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ELECTROCHEMICAL SYNTHESIS OF MULTIDIMENSIONAL NANOPARTICALES AND THEIR ELECTROCATALYTIC APPLICATIONS FOR SUSTAINABLE FUTURE

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Abstract

Copper and copper oxide nanoparticles (NPs) have been synthesized by electrochemical route using the Tri-Sodium Citrate 150 mM (TSC) as a capping and reducing agent. The synthesis has been done at 3.2 V, 311 K using Copper rod as a working electrode and Platinum wire as a reference electrode. The electrochemical set up has been kept in air as well as under inert Nitrogen-purged conditions. The NPs have been characterized by using UV-visible absorption spectroscopy, Scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques. This new kind of synthesis method shows the excellent stability compared with that of another chemical method of Copper nanoparticles. These particles have been used in electro-oxidation of Methanol. Methanol oxidizes completely in CO_2 and H_2O.

Keywords: Tri-Sodium Citrate (TSC), Working electrode, Platinum wire, Reference electrode.

Introduction

Copper and their oxide nanoparticles (NPs) especially cuprous oxide have wide application range as a catalyst such as in photo-electrochemical water splitting, photovoltaics, opto-electronics, biosensors, etc. The Cu_2O NPs have been used as a photo-catalyst for enhanced organic contaminant degradation under visible light irradiation (Liu, 2016). The pH-dependent single-step rapid synthesis of CuO and Cu_2O nanoparticles have been done by using microwave irradiation (Nikam, 2014). These CuO nanoparticles displayed good hole mobility under ambient conditions making it a good candidate to be used in FET devices. The NPs of CuO with flower like structure have been prepared by a domestic hydrothermal microwave (Volanti, 2008) Magnetic nanoporous $Cu/(Fe,Cu)_3O_4$ composites with excellent electrical conductivity have been investigated by one-step dealloying (Gawande, 2016) Cu and Cu-based nanoparticles with applications in catalysis have been reviewed by Manoj B. Gawande. Synthesis of Copper/Copper-oxide nanoparticles have been synthesized and have been studied for optical properties (Kim, 2012). The Copper ion has antibacterial effect on Pseudomonas aeruginosa, Salmonella typhimurium, Helicobacter pylori and also reported for optical and mechanical properties respectively (Huang, 2015). The graphene oxide/metal (Cu, Ni, Co) nanoparticle hybrid composites have been synthesized via a facile thermal reduction method (Qi, 2011). Preparation of nanocrystalline Cu_2O thin film has been done by pulsed laser deposition and sol-gel like dip technique (Ray, 2001; Jawad, 2011).

Materials and Methods

Tri-Sodium Citrate capped Copper nanostructures of ($CuCu_2O$) have been

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synthesized via electrochemical route. Electrochemical cell has been formed by immersing the Copper electrode and Platinum wire in solutions of 2.55mM of Tri-Sodium Citrate (TSC). The solution has been prepared in double de-ionised water. The electrochemical set up has been kept in air as well as under inert Nitrogen-purged conditions equipped with a magnetic stirrer at 350 rpm. The powder present in the solution has been obtained by filtering with Whatman paper of 42 number and has been washed several times by de-ionized water then dried in atmospheric condition and the reddish-brown powder deposited on platinum electrode can be easily separated. In this synthesis first Copper gets oxidised in +2 state from working Copper electrode when potential is applied or we can say dissolution process take place first after that Cu and Cu_2O form due to reduction process and size of particles has been controlled by capping agent.

Characterization

Nanoparticles have been characterized by using UV-visible absorption spectroscopy, Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The UV-Visible absorption measurements have been done with Parkin Elmer UV/vis spectrophotometer LambdoBio20 at a resolution of 1 nm. X-ray diffraction measurements of the electro-reduced dried powder has been done by filling it in to the groove of quartz glass sample holder using Bruker made X-ray diffractometer instrument operating at a voltage of 40 kV and a current of 30 MA with Cu Ka radiation. The field emission scanning electron microscope (FE SEM) attached with Oxford-EDS system IE 250X :nax 80 with latest 80 mm 2 model FEI Quanta 200 have been used to determine morphology and elemental composition of the prepared materials. The electrocatlytic activity has been studied by AutoLab.

Result and discussion

UV-visible absorption spectra of Copper nanoparticles in aqueous solution have been recorded. The characteristic absorption band at around 270 nm and 462-466 nm (surface-plasmon) have been found due to Cu_2O and Cu nanoparticles respectively. The value of absorption band has been found same as reported in the literature. But the value for surface -plasmon has been obtained less than 519nm-573nm.The sharpness of absorption band and surface -plasmon probably arises from the narrow size distribution of Copper nanoparticles.

The XRD pattern recorded on the reddish brown powder obtained after precipitation and drying is shown in figure 1(a). The diffraction pattern shows peaks at 2? values and corresponding (hkl) planes of 43.3° (111), 50.5° (200), 74.1° (220) that matches with the fcc metallic Cu (JCPDS, File No. 85-1326) and the other peaks in the same diffraction pattern at 2θ values of 29.56° (110), 36.44° (111), 42.3° (200), 61.4° (220), and 73.9° (311) that matches with the Cu_2O (JCPDS, File No. 65-328), indicating that Cu_2O also coexists together with metallic copper particles. These (hkl) values also match with the reported values in the literature (Nikam, 2014). The coexisting Cu_2O is also considered to be due to some oxidation in air environment in addition to Cu-hydroxide reduction process. No impurity diffraction peaks have been detected confirming the high purity of the product obtained by this method. Additionally, high reflection peak intensities for all the samples suggest that these are highly crystalline in nature.

Figure 1 (b) shows the SEM images of copper/ copper oxide NS prepared with 150 mM of TSC and an applied voltage of 3.2 V. This image shows that synthesized NPs are agglomerated in nature. The approximate size of particles has been found to be 50-60 nm. The size has been calculated with Sherrer equation. These particles are elongated and spherical in shape. The cyclic voltammetry study has been done for testing electrocatalytic activity of prepared NPs. This study has been done by drop casted Copper particles on disk of Gold electrode

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which acts as working electrode, Ag/AgCl reference electrode and Pt wire as a counter electrode. The results of this analysis shows that oxidation current increases with increased scan rates. The cyclic voltammetry curve shows that electrocatalytic activity of methanol oxidation increases with scan rate. One oxidation peak is obtained in this case which shows methanol oxidizes completely in CO_2 and H_2O in one step which is an example of direct methanol fuel cell.

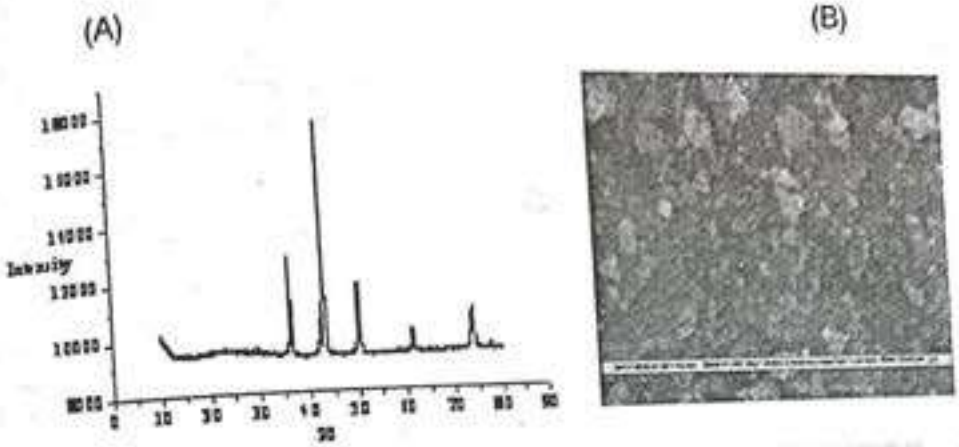

Figure 1: Powder XRD pattern of copper/copper oxide NPs prepared with 150 mM of tri-sodium citrate at 3.2 V, and 311 K. (a) and (b) SEM images of copper/copper oxide NPs prepared with 150 mM of tri-sodium citrate at 3.2 V and 311 K, Scale bar 200nm.

Conclusion

We have prepared Copper and copper oxide nanoparticles in different shape and size by a novel electrochemical synthesis technique which is simple and environment friendly. It is an easy, fast and cost effective technique and doesn't involve any harmful and environmentally toxic chemicals used previously in conventional chemical reduction methods. These particles can be used in electro-oxidation of Methanol.

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