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PREPARATION OF NICKEL OXIDE NANOPARTICLES BY THERMAL DECOMPOSITION OF Ni (2-MERCAPTOBENZOTHIAZOLE)$_2$ COMPLEX AS SINGLE SOURCE PRECUSOR AND ITS APPLICATION IN DEGRADATION OF ORGANIC NITRO COMPOUND

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ABSTRACT

Nickel oxide nanoparticles are very important materials due to its various applications in preparation of smart windows and piezoelectric devices, as p-type semiconductors with wide band gap 3.6-4.0 eV, in fuel cells and supercapacitor coatings for the passivation of surfaces against corrosion, as catalysts and magnetic materials and as sensors. The tuning of morphology is the current research interest, therefore the ability to synthesize nanoparticles with precisely controlled size, composition and shape is the task. Thermal decomposition of Ni(2-Mercaptobenzothiazole)$_2$ in horizontal furnace is one of simplest way to prepare nanoparticles. Nickel-2-mercaptobenzothiazole complex was synthesized by the reaction between nickel chloride hexahydrate and 2-mercaptobenzothiazole in methanol. As prepared complex was characterized using UV, IR Spectroscopy. It was found that the stoichiometry of metal and ligand is in the ratio of 1:2 that is [NiL$_2$]. Nickel oxide nanoparticles were prepared by thermal decomposition in horizontal furnace at 400, 450 and 500^{o}C. Further nanoparticles were characterized by powder X-ray diffraction(XRD) and transmission electron microscopy(TEM). The formation of phase pure cubic NiO (JCPDS: 78-0643) was evident from the powder XRD patterns. TEM shows spherical morphology from particle size

ranging from 4-40 nm. Nitrobenzene is primarily used as a precursor for aniline.[1a,b,c,d.e] It is also used as an organic solvent and a fragrance for cheap soaps. It is responsible for cancer in human being and animals, also it binds to protein of haemoglobin which leads to Methaemoglobinaemia. NiO nanoparticles are best candidate for photocatalytic degradation of nitrobenzene as it is wideband gap semiconductor.

KEYWORDS: Nickel oxide, chalcogenato complex, 2-mercaptobenzothiazole, nanoparticles, nitrobenzene, pyrolysis.

INTRODUCTION

In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors for detecting various toxic gases, smart windows, piezoelectric devices, fuel cells, supercapacitors, coatings for the passivation of surfaces against corrosion, as catalysts and magnetic materials.[2a, b, c, d, e, f, g, h] Specifically, nickel oxide nanoparticles have a wide range of applications in the manufacturing of magnetic materials, drug delivery, alkaline battery cathodes, dye-sensitized solar cells, semiconductors, solid oxide fuel cells (SOFCs), antiferromagnetic layers, p-type transparent conducting films, non-volatile memory in MIM as ReREM, electrochromic films, heterogeneous catalytic materials and gas sensors.[3a-j]

Recently, several methods have been developed to synthesize nickel oxide nanoparticles with the help of multiple or dual source precursor; for example, low-pressure spray pyrolysis[4a], surfactant - mediated method[4b], simple liquid phase process[4c] and other techniques.[4d-h] Some of the methods for the formation of NiO nanostructures are technically complex, require high temperature, harsh growth conditions, expensive experimental setup, complicated control processes and have made frequent use of organics.

The development of systematic method for the synthesis of oxide nanocrystallites is a current challenge. A major barrier at this moment is the ability to synthesize nanoparticles with precisely controlled size, composition and shape in a way that is economically and ecologically well-considered. Therefore, the tuned morphology of nanoparticles is the key research area in recent years. One can make use of single source precursors to prepare nanoparticles because they give clean decomposition and control over stoichiometry of the materials.

Literature survey reveals that metallo-complexes of 2-mercaptobenzothiazole (2-MBT) and their related 2-MBT compounds have proved a fertile area for the study over years stimulated both by the diversity of their commercial application and the richness of their structural chemistry. In heterocyclic thiones, both the exocyclic sulphur atom and endocyclic nitrogen may act as donor atoms[5a] and hence these ligands have great ability to adopt different bonding modes, unidentate, bidentate or bridging; sometimes in more than one way in the same compound.[5b] It also shows tautomerism as keto and enol form. Further, enol form can chelate to transition metal atom by forming pentacyclic structure which has enhanced stability. This led to the interest in the coordination chemistry of heterocyclic thiones. 2-MBT has a high molecular weight and has been proved as an excellent chelating agent[5c-h] for the estimation of transition metal complexes at ppm level.

Nitrobenzene is primarily used as a precursor for aniline, which is an aromatic compound with an $-NH_2$ group. The nitro group $-NO_2$ gets reduced to the amino group $-NH_2$ in the presence of tin and concentrated hydrochloric acid. Nitrobenzene is also used as an organic solvent and a fragrance for cheap soaps. It is responsible for cancer in human beings and animals. It binds to the protein of haemoglobin which leads to Methaemoglobinaemia[6], with cyanosis, headache, dyspnoea, weakness and ultimately coma and death, which is the main characteristic of acute nitrobenzene poisoning. Nitrobenzene may also induce haemolysis and shows poisoning to liver, lung and splenic internal organs. So it must be treated before putting to environment. NiO nanoparticles are best candidate for photocatalytic degradation of nitrobenzene.

EXPERIMENTAL

Synthesis of single source precursor

In a typical synthesis, in a 20 cm^3 round bottom flask, 0.705 mmole of nickel chloride hexahydrate was dissolved in methanol. In another round bottom flask, 2.370 mmole of 2-MBT was dissolved in methanol (Fig.1).

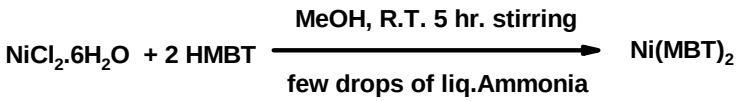

Figure 1: Reaction of synthesis of single source precursor.

The ligand solution was added to the metal salt solution with constant stirring for 5 hr. To this reaction mixture, few drops of liquor ammonia was added till we get the distinct color change

i.e. chocolate brown color. A brown colored precipitate implies the formation of complex (Fig.2). Product was filtered and air dried. Further, the complex was characterized by elemental analysis, UV and FTIR spectroscopy and the structure of complex was proposed.

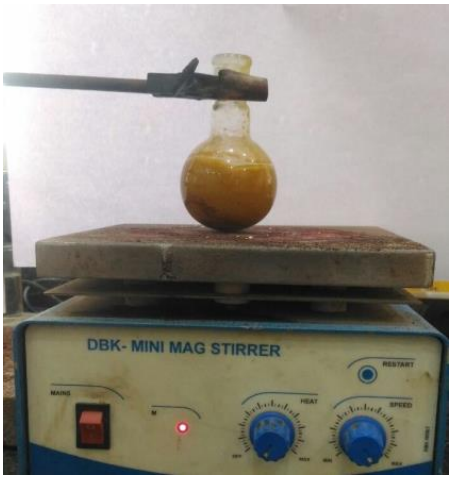

Figure 2: Brown colored single source precursor.

Characterization of single source prescursor by UV-visible and FTIR spectroscopy

The elemental analysis was done by using CHNS (O) Analyzer of Thermo finnigan, Italy make, FLASH EA 1112 series model which is based on the principle of Dumas method. The complex was opened in aquaregia and evaporated nearly to dryness. Estimation of nickel was carried out by titrating nickel with ethylene diammine tetracetic acid (complexometric titration) using pyrogallol red as an indicator. Elemental analysis of complex observed (calculated): Ni: 15.05% (15.07%), C:43.01% (42.95%), H: 2.04% (2.05%), N: 7.14% (7.15%), S: 32.50% (32.65%), Melting point of complex: 272 ^{0}C (Melting point of ligand:179 ^{0}C), Yield: 79.00%. To find out the λ_{max} of the complex, UV spectra was carried out in Dimethyl sulphoxide solvent using Perkin Elmer, model-LAMBDA 25 which showed the λ_{max} at 370 nm (Fig.3).

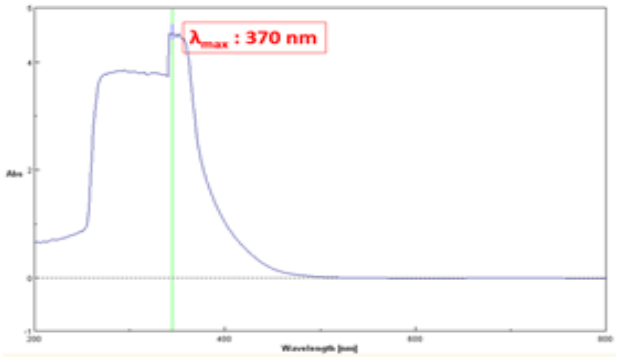

Figure 3: UV-Visible Spectra of Single Source Precursor.

FTIR studies were carried out for both the ligand as well as the complex using FTIR - Jasco – 460 Plus model by taking 3 mg of complex in KBr. The FTIR spectra of the complex showed peaks (Fig.4) at 718.354 cm^{-1} assigned for C-S bond, 1339.32 cm^{-1} assigned for N=C-S, 1503.24 cm^{-1} assigned for C=N, 1015.34 cm^{-1} assigned for C=N and 504.29 cm^{-1} assigned for Ni-N. Bands were observed at 718 cm^{-1} for C-S bond, 1015 cm^{-1} and 1579 cm^{-1} for C=N, 1339 cm^{-1} and 1313 cm^{-1} for N=C-S at lower wave number compared to their positions in FTIR spectra of ligand. These observations implies that the co-ordination is through thiolsulfur atom and azomethine nitrogen atom. From these observations, a proposed structure of $Ni(MBT)_2$ complex is as shown in Fig.5.

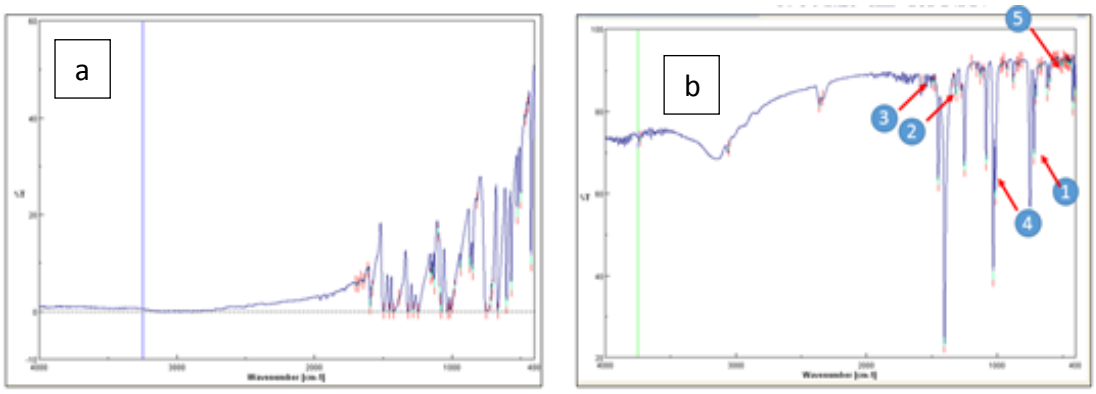

Figure 4: a) FTIR spectra of ligand b) FTIR spectra of single source precursor.

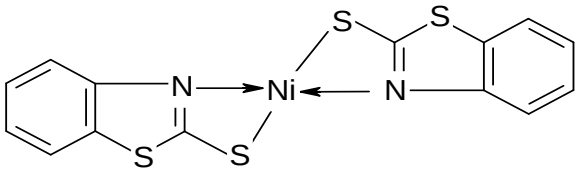

Figure 5: Proposed structure of $Ni(MBT)_2$ complex.

It has been observed that $Ni(MBT)_2$ complex is paramagnetic (d^8 system) in nature and hence proton and C_{13} NMR is not possible.

Synthesis of nickel oxide nanoparticles

0.300 g of $Ni(MBT)_2$ complex was weighed, transferred in silica crucible and placed in horizontal furnace. Temperature was raised to 400 ^oC and it was kept in the furnace at same temperature for annealing process. After two hours, furnace was allowed to attain room temperature. The procedure was repeated at 450 ^oC and 500 ^oC. The black colored product was air dried which weighed 0.064 g. The practical yield was in agreement with theoretical yield.

Characterization of nanoparticles by XRD, TEM and SAED pattern

XRD of black colored NiO nanoparticles (Fig.6a) was carried out by using Panalytical Xpert PRO X Ray Diffractometer, Model: Xpert Pro MPD, Anode: Copper, Wavelength: 1.5405 Angstorm, Power: 40KV / 30mA, Detector: Xcelerator Detector with Diffracted Beam Monochromator. It showed the peaks at (111), (200), (220) and (222) which matches with cubic phase of Nickel Oxide (JCPDS:78-0643) (111), (200), (220) and (222). This indicates that phase pure cubic nickel oxide was obtained with growth direction (200). SAED pattern of nickel oxide nanoparticle (Fig.6b) peaks (111) (220) (311) matches with the cubic phase of NiO (JCPDS: 36-1450).

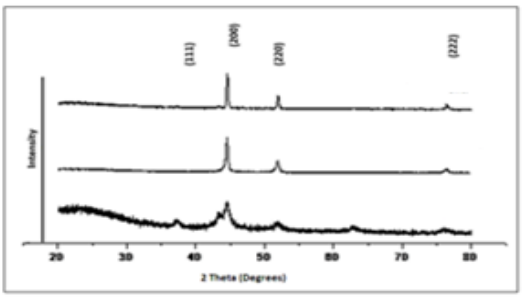

Figure 6: a) Powder XRD of NiO nanoparticles obtained 400 ^{o}C, 450 ^{o}C and 500 ^{o}C.

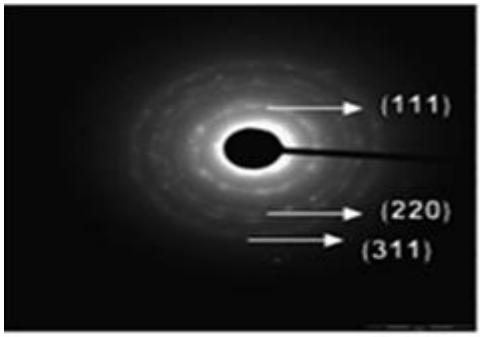

Figure 6: b) Powder SAED of NiO nanoparticles obtained 500 ^{o}C.

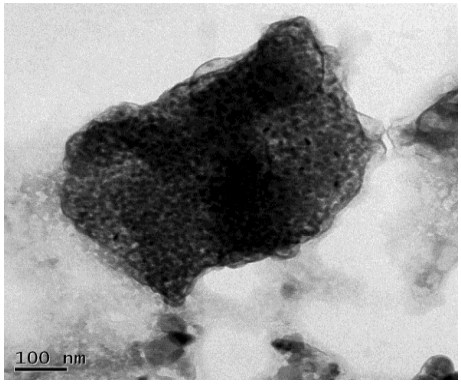

Figure 7: TEM image of NiO nanoparticles obtained at 400 ^{o}C.

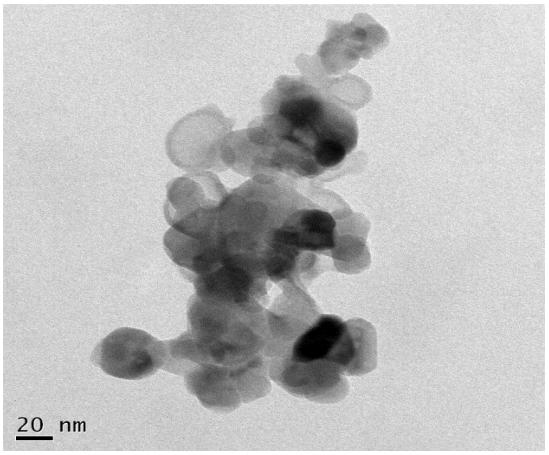

Figure 8: TEM image of NiO nanoparticles obtained at 450 ^{o}C.

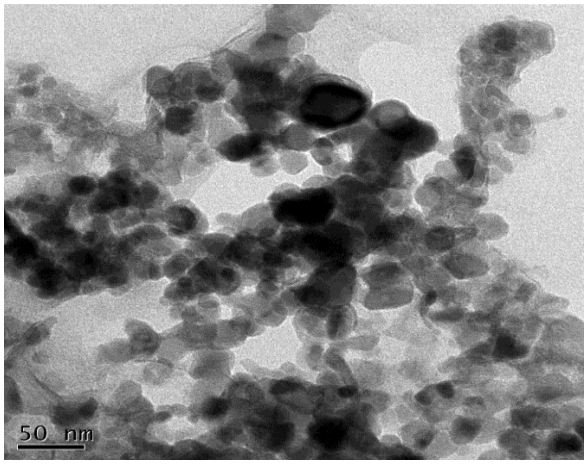

Figure 9: TEM image of NiO nanoparticles obtained at 500 ^{o}C.

TEM analysis was carried out by sonicating 5 mg of nanoparticles in 10 cm^3 of methanol for half an hour. 2 drops was taken on copper grid by using TEM CM 200, Make: PHILIPS, Model: CM 200, Operating voltages: 20-200 kv. Grid was air dried and the images were recorded. The TEM image of NiO nanoparticles obtained at 400 ^{o}C shows spherical morphology with particle size 5-10 nm (Fig.7), Nickel oxide nanoparticles obtained at 450 ^{o}C shows spherical morphology with particle size 20-30 nm (Fig.8) and NiO nanoparticles obtained at 500 ^{o}C shows spherical morphology with particle size 10-40 nm (Fig.9). The size of nanoparticles increases with increase in temperature.

Application of NiO nanoparticles for degradation of Nitrobenzene

The synthesized NiO nanoparticles were successfully used for degradation of nitrobenzene up to 100 cycles. Also, the time required for degradation was 10 min which marks the additional advantage of the proposed method with one pinch of NiO nanoparticles.

An aliquot of 5 cm^3 of Nitrobenzene solution was taken in a test tube. The degradation of Nitrobenzene was carried out by adding a pinch of prepared NiO nanoparticles to the above aliquots and further shaking the solution and by doing the process of sonication in some cycles.

Further, the nanoparticles which were used in the first cycle for degradation of nitrobenzene were separated out with the help of centrifugation method. The residue left behind after centrifugation contained nanoparticles which were collected and used for next cycle of degradation. (Fig. 10) The percentage of degradation was calculated using the same procedure as mentioned above. The degradation studies were carried out till 100 cycles.

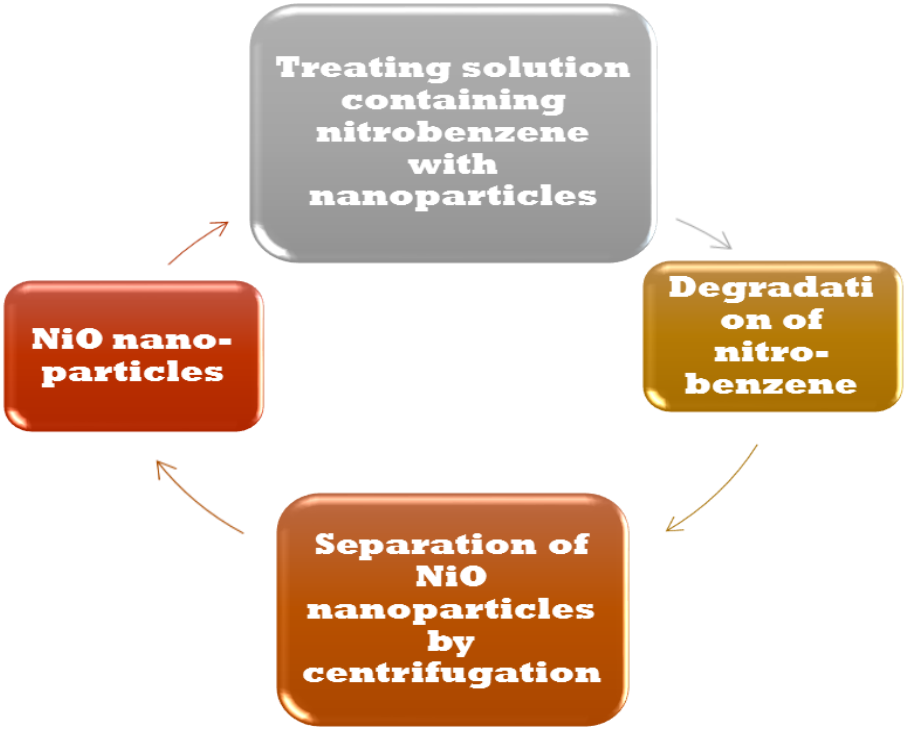

Figure 10: Degradation of NiO nanoparticles with nitrobenzene.

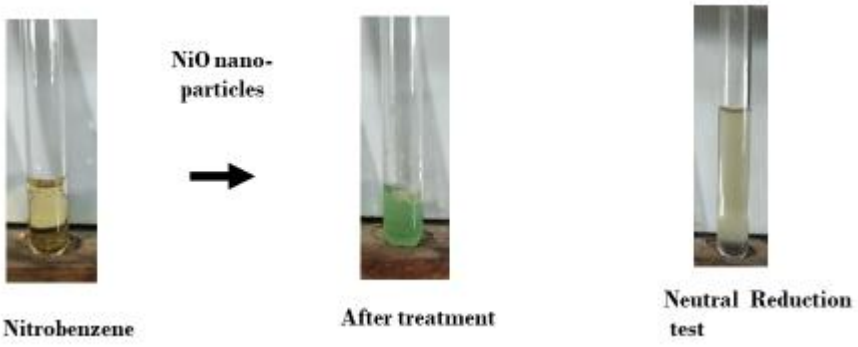

Figure 11: Treating NiO nanoparticles with nitrobenzene.

The presence of nitro group was checked by neutral reduction test and it was observed that no black precipitate was formed. This confirms that NiO nanoparticles has successfully degraded nitrobenzene.

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