

Synthesis, Characterization and Application of Nanoparticles of Cr, Mo and W Ions Using Biogenic and Chemical Routes

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Abstract: The reactants $[\text{CH}_2\text{-OH}]_2$, $\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{MoO}_4$ refluxed at 180°C yielded a red color solution of $\text{Mo}(\text{SH})_4$ indicating reduction of $\text{Mo}(\text{VI})$ to $\text{Mo}(\text{IV})$ ion, in chemical route. Similarly green color solution of $\text{Cr}(\text{SH})_3 \cdot \text{H}_2\text{O}$ and blue color solution of $\text{W}(\text{SH})_4$ were obtained. It shows the involvement of two electrons, in similar way as in bio-genic route for $2e^-$ process for member of the sulphite oxidase family in chicken liver. *Aspergillus niger* too plays as an oxidase during the formation of nanoparticles of all the metal ions. UV visible spectrum shows the presence of ${}^4\text{T}_{1g} - {}^4\text{T}_{2g}$, ${}^4\text{A}_{2g}$, ${}^4\text{T}_{1g}$, (P) transitions for Cr^{+3} ion IR spectra of all the compounds show the presence of $\nu \text{S} - \text{H}$ band of T_d symmetry. SEM and TEM photographs show the presence of nanoparticles in $10 - 20 \text{ nm}$ range in biogenic route. Since the evolution of oxygen takes place in chemical route this places the chemical reactions in the category of green chemistry. In presence of *Aspergillus niger*, synthetic route is ecofriendly.

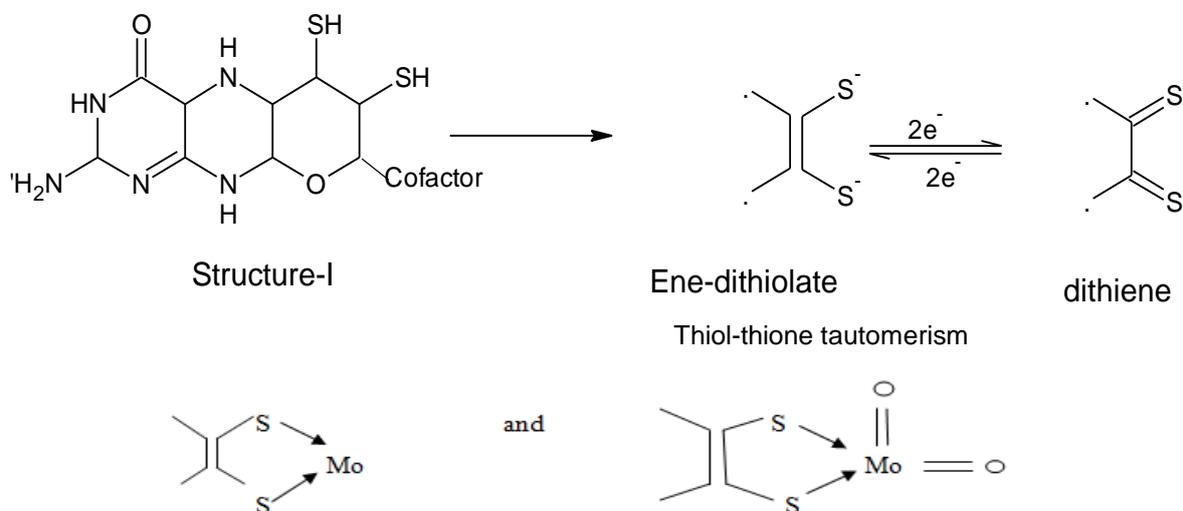
Keywords: Bio-genic route, *Aspergillus niger*, $\text{Mo}(\text{SH})_4$, $\text{Cr}(\text{SH})_3 \cdot \text{H}_2\text{O}$ and $\text{W}(\text{SH})_4$ nanoparticles.

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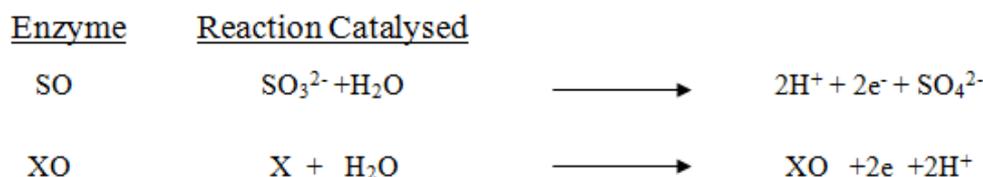
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I. Introduction

Molybdenum is the only 4d transition metal required for all forms of life. Fungi make use of the constituent elements, C, O, H, M, P, K, Mg, S, Mn, Mo, Cu and Fe, where hydrogen and oxygen are supplied in the form of water which is the major constituent of fungus mycelium. The element Mo is found as mononuclear active center, where the ion is coordinated by especially modified pyranopterin co-factor (structure-1). Mononuclear molybdenum enzyme catalyze wide variety of reactions e.g. oxidation of sulphite to sulphate[1]. The dithiolene moiety of the pyranopterin co-factor coordinates the Mo center in a bidentate mode[1]. Rees et al have discussed the redox chemistry[2,3] and crystallographic confirmation of such Mo mononuclear active center.



According to Hille[4] molybdoenzymes can be classified into two families represented by xanthine oxidase (XO) and sulphite oxidase (SO). Member of sulphite oxidase family contain an Mo-O unit in contrast of the S-Mo-O in XO family. These enzymes function via an oxygen atom transfer process. Only one crystal structure of this family is known, which is the chicken liver sulphite oxidase[5]. Past studies have defined the xanthine oxidase family as the enzyme that catalyze the hydroxylation of the substance in the presence of an electron acceptor and include XO and, SO oxides.



In presence of *Aspergillus niger* synthetic route is ecofriendly[6-10]. While from chemical route nano particles of Cr, Mo and W ions are synthesized very rapidly using either ethylene glycol (EG) or methanol as reducing agent and polyvinyl pyrrolidin (PVP) as capping agent[11-13]. Since the evolution of oxygen takes place in chemical route this places the chemical reactions in the category of green chemistry [14]. This paper presents the recent development of the bio-synthesis of mercaptyl nanoparticles of Cr, Mo and W ion in ethylene glycol and toluene solvent respectively.

II. Experimental Procedure

Potassium dichromate [$\text{K}_2\text{Cr}_2\text{O}_7$], ammonium molybdate [$(\text{NH}_4)_2\text{MoO}_4$], sodium tungstate [Na_2WO_4] of A.R. grade purity 99.98 (BDH) and sodium sulphide ($\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$) purity 99.98 (Emerk) were used for preparing final product from a mixture of ($\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$) and corresponding metal salts by chemical as well as biogenic route. In chemical route the solution of corresponding salts were filtered and refluxed in ethylene glycol (EG) at 180°C for 10 minute in presence of PVP. The nanoparticles of the metal ions were stabilized in presence of toluene. In biogenic route nanoparticles of Cr, Mo and W ions were synthesized by using fungus *Aspergillus niger*. The procedure is described bellow.

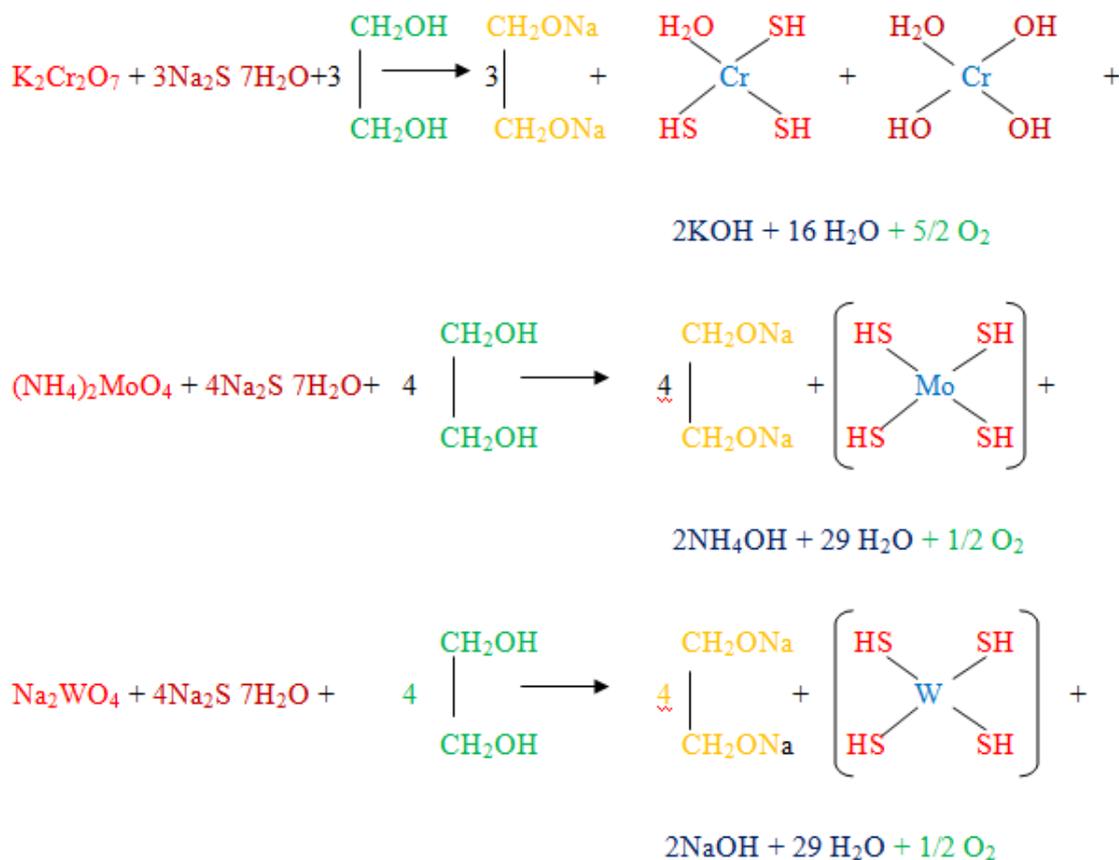
Fresh culture of *Aspergillus niger* was taken and maintained on potato–dextrose agar slants at 25°C . The fungus was grown in 500 ml Erlenmeyer flask each containing 100 ml MGY medium, composed of malt extract (0.2%) glucose (1.0%) yeast extract (0.3%) and peptone (0.5%) at $25\text{--}28^\circ\text{C}$ under shaking condition for 96h. After 4 days of fermentation, mycelia were separated from the culture broth by centrifugation (5000 rpm) at 10°C for 20 minutes and the settled mycelia were washed thrice with sterile distilled water. Ten grams of the harvested mycelial mass was then re-suspended in 100 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$ in aqueous solution ($1 \times 10^{-3}\text{M}$) at pH 8. The whole mixture was there after put into a shaker at 28°C (200 rpm) and reaction was carried out for a period of 72h. Similar experiments was carried out for the salt of $(\text{NH}_4)_2\text{MoO}_4$ and Na_2WO_4 . The bio-transformation was routinely monitored by visual inspection of the biomass as well as measurement of the UV visible spectra from solution of the fungal cell [15]. In our case also we have measured UV visible spectra from fungal cell.

A Philips transmission electron microscope CM12 equipped with a LaB_6 cathode and a scanning unit was used for the TEM investigations ($\lambda = 36.784\text{A}$ mm) and measurements were performed at 120 kV. Sample preparation was performed by ultrasonically dispersing powder particles and subsequent use of a carbon filmed copper grid as carrier. TEM photographs have been produced from Transmission Electron Microscope, JEOL 2000 EX JEOL, corporation, Japan. The films were cut in appropriate size (10 mm approx.) and coated with gold to avoid charge accumulation on the surface of film. SEM photograph has been produced from Scanning Electron Microscope, JEOL-840, JEOL corporation Japan. UV visible spectra were performed by UV visible spectrometer model – Hitachi – u – 2000. IR spectra of solutions were run in the range 4000 cm^{-1} to 400 cm^{-1} using polythene container on a Perkin FT-IR spectrophotometer RX- IB UK.

III. Result And Discussion

One co-factor per Mo, in oxidized form and dioxo-Mo-centre is coordinated by one ene dithiolate moiety [16,17]. In similar way chemical route shows coordination of thiol group in our case instead of sulphide ion after hydroxylation by accepting two electrons in basic medium at pH 8, imparting +4 oxidation state to molybdenum and a tetrahedral symmetry instead of octahedral[18] symmetry. The compound in ethyleneglycol and toluene solvent shows the surface[19] modification by formation of stable nanoparticles due to existence of sharp splitting at $3623, 2923\text{ cm}^{-1}$ instead of broad band at 3651 cm^{-1} in ethylene glycol (Fig.4,5,6)..

Chemical route shows evolution of $1/2\text{ O}_2$ which places the chemical reaction in the category of green chemistry [14] and matches with enzyme function via oxygen transfer in biological process. In biological process fungus *Aspergillus niger* was used which converts sulphate to sulphite by sulphatase enzyme which is secreted extracellularly and formation of nanoparticles of Cr, Mo and W ions were completed. The only product of the enzyme is indeed free sulphite that thiol intermediate was most likely artifact due to presence of oxidized thiol in the reaction medium [20]. Mechanism of reduction in presence of ethylene glycol (EG) has already been reported [11]. On the basis of reduction mechanism chemical route equations are given below.



Reaction of ammonium molybdate with sodium sulfide in EG refluxed at 180 °C yielded a red color solution indicating reduction of Mo VI to Mo IV which is shown in above chemical equations.

UV visible spectra of green solution of chromium compound (Table-1) and (Fig.7) shows band at 244 and 374 nm for Cr(SH)₃ H₂O and similar band do appear in red solution of molybdenum compound and blue solution of tungstate compound indicating tetrahedral symmetry of Mo(SH)₄ and W(SH)₄. Similar results have been observed in biogenic route which are given in Table-2, (Fig.7) No metal-metal bond is present in case of chromium compound indicating paramagnetic character ($\mu=3.7$ BM) due to 3d³ (Cr⁺³) ion after reduction of (Cr⁺⁶) in K₂Cr₂O₇ in presence of reducing agent (EG) which shows ⁴T_{1g} – ⁴T_{2g} transition at 610 nm, while Mo⁺⁴ (4d²) system has Mo-Mo bond due to clustering and diamagnetic nature with d-d transition [17] at 591 nm and W –W bond at 600 nm. Presence of mercaptyl group has been ascertained by stretching band ν SH at 2900 cm⁻¹ in IR spectra (Fig.4, 5, 6.). In order to control the shape and size of nanoparticles chemical route reaction has also been carried out in different solvent viz. toluene [19] in place of ethylene glycol. SEM (Fig.3) and TEM (Fig.2) photographs ascertain the formation of nanoparticles in 10 to 20 nm range. Many fungi exhibit reductase characteristic properties, beside these extracellular enzymes, naphthaquinones [21-23] and anthraquinones [24] which have excellent redox properties act as electron shuttle.

IV. Conclusion

Potassium chromate, ammonium molybdate and sodium tungstate are oxidizing agent and itself gets reduced. Therefore the two electrons in biological process showed the reduction of sulphate ion to sulphite ion which are being assimilated by the oxidizing agent and therefore color changes e.g. K₂Cr₂O₇ changes from orange to dirty green, molybdenum from colorless to dirty redish color and tungsten from colorless to dirty blue color.

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Table: 1. Data of electronic spectra of green, red and blue solution of nanoparticles by chemical route

Wave length λ_{\max} nm	Symmetry	Transitions
610 374 244	T_d	Green solution of Cr^{+3} ($3d^3$) ion ${}^4T_{1g} - {}^4A_{2g}$ (F) ${}^4T_{1g} - {}^4T_{2g}$ (F), ${}^4T_{1g} - {}^4T_{1g}$ (P)
591 372 250	T_d	Red solution of Mo^{+4} ($4d^2$) Mo-----Mo bond
600 280 352	T_d	Blue solution of W^{+4} ($5d^2$) W-----W bond
207 277 352		EG = Ethylene Glycol

Table: 2. Data of electronic spectra of green, red and blue solution of nanoparticles by biochemical route

Wave length λ_{\max} nm	Symmetry	Transitions
603 386 242	T_d	Green solution of Cr^{+3} ($3d^3$) ion ${}^4T_{1g} - {}^4A_{2g}$ (F) ${}^4T_{1g} - {}^4T_{2g}$ (F) ${}^4T_{1g} - {}^4T_{1g}$ (P)
284 241	T_d	Red solution of Mo^{+4} ($4d^2$) Mo-----Mo bond
287 252	T_d	Blue Solution of W^{+4} ($5d^2$) W-----W bond

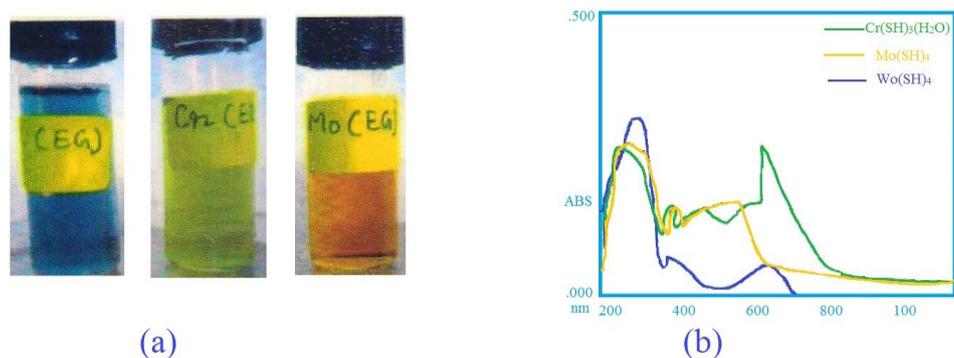


Fig. 1a. Sample tube containing nanoparticles of $\text{Cr}(\text{SH})_3(\text{H}_2\text{O})$, $\text{Mo}(\text{SH})_4$ and $\text{W}(\text{SH})_4$
 1b. UV - Visible spectra of nanoparticles of $\text{Cr}(\text{SH})_3(\text{H}_2\text{O})$, $\text{Mo}(\text{SH})_4$ and $\text{W}(\text{SH})_4$ in ethylene glycol

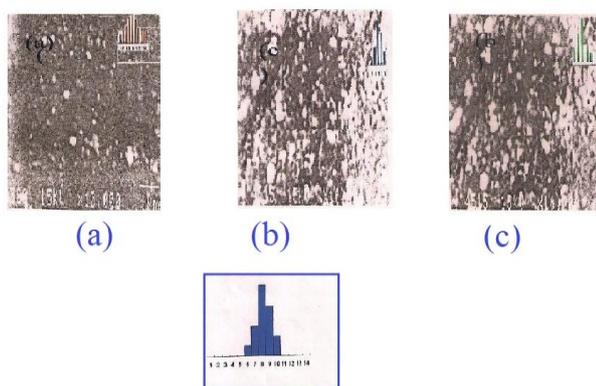


Fig. 2. TEM image of (a) $\text{Cr}(\text{SH})_3(\text{H}_2\text{O})$ (b) $\text{Mo}(\text{SH})_4$ and (c) $\text{W}(\text{SH})_4$ nanoparticles obtained by biochemical route using solvothermal method in reducing solvent ethylene glycol

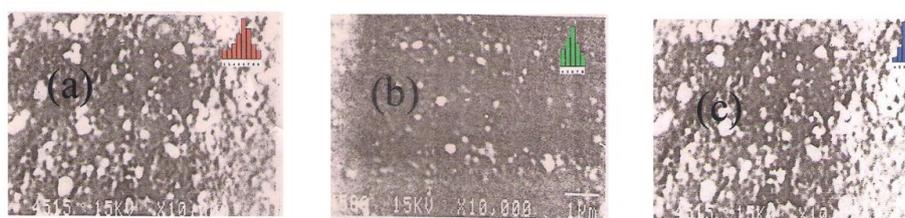


Fig 3 SEM images of (a) $[\text{Cr}(\text{SH})_3 \text{H}_2\text{O}]$ (b) $\text{Mo}(\text{SH})_4$ and (c) $\text{W}(\text{SH})_4$ indicating the nanoparticles of 10 - 20 nm range by biochemical route using solvothermal method in reducing solvent, ethylene glycol.

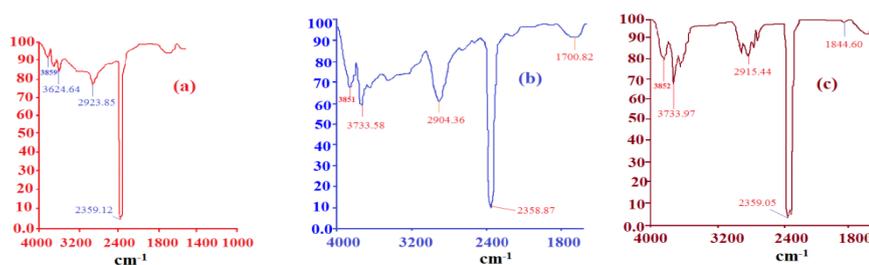


Figure. 4 IR spectra of NP of (a) $\text{Cr}(\text{SH})_3\text{H}_2\text{O}$ in EG by chemical route (b) $\text{Cr}(\text{SH})_3\text{H}_2\text{O}$ in EG by bio - chemical route (c) $\text{Cr}(\text{SH})_3\text{H}_2\text{O}$ in Toluene by chemical route

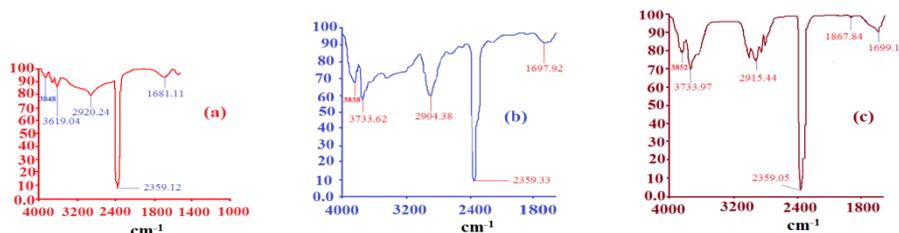


Figure. 5 IR spectra of NP of (a) $\text{Mo}(\text{SH})_4$ in EG by chemical route (b) $\text{Mo}(\text{SH})_4$ in EG by bio - chemical route (c) $\text{Mo}(\text{SH})_4$ in Toluene by chemical route

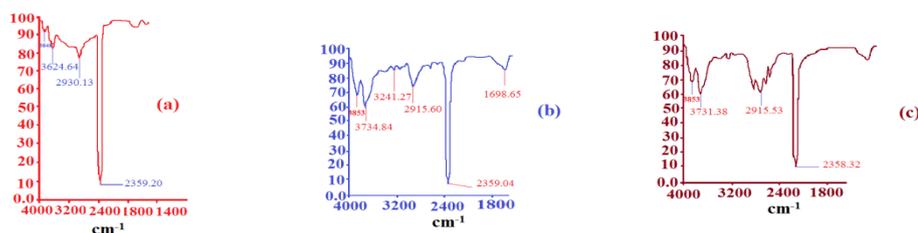


Figure. 6 IR spectra of NP of (a) $\text{W}(\text{SH})_4$ in EG by chemical route (b) $\text{W}(\text{SH})_4$ in EG by bio - chemical route (c) $\text{W}(\text{SH})_4$ in Toluene by chemical route

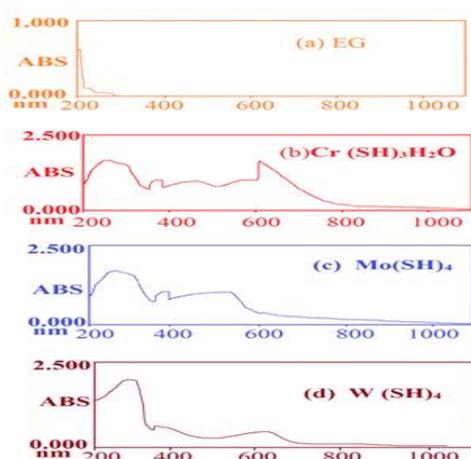


Figure. 7 Electronic spectra of (a) EG, (b) NP of $\text{Cr}(\text{SH})_3\text{H}_2\text{O}$ (c) NP of $\text{Mo}(\text{SH})_4$ and (d) NP of $\text{W}(\text{SH})_4$ by chemical route

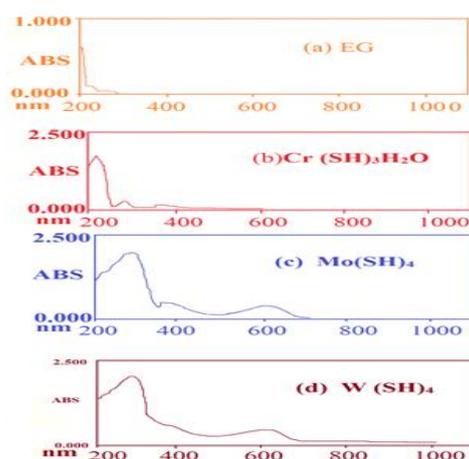


Figure. 8 Electronic spectra of (a) EG, (b) NP of $\text{Cr}(\text{SH})_3\text{H}_2\text{O}$ (c) NP of $\text{Mo}(\text{SH})_4$ and (d) NP of $\text{W}(\text{SH})_4$ by bio - chemical route

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