^{-1} is due to Cu–O bonds [2].

The morphology and elemental confirmation were investigated with SEM made of ZEISS EVO 18 Research attached with BRUKER-X Flash 6130 EDS. The morphology of the prepared sample was examined by SEM and displayed in Fig. 3. SEM images were attained in the absence of surfactant. It illustrates that sample have formed by assembling of small spherical shaped NPs which have resulted in formation of fine nanoclusters with agglomeration of the NPs. The noticed agglomeration may be due to the magnetic relationship with in the $Cu_3Mo_2O_9$ particles. Moreover, EDS spectroscopy have been used to analyze the elemental distributions in the $Cu_3Mo_2O_9$ NPs. The EDS spectrum confirms the occurrence of Cu, Mo, and O elements in the prepared sample, as shown in Fig. 4. The elemental composition of each element is tabulated in the table I.

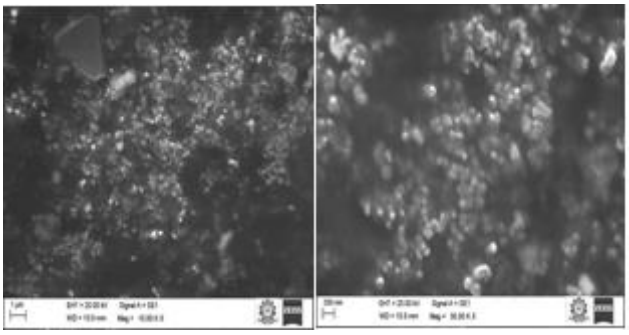

Fig. 3. SEM pictures of nano-spherical $Cu_3Mo_2O_9$ NPs.

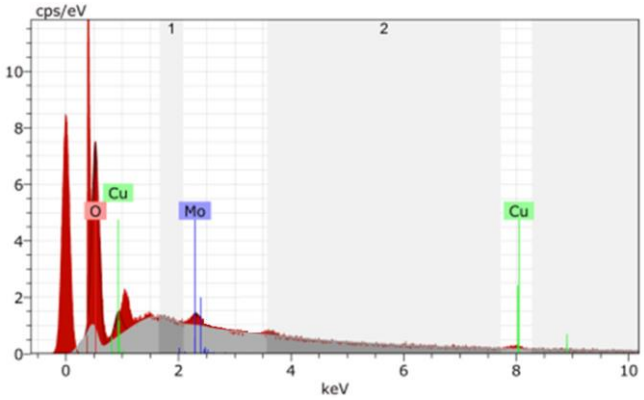

Fig. 4. EDS spectrum of spherical $Cu_3M0_2O_9$ nanoparticles

Table- I: Elemental composition of $Cu_3M0_2O_9$ NPs in weight %

Elements	Weight %
Copper	21.43
Molybdenum	14.29
Oxygen	64.28

B. Photocatalytic degradation:

The photocatalytic degradation efficiency of as-prepared $Cu_3Mo_2O_9$ NPs was assessed towards degradation of MB dye under direct sun light irradiation. In this present study, 1×10^{-5} mole concentration of MB in aqueous medium and 50 mg of $Cu_3Mo_2O_9$ nanocatalyst was loaded to the earlier prepared MB solution and allowed to stir for 30 min. to attain equilibrium condition and eradicate the adsorption's effect on photodegradation efficiency of MB solution in a dark condition. Later, 4 ml of the resultant mixture solution was collected for UV analysis termed as dark reaction expressed as 0 min. (control). The photocatalytic experiment was carried out in direct sun light irradiation (visible light λ >400 nm). During the process, 4 ml of the reaction solution withdrawn periodically at the equal time interval of 10 min. and the changes in the concentration of aqueous MB was measured using UV–Vis. spectroscopy.

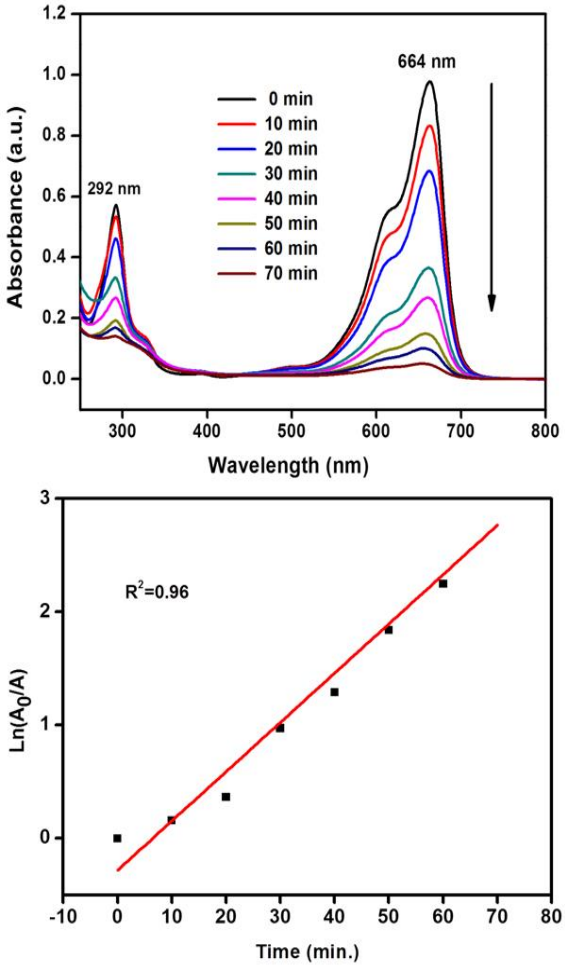

Fig. 5. (a) Photodegradation absorbance spectra of MB dye using 50 mg of $Cu_3Mo_2O_9$ nanocatalyst under sun light and (b) Calibration plot of MB degradation ($Ln(A_0/A)$ Vs time).

The photocatalytic mechanism recommends both the photocatalyst and light source are essential for the photocatalytic reaction. The typical absorption peak of MB at 664 nm is utilized to investigate the degradation process [18]–[20]. Fig.5(a) represents the photodegradation absorption spectra of MB dye solution and the intensity of the major absorption peak of MB at 664 nm declines with the rise in irradiation time. In addition, Fig 5(b) shows the calibration plot of MB degradation in aqueous medium. After 70 min, the intensity peaks almost vanish which represents that the complete degradation of MB. The degradation plot of $Ln(A_0/A)$ Vs time represents linear fit which propose the first order kinetics degradation with a linear regression coefficient (R^2) 0.96 [19], [20]. The prepared sample has good catalytic property, finally a complete degradation of MB dye. Thus, the as-prepared $Cu_3Mo_2O_9$ photocatalyst act to be a good candidate for environmental remediation.

IV. CONCLUSION

Copper molybdate was successfully prepared by one-pot microwave combustion technique and characterized by powder XRD, FT-IR, SEM and EDX analyses. The spherical shaped 18 nm $Cu_3Mo_2O_9$ NPs were found from SEM and XRD results. As-prepared $Cu_3Mo_2O_9$ active catalyst has improved absorption in the visible region and thus evidenced as a better visible photocatalyst for the decomposition of industrial contaminants methylene blue. The pseudo first order kinetic reaction was followed with R^2 is 0.96. In comparison, the prepared method is cost effective with simple, involves materials with less toxicity, less solvent and reaction time.

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AUTHORS PROFILE

A. Shameem is a Research scholar in the Department of Physics, School of Advanced Sciences at Kalasalingam Academy of Research and Education, India. He received his B.Sc. degree in Physics from Jamal Mohamed College, Tiruchirappalli, in 2010, and his M.Sc. degree in Physics from Government Arts College (Autonomous), Coimbatore, in 2012. His research interest is in the field of nanomaterials for energy and environmental applications.

Dr. V. Siva obtained Ph.D. in Physics from Kalasalingam Academy of Research and Education in 2018. He has received his Bachelor's Degree and Master's Degree in Physics from Government Arts College (Autonomous), Coimbatore, which is affiliated to Bharathiar University in the years 2010 and 2012, respectively. He has expertise in the areas of Crystallography, Crystal growth and Computational Physics. To his credit, he has published more than 20 articles in journals of international repute besides ten more as proceedings. Further, he has presented papers in various conferences and seminars. His current research interestisthe development of Metal-Organic Frameworks (MOFs) for sensor and energy storage applications.

A. Murugan is a Senior Research Fellow in the Department of Physics at Kalasalingam Academy of Research and Education. He has joined as Junior Research Fellow in the Department of Physics under DST-SERB funded project, Govt. of India in the year of 2017. He has received his Master's Degree in Physics from Government Arts College (Autonomous), Coimbatore, which is affiliated to Bharathiar University in the year 2013.His research focus is thin film for solar cell applicationsand the design of materials enhanced for energy applications.

Dr. Shamima Hussain is a Scientist in UGC-DAE Consortium for Scientific Research, Kalpakkam Node Kokilamedu-603104, Tamil Nadu, India since 2011. She had worked as a Postdoctoral Fellow, Semiconductor and Material Spectroscopy Lab, KAUST, Saudi Arabia, 2009 - 2010. Her research interest is on synthesis and characterization of materials especially thin films of II-VI III-V semiconductors, composite materials, materials for photovoltaics, and functional materials.

Dr. S. Asath Bahadur is a Senior Professor in the Department of Physics, School of Advanced Sciences at Kalasalingam Academy of Research and Education, India. He has obtained Ph.D. in the area of X-ray crystallography from Madurai Kamaraj University in 1994 and also received his M.Phil. and M.Sc. Degree in physics from Madurai Kamaraj University. He has expertise in the areas of Crystallography and Material science. He has published more than eighty-five peer-review research articles in journals of international repute besides seventy more as proceedings.