

Cobalt Oxide Nanoparticles: Characterization and its Electrocatalytic Activity towards Nitrobenzene[†]

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Abstract: Cobalt oxide (Co₃O₄) nanoparticles were successfully prepared by thermal decomposition of cobalt hydroxide synthesized from cobalt acetate, ammonium hydroxide and 10% glycerol. The cobalt oxide nanoparticles calcined at 450 °C were characterized by using XRD. The XRD confirms the crystallinity and crystal structure of the sample. It also shows that the diffraction peak are broadened which reveals the narrow size distribution of the cobalt oxide nanoparticles. In addition, the average grain size, lattice parameter values also calculated using XRD. The FT-IR analysis confirms the functional group presents in the cobalt oxide nanoparticles. The SEM image of cobalt oxide nanoparticles shows the nanosized agglomerated particles. The electrochemical detection of nitrobenzene (NB) by cobalt oxide nanoparticles was investigated by cyclic voltammetry. The result concludes that the cobalt oxide nanoparticles have higher activity for the detection of nitrobenzene.

Keywords: Cobalt oxide, Thermal decomposition, Cyclic voltammetry, Nitrobenzene.

Introduction

Nanostructured materials have been widely investigated for the fundamental scientific and technological interests in accessing new classes of functional materials with unprecedented properties and applications¹⁻³. In recent years, there has been an increasing interest in the synthesis of nanosized crystalline metal oxides because of their large surface areas, unusual adsorptive properties, surface defects and fast diffusivities. Co₃O₄ is a very important material extensively used in catalysis, gas sensors, electrochromic films, battery cathodes, heterogeneous catalytic materials and magnetic materials^{4,5}. Due to their small size, nanoparticles exhibit novel material properties that are significantly different from those of their bulk counterparts. Co₃O₄ nanoparticles have been synthesized by various methods like sol-gel, surfactant-mediated synthesis, thermal decomposition, polymer-matrix assisted

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synthesis and spray-pyrolysis^{6,7}. Some of the above methods suffer from the difficulty in size-homogeneity and well dispersion of Co_3O_4 nanoparticles. Recently, several methods have been developed to prepare ultrafine Co_3O_4 powder, including low pressure spray pyrolysis, optical gas sensors, antiferromagnetic layers, solar thermal absorbers, *etc.* In this study, we have reported the synthesis of Co_3O_4 nanoparticles using thermal decomposition method and characterized its structural, morphological properties. Additionally we have performed the electrocatalytic activity of the synthesized Co_3O_4 towards the detection of NB.

Experimental

Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), nitrobenzene, ammonium hydroxide, potassium hydroxide and glycerol were purchased from Qualigens. Double distilled water was used as the solvent throughout the experiment.

Characterization methods

The crystal structure of Co_3O_4 nanoparticles was analyzed by a Rich Siefert 3000 diffractometer with $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). FT-IR spectrum of the Co_3O_4 was recorded on Shimadzu FT-IR 8300 series instrument by using potassium bromide pellets. The morphology of the materials was analyzed by SEM HITACHI SU6600 scanning electron microscopy respectively. The electrochemical experiments were performed on a CHI 600A electrochemical instrument using the as-modified electrode and bare GCE as working electrode, a platinum wire was the counter electrode, and saturated calomel electrode (SCE) was the reference electrode.

Synthesis of Co_3O_4 nanoparticles

Co_3O_4 was prepared by thermal decomposition of cobalt hydroxide. The cobalt hydroxide was prepared by reacting aqueous solutions of 0.01 M cobalt chloride and 0.01 M ammonium hydroxide. The 0.01 M cobalt chloride was dissolved in 500 mL distilled water and 10% of glycerol. This suspension was stirred for 20 min at 50 °C in magnetic stirrer. After 20 min, the dissolved ammonium hydroxide solution (50 mL) was slowly added to control the agglomeration. The obtained cobalt hydroxide is calcined in air for 3 h at 450 °C, which results the Co_3O_4 nanoparticles.

Electrode modification

Ultrasonically dispersed Co_3O_4 nanopowder in 5 mL of water was drop coated onto the GCE and dried at room temperature. The Co_3O_4 coated electrode prepared by electrochemical deposition techniques and used for electrocatalytic reduction of nitrobenzene. CV's were run in electrochemical cell containing 50 mL DD water and 0.1 M KOH in presence of SCE reference electrode and Pt wire as counter electrode.

Results and Discussion

Structure and morphology

XRD patterns of the Co_3O_4 nanoparticles calcined at 450 °C, is shown in Figure 1, which indicates the cobalt oxide has cubic phase structure. The peak positions ($2\theta = 19.02^\circ, 31.3^\circ, 36.88^\circ, 38.59^\circ, 44.85^\circ, 59.41^\circ$ and 65.30°) and relative intensities obtained for the Co_3O_4 match with the JCPDS card No: 073-1701 file, identifying it as Co_3O_4 with a cubic structure with Fd-3m (227) space group and lattice constant $a = 8.08 \text{ \AA}$. There was no characteristic peaks of impurity were observed. The average grain size of Co_3O_4 is determined using Scherrer relation, and it was found to be around 49 nm.

FT-IR spectrum of Co_3O_4 nanoparticles (Figure 2) showed significant absorption peaks at 1607 and 525, 647 cm^{-1} . The absorption band at 525 cm^{-1} was assigned to Co-O stretching

vibration mode⁸ and 647 cm^{-1} was assigned to the bridging vibration of O-Co-O bond⁹. The weak band near 1635 cm^{-1} is assigned to H-O-H bending vibration mode were presented due to the adsorption of moisture, when FTIR sample disks were prepared in an open air atmosphere. These observations provided the evidence for the presence of hydration in the structure¹⁰.

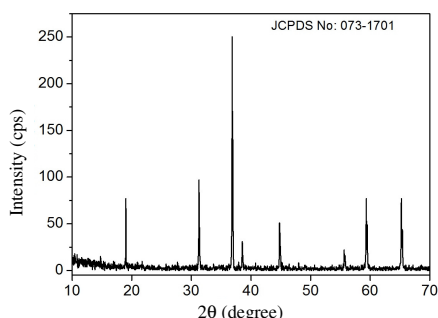


Figure 1. XRD pattern of the Co_3O_4 nanoparticles prepared at $450\text{ }^\circ\text{C}$

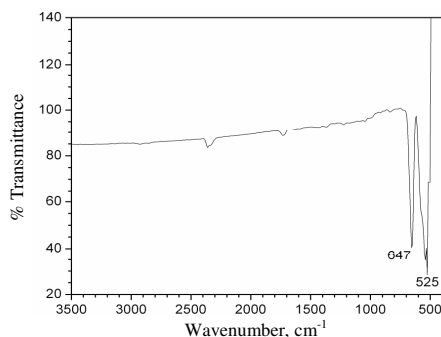


Figure 2. FT-IR spectrum of Co_3O_4

The SEM micrograph of the Co_3O_4 calcined at $450\text{ }^\circ\text{C}$ is shown in Figure 3. It can be seen that the particles adopt irregular morphology with different sized particle. In addition, Co_3O_4 nanoparticles show rod shape with smooth surface. It clearly indicates the fine rod like particles adsorbed on the surface due to the aggregation. It shows the rod like agglomerates were purely due to the magnetic induction between the particles¹¹.

Electrochemical property

The electrochemical behaviour of 1 mM NB at $\text{Co}_3\text{O}_4/\text{GCE}$ was tested with cyclic voltammetric (CV) measurements in 0.1 M KOH. Figure 4b shows the CV of $\text{Co}_3\text{O}_4/\text{GCE}$ in KOH electrolyte. It can be seen that the Co_3O_4 is non-electroactive in the selected potential region. Figure 4b shows broad peaks in the potential range from -0.4 to -0.6 V . Figure 4b shows reduction of NB at $\text{Co}_3\text{O}_4/\text{GCE}$. It shows the cathodic peak at -0.8 V with enhanced current response relative to that of $\text{Co}_3\text{O}_4/\text{GCE}$. At the same time, we have noticed that the $\text{Co}_3\text{O}_4/\text{GCE}$ shows higher current response at the positive potential region 0 to 0.2 V , which was indicative of the electron transport property of nitrobenzene. It indicated that the Co_3O_4 were catalytically more active toward electrochemical reduction of nitrobenzene to aniline¹².

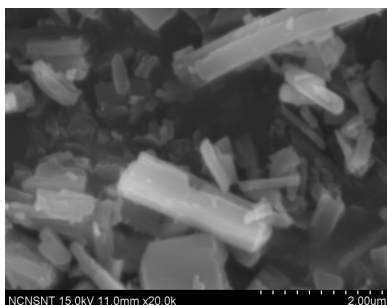


Figure 3. SEM image of Co_3O_4

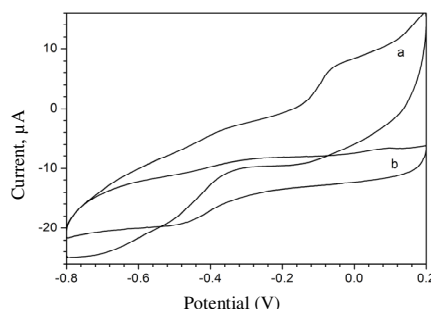


Figure 4. Cyclic voltammograms (CV) of (a) Cobalt oxide modified GCE (b) Bare GCE for the reduction of 0.001 M nitrobenzene in 0.1 M KOH electrolyte at 50 mVs^{-1}

Conclusion

The Co₃O₄ nanoparticles were prepared by thermal decomposition method. FT-IR analysis confirms the formation of the Co₃O₄ nanoparticles. The calcined cobalt oxide nanoparticles at 450 °C were characterized by using XRD. The XRD confirms the crystal structure and of the samples. The SEM of Co₃O₄ nanoparticles shows the spherical agglomerated particles. The optical absorption spectrum of cobalt oxide sample was studied by UV-Visible spectroscopy. The electrochemical detection of nitrobenzene by cobalt oxide nanoparticles was investigated by cyclic voltammetry. The results conclude that the cobalt oxide nanoparticles have higher activity for the detection of nitrobenzene.

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