

Electrochemical Synthesis and Characterization of Molybdenum Oxide Nanoparticles

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ABSTRACT

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Molybdenum oxide nanoparticles were prepared by electrochemical reduction method using tetra butyl ammonium bromide (TBAB) as a stabilizing agent in an organic medium i.e. tetra hydro furan (THF) and acetonitrile (ACN) in 4:1 ratio and at current density 14 mA/cm², and molar concentration of the ligand. The reduction process takes place under inert atmosphere of nitrogen over a period of 2h. Such nanoparticles are prepared using simple electrolysis cell in which the sacrificial anode as a commercially available Molybdenum metal sheet and platinum (inert) sheet act as a cathode. The synthesized molybdenum oxide nanoparticles were characterized by using ultra violet-visible spectroscopy, Infra-red spectroscopy, scanning electron microscopy, and energy dispersive spectroscopy analysis techniques.

Keywords : Electrochemical cell, Tetra butyl ammonium bromide, Molybdenum oxide nanoparticles, UV-visible spectroscopy, IR spectroscopy, and SEM.

I. INTRODUCTION

The recent interest in the synthesis and characterization of nanomaterials is due to diverse areas of applications, including catalysis, sensing, and electrochemistry [1-3]. The electrochemical method for production of nanoparticles has been widely studied since early work of Reetz [4-5]. This indicated that size selective nanosize transition metal particles could be prepared electrochemically using tetra alkyl

ammonium salts as stabilizers of metal cluster in a nonaqueous medium. The electrochemical technique has been shown to be better than other nanoparticles synthesis methods because of simple equipment set up, low cost and high yield & purity of nanoparticles [6-7]. In recent years much exertion has been committed to the investigation of molybdenum oxides and related materials. Molybdenum oxide, has attracted intensive attention because of its certain chemical and physical properties [8-9]. Molybdenum oxides possess

unique catalytic and electronic properties and have potential applications in chemical synthesis, petroleum refining, recording media and sensors [10-13]. They are also used in the optical device applications [14-16] and a promising material for photo electrochemical energy production with high surface area having higher photo efficiencies [17,18]. In this report, we describe the synthesis of Molybdenum oxide nanoparticles by electrochemical method with tetra butyl ammonium bromide as stabilizing agent and their characterization.

II. EXPERIMENTAL METHOD

2.1. Materials:

Tetra Butyl ammonium bromide (TBAB) (A.R.), tetrahydrofuran (THF) and acetonitrile (ACN) were purchased from Aldrich and S.D. Fine chemicals and used as such. The sacrificial anode in the form of molybdenum sheet and platinum sheet as inert cathode having thickness 0.25 mm and purity 99.9% were purchased from Alfa Aesaer. The specially designed electrolysis cell with a volume of 30ml was used.

2.2. Synthesis of MoO₃ Nanoparticles:

In electrochemical reduction method for oxidation of bulk metal and reduction of metal ions for size selective preparation of tetra butyl ammonium salt stabilized metal nanoparticles. In the initial experiment we have used a molybdenum metal sheet (1x1 cm) as anode and a platinum sheet (1x1 cm) as the cathode. These two electrodes were placed parallel to one another and were separated by 1.0cm in 0.01 M solutions of TBAB prepared in ACN/THF(4:1) which also served as the supporting electrolyte (scheme-1). The electrolysis process was then carried out at current density of 14 mA/cm² for 2.0 hrs. For UV-visible spectroscopic study, 2.0 ml of the sample solution was withdrawn after completion of electrolysis process and solution was allowed to settle for one day. The agglomerated solid sample was separated from the solution by decantation and

washed three to four times with THF. The washed samples were then dried under vacuum desiccator and store in air tight containers. As obtained MoO₃-TBAB crystallite compound was used as precursor to prepare MoO₃ nanorods. The dried sample of MoO₃-TBAB crystallite compound was placed in a silica crucible which was then put into the electric muffle furnace and kept at 500°C temperature for 2 hours. After natural cooling down to room temperature gave bright pale yellowish crystals of molybdenum oxide nanorods were obtained.

III. CHARACTERIZATION OF NANOPARTICLES

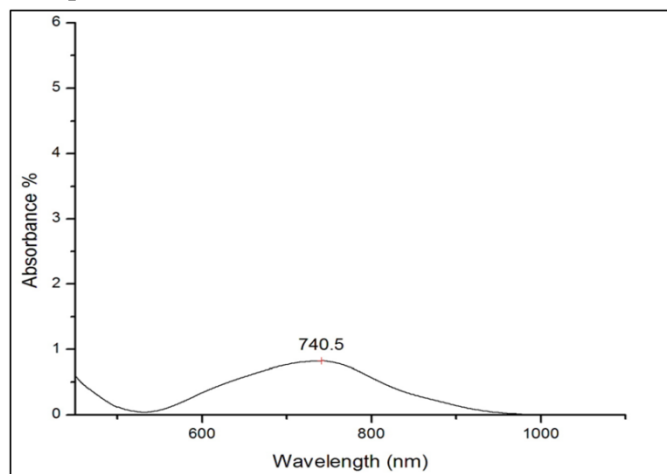
The prepared molybdenum oxide nanorods were characterized by UV-Visible, FT-IR, SEM-EDS techniques. The UV-Visible spectrum was recorded on spectrophotometer [JASCO 503] with a quartz cuvette using ACN / THF (4:1) as reference solvent. The IR spectra were recorded on FT-IR spectrophotometer [JASCO FT-IR/4100] Japan using dry KBr as standard reference in the range of 400–4000 cm⁻¹. To study the morphology and elemental composition, molybdenum oxide nanorods were examined using SEM and energy dispersive spectrophotometer (EDS), The SEM analysis were carried out with JEOL; JSM- 6330 LA operated at 20.0kV and 1.0000nA.

IV. RESULTS AND DISCUSSION

4.1. UV-visible Spectroscopy

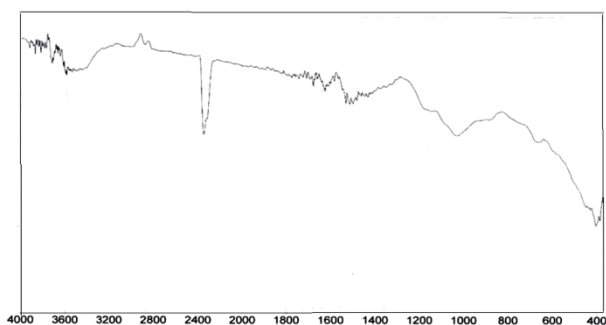
The UV-visible absorption spectrum recorded for molybdenum oxide nanoparticles is shown in Fig 4.1a exhibits maximum absorption at 740nm for TBAB at 14mA. The metal nanoparticles exhibit absorption bands or broad regions of absorption in the UV-visible range due to the excitation of surface plasmon resonances (SPR) or interband transitions; these SPR are characteristic properties for the metallic nature of particles. The particles showed hardly any change in the absorption spectra even after a month of ageing time indicating highly stable nature of particles. The

broadening of SPR peak was due to the agglomeration of the nanoparticles in the sample and high width of these particles' distribution.

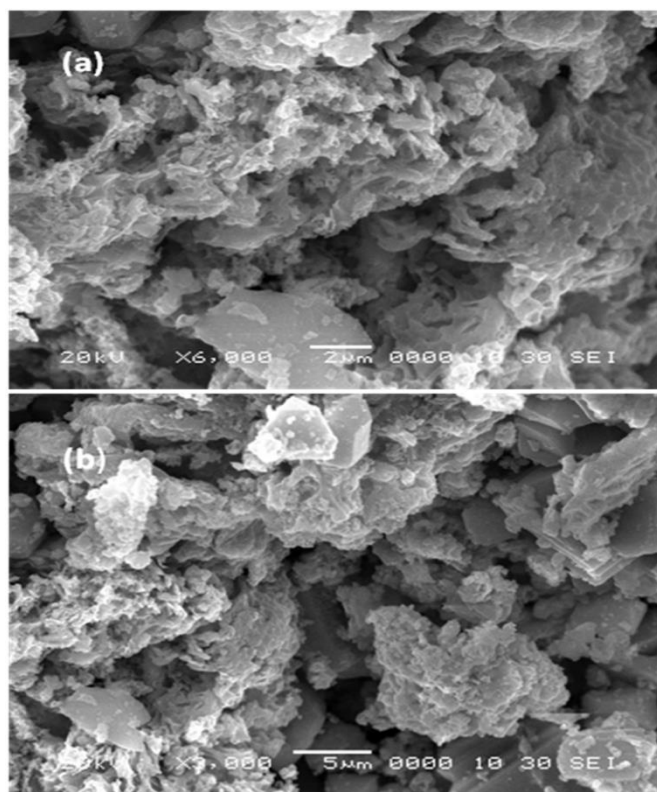


4.2. IR Specoscopy:

The IR spectra in fig.4.2 of molybdenum nanoparticles capped with TPAB as capping agent shows peaks at 2956cm^{-1} indicating the C-H stretching. The frequencies corresponding to 1591cm^{-1} and 1464cm^{-1} are due to symmetrical (ammonium ion) bending and C-H bending respectively. The unconjugated C-N linkage gives medium bands at 1376cm^{-1} and at 1264cm^{-1} . The mixed phase of molybdenum and molybdenum oxide is characterized by the peaks at 499cm^{-1} , 806cm^{-1} and 1079cm^{-1} .



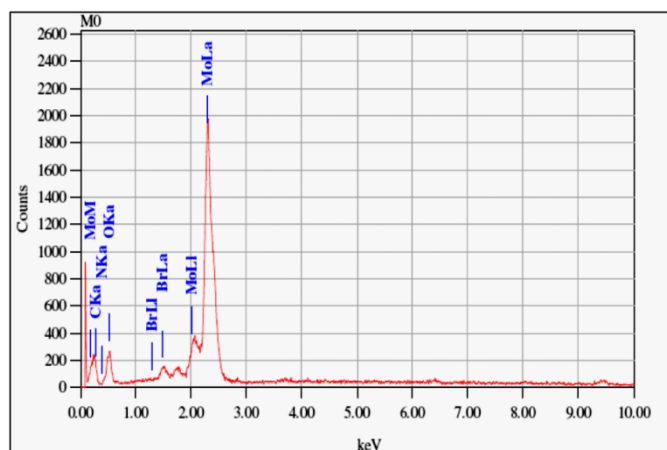
4.3. Scanning Electron Microscopy:



The evaluated morphology of molybdenum oxide nanoparticles capped with TBAB studied by SEM which is shown in Fig.4.3(a) and (b) respectively. The scanning electron microgram and the particle size distribution for the sample of molybdenum nanoparticles capped with TBAB at current density of 14 mA/cm^2 is obtained for various resolutions. Fig.(a) and (b) SEM microstructure of the electrochemical reduction derived molybdenum oxide nanoparticles reveals the presence of dense agglomerations. It shows these particles having irregular shape and their distribution is not uniform. This is probably due to the partial solubility of the surfactant in the solvent under the given experimental conditions. The single molybdenum nanoparticle having the average particle size of is 1 to 20nm in range.

4.4. Energy Dispersive Spectrophotometer:

Molybdenum nanoparticles synthesized with capping agent TBAB at current density 14 mA/cm^2 were analyzed qualitatively and quantitatively by EDS.



Constituents	Mass (%)	Atom (%)
Mo	51.65	13.66
O	24.56	38.96
Br	1.62	0.51

Fig.4.4 shows that molybdenum, oxygen and bromine are present in the sample. Here trace amount of Bromine is present because of addition of tetra butyl ammonium bromide.

V. CONCLUSIONS

In summary, we have demonstrated the efficiency of electrochemical reduction method for the synthesis of molybdenum oxide nanoparticles. The TBAB salts used as ligands have played a significant role on controlling the particle size. The procedure offers several advantages including control the particles size (1–10 nm), excellent yields, operational simplicity, minimum environmental effects and above all.

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