Synthesis and evaluation of antioxidant behavior of MoO_3 nanoparticles

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ABSTRACT: *Modified co-precipitation method was used to synthesized α-molybdenum oxide nanoparticles (α-MoO_3 NPs). The Polyethylene glycol used as stabilizer in an aqueous medium. These synthesized NPs were characterized by TGA, XRD and SEM analysis. The synthesized NPs are long rod and average grain size is in the range of 3.00-10.00 nm. The antioxidant activity of these nanoparticles was evaluated using in vitro modified DPPH method.*

Key Words: *Modified co-precipitation method, Polyethylene glycol, α-MoO_3 nanoparticles, in vitro antioxidant,*

Introduction

During normal cellular metabolic reactions, reactive oxygen species (ROS) like hydroxyl radical (ȮH), hydrogen peroxide (H_2O_2) and superoxide radicals ($\dot{O}_2$) are formed. These metabolic species help to maintain homeostasis when they are not in excess concentration. Mammalian cells have a defense mechanism which detoxifies these radicals. Formation and detoxification of these ROS is maintained in healthy state. Several antioxidant species like catalase, superoxide dismutase, glutathione-s-transferase, glutathione peroxidase, non enzymatic species including vitamin E, glutathione[1,2] are the integral part of cellular defense mechanism. Dysfunctioning of antioxidant mechanism leads to cellular damage[3]. These excess ROS are known to interact with proteins, lipids, nucleic acids and cell structure[4,5] resulting in structural and functional changes in proteins, genetic disorders and loss of membrane integrity[6]. ROS are also known to cause disorders like cancer[7] and atherosclerosis[8], neurodegenerative disorder and aging[9] and diabetic disorders[10]. Natural antioxidant like vitamin A, C and E play an important role in neutralizing these ROS. In present days the need of external antioxidants is increasing. Development of newer antioxidants is an emerging research area today.

Nanotechnology, the leading branch which is of prime importance for researchers. The research efforts in this field are constantly increasing because of the wide applications of nanoparticles. Along with the various applications, nanoparticles have shown antioxidant properties also. Antioxidant properties of metal oxide nanoparticles have been investigated by different researchers. Report on antioxidant activity of Y_2O_3, Al_2O_3[11], CuO[12-14], Ag[15,16], NiO[17] and Fe_2O_3[18] are available. α-MoO_3 have been less studied for their antioxidant property. In focus of this literature survey we decided to synthesize and evaluate the α-MoO_3 NPs for their antioxidant behavior.

Experimental

Materials and methods:

All the chemicals were of AR grade and used without purification. Ammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$, Polyethylene glycol (4000), 2, 2-Diphenyl-1-picrylhydrazyl (DPPH) and Concentrated Nitric acid was purchased from Aldrich. Methanol (HPLC grade) and distilled water were used as a solvent.

Method:

To synthesize molybdenum oxide nanoparticles, firstly prepare 25.00 ml 0.05M of ammonium heptamolybdate tetrahydrate (AHM) solution. Subsequently, add 0.7 gm Polyethylene glycol (PEG) as capping agent and 1.5 ml of concentric HNO_3 acid drop wise to the above solution with continuously stirred for 48 h at room temperature. After this, white color precipitate was obtained, which was washed with distilled water and ethanol several times to remove the residues from the product. Finally, the product was dried for 3 h through in an oven maintained at 80 ºC. The prepared sample was calcined to 600ºC with the help of a muffle furnace for 2 h.

Reaction Mechanism:

The AHM and conc. HNO_3 acts as reaction partner and PEG as capping agent for the formation of MoO_3. The formation of MoO_3 can be understand as per the following reaction mechanism [19]. Steps involved in reaction mechanism

Step 1: Dissociation of AHM takes place to produce 6 NH_4^+ and $Mo_7O_{24}^{-6}$ ion.

$$(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O \longrightarrow 6\,NH_4^+ + Mo_7O_{24}^{-6} + 4\,H_2O$$

Step 2: concentrated nitric acid ionizes to H^+ and NO_3^- ions.

$$6\,HNO_3 \longrightarrow 6\,H^+ + 6\,NO_3^-$$

Step 3: The ionization of AHM released NH_4^+ and NO_3^- ions combine together to form NH_4NO_3.

$$6\,NH_4^+ + 6\,NO_3^- \longrightarrow 6\,NH_4NO_3$$

Step 4: Finally solid MoO_3 get separated as nanocrystallites in acidic medium.

$$Mo_7O_{24}^{-6} + 6\,H^+ \longrightarrow 7\,MoO_3 + 3\,H_2O$$

Overall Reaction

$$(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O_{(aq.)} + 6\,HNO_3 \longrightarrow 7\,MoO_3 + 6\,NH_4NO_{3\,(aq.)} + 7\,H_2O$$

Assessment of antioxidant activity:

Antioxidant behavior of α-MoO_3 NPs was assessed by DPPH method for insoluble materials as reported by Serpen *et al* [20]. In a test tube was taken 100 mg of powder α-MoO_3 NPs and 2.5 mL (100µM) methanolic solution of DPPH. The mixture was further sonicated for 5 min. and kept in dark to increase the rate of contact between α-MoO_3 NPs and DPPH reagent. The contents were centrifuged at 15,500 rpm for two min. The DPPH scavenging activity was evaluated by measuring absorbance of supernatent liquid at 517 nm at different time intervals. The percent inhibition was calculated using the equation

$$\%\ \text{inhibation} = \frac{[(\text{Acontrol} - \text{Asample}]}{\text{Acontrol}} \text{X}100$$

Where $A_{control}$ and A_{sample} are absorbance of Control and supernatant DPPH solvent respectively.

The SC 50 (amount required to scavenge 50% DPPH) value was evaluated by taking 0.004 % DPPH solution in methanol and stored at 4 ºC in dark until use. Prepare stock solution of MoO_3 NPs (1mg/ml) was diluted to final concentration of 100 µg/ml to 1000 µg/ml in their methanol. Volume was made upto 2.00 ml with methanol. 2.00 ml of 0.004 % of DPPH methanol was added to the sample solution of different concentration. These were test samples. 2.00 ml of methanol was added to the sample solution of different concentration. These were blank solutions. 2.00 ml of DPPH solution was added to 2.00 ml of methanol and used as control. The blank for this solution was methanol. As DPPH is sensitive to light, it was exposed to the minimum possible light. These solutions were kept at room temperature in dark for 30.00 min to complete the reaction. The absorbance was measured at 517 nm and converted into the percentage antioxidant activity using the following equation:

$$\text{Scavenging capacity}\ (\%) = \frac{\text{Absorbance of negative control} - \text{Absorbance of test}}{\text{Absorbance of negative control}}\ \text{X}\ 100$$

Characterization of α-MoO_3 nanoparticles:

The thermogram of synthesized solid nanoclusters were recorded in the range of 27 °C to 1000 °C on Shimadzu TA 60 WS. Powder samples in the size of 45-50 mg were placed in a platinum pan. The calcinations temperature of the synthesized sample determined by TGA. The determination of average particle size and crystal phase was done by powder X-ray diffractometer with Cu-K_α radiation (λ = 1.5406 Å) recorded using Bruker D8 Advance. The surface morphology of α-MoO_3 NPs were examined by using SEM technique. The SEM analysis was carried out with JEOL-LED 2300 (LA). The DPPH scavenging activity was evaluated using Shimadzu 1800 UV-visible spectrophotometer.

Result and Discussion

Thermogravimetric Analysis:

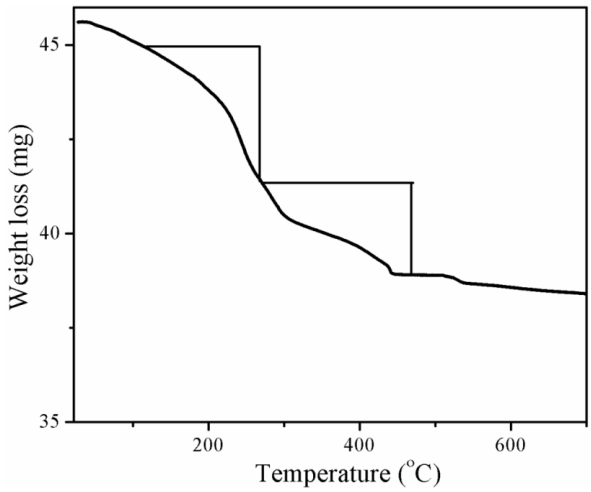

Fig. 1 Thermo gram of synthesized sample

TGA analysis was performed in order to understand the thermal behavior of MoO_3. Fig. 1 shows TGA curve in the temperature range of 27˚C to 700˚C for α-MoO_3. The first weight loss equivalent to 3.802 % in temperature range of 100-220˚C was due to the desorption of physically adsorbed water molecules at the surface of α-MoO_3 sample. The next weight loss equivalent to 9.068 % in temperature of 230-430 °C corresponds to the decomposition of capping agent; loss of ammonia and other nitrates. We observe no weight loss in 430-700℃ temperature range. It indicates the formation of thermodynamically stable α-MoO_3. Therefore according to the TGA analysis it is clear that the α-MoO_3 is a thermodynamically stable phase [21].

X-ray diffraction analysis:

Fig. 2 shows X-ray diffraction analysis at 20°-80° confirms the crystal phase and grain size of synthesized α-MoO_3 NPs. The nanocrystalline α-MoO_3 structure was confirmed by broad peaks obtained at corresponding its 2θ and planes observed at 24.721° (0 1 1), 26.911° (0 2 1), 30.849° (0 3 1), 34.388° (1 4 0), 40.220° (0 5 1), 47.198° (1 5 1), 53.974° (2 2 1), 59.792° (0 9 0), 66.097° (0 9 1) and 78.400° (2 9 0) respectively indicating the orthorhombic structure of α-MoO_3 nanoparticles. All peaks obtained were in good agreement with the JCPDS file no. 76-1003. The lattice parameter observed a = 3.962, b = 13.85, c = 3.696 at α = β = γ = 90. The average grain size is calculated by Scherrer's equation and was estimated to be 6.82 nm.

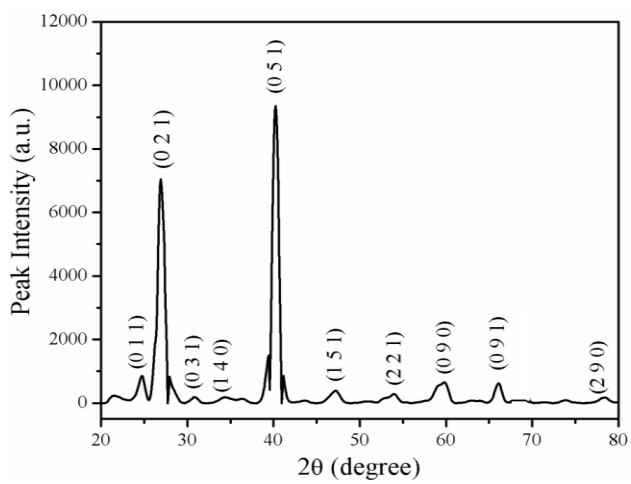

Fig. 2 XRD pattern of Molybdenum oxide nanoparticles

Scanning Electron Microscopy:

Surface morphology of the sample was carried out using scanning electron microscopy (SEM). The morphology of the synthesized α-MoO_3 nanoparticles capped with PEG at various resolutions shown in Fig. 3. The SEM image for α-MoO_3 nanoparticles showed that the obtained nanoparticles had irregular shape and

their distribution is not uniform. Fig.3 shows a microgram at a resolution of 10μm and 5μm. The microgram appears to be broad rod like nanoparticles are formed.

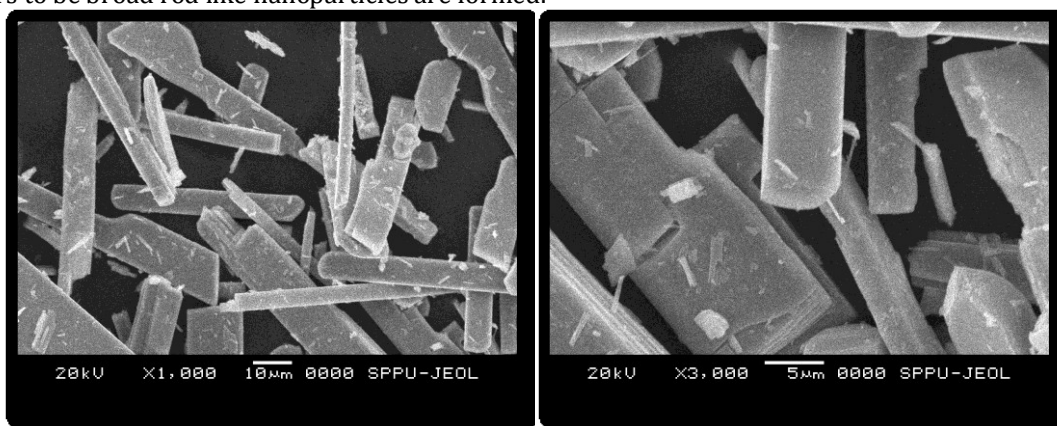

Fig. 3 SEM images of α-MoO_3 nanoparticles

Antioxidant Activity Result:

The DPPH reagent used as control and it does not show any change of absorbance with time. In presence of α-MoO_3 NPs, DPPH containing solution changed from deep violet to pale yellow. Fig. 4 (a) shows a steady decrease in absorbance at 517 nm in DPPH with α-MoO_3 NPs. As seen in Fig. 4 (a) the DPPH scavenging percentage of α-MoO_3 NPs increase from 68.32 to 81.30 % as time increase from 30 to 60 min for 100 mg of α-MoO_3 NPs. From Fig. 4 (b) the SC 50 value was determined graphically and was found to be 400 μg that is 0.4 mg. The observed antioxidant activity might be due to neutralization of free radical character of DPPH by the transfer of an electron.

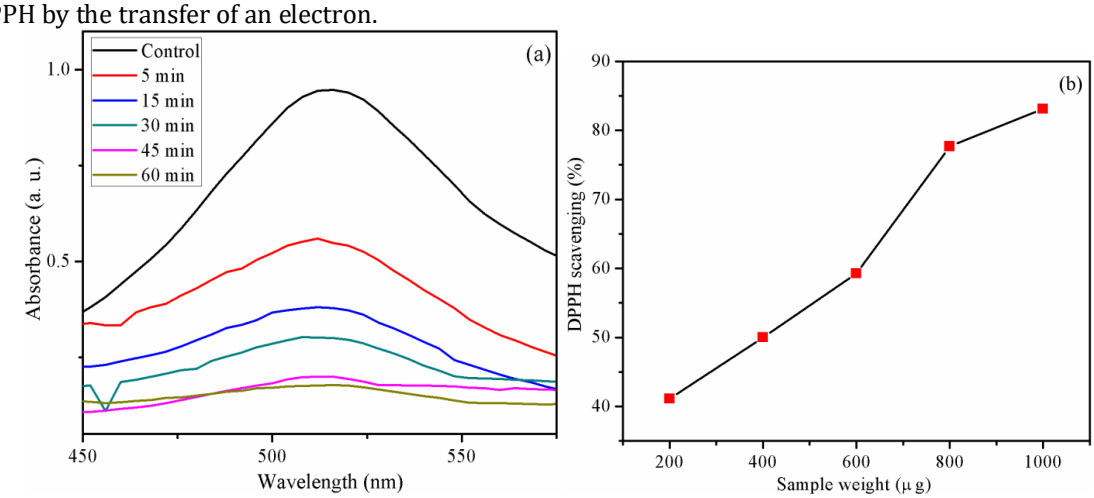

Fig. 4 Antioxidant activity: (a) Time dependent free radical scavenging by α-MoO_3 NPs (b) DPPH scavenging (%) at different amount of α-MoO_3 NPs

Conclusion:

In summary, we have studied the efficiency of co-precipitation method for broad rod like molybdenum oxide NPs synthesis and studied their antioxidant behavior. The PEG used as stabilizing agent played an important role on controlling the particle size, prevent agglomerization and well dispersed morphology. The method offers several advantages such as simple processing, easy isolation, high purity sample is obtained, easy to control particle size, large quantity of yield and absence of side product. In 1 h MoO_3 NPs show 81.30 % free radical scavenging activity which is relatively higher in comparison to other metal oxide nanoparticles reported in literature.

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