Rod-shaped copper (Cu, Cu_2O) nano catalyst for the facile oxidation of methanol

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Abstract

Copper and copper oxide (Cu_2O) nanoparticles (NPs) were synthesized by electrochemical route using 2.55 mM tri-sodium citrate (TSC) as a capping and reducing agent. Synthesis was conducted at 15 V and 373 K in the presence of pH 4.22 using a copper rod as a working electrode and a platinum wire as a reference electrode. The electrochemical set-up was kept in the air, as well as under inert nitrogen-purged conditions. Cu NPs were synthesized for the first time by the direct dissolution of Cu^{2+} into the solution of the capping agent from the copper electrode in to the electrochemical cell. This means salt of copper was not used. NPs were characterized using UV–visible absorption spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) techniques. High-resolution TEM pictures showed the formation of a rod-shaped nanostructure. The lengths of copper rods were from 56.9 nm to 61.9 nm and the widths of nano-rods were, from 8.11 nm to 9.57 nm. Furthermore, the rod-shaped Cu_2O NPs were tested for their catalytic applications in the electro-oxidation of methanol, where they showed excellent activity in terms of higher efficiency as well as kinetically low over-potential values.

Keywords: Copper, cuprous oxide NPs, rod shape, electrochemical cell, methanol oxidation.

Introduction

Copper and their oxide nanoparticles (NPs), especially cuprous oxide, have a wide application range as a catalyst, such as in photo-electrochemical water splitting, photovoltaics, opto-electronics, biosensors and humidity sensor [**1**]. Interests in cuprous oxide is continuously growing due to exotic electronic properties and excellent electrical and thermal conductivities associated with their nano-dimensions that are dependent on stoichiometry, such as vacancies due to copper and oxygen. Additionally, its base material i.e., copper is inexpensive, abundant, and non-toxic and it can be prepared in bulk quantities. Besides the nano-dimension of Cu/CuO NPs, the shape brings in another degree of freedom to vary and control their properties which exert tremendous impact on their applications. For example, the atomic arrangement in different facets that are exposed due to variations in shape will have a profound effect on their catalytic properties. Therefore, the activation of cuprous oxide by changing its particle shape to expose its most active catalyst site would yield an economic and efficient catalyst material which in turn can be achieved by developing a facile, cheap, and sustainable synthetic protocol for cuprous oxide NPs with various shapes.

Recently several methods are being applied to prepare copper and cuprous oxide NPs, such as chemical reduction, evaporation deposition, a plasma approach, mechano-chemical synthesis, electrical explosion, micro-emulsion, and electrochemical processes. Among these methods, the electrochemical technique which involves a lower cost and has a lesser environmental impact which is considered more attractive. The copper NPs have conventionally been prepared in aqueous media by electro-deposition, which can be obtained at higher over-potentials corresponding to the limiting diffusion current density. Particularly, electrolysis has been commonly used to prepare cuprous oxide in powder form due to its simple process and operations that are easy to control. Few reports describing the electrochemical synthetic protocol for cuprous oxide NPs with varying shapes have been published in the literature.

Nano-ultra fine copper particles have been synthesized by a novel electro-deposition method, and the effect of electrolysis parameters on the morphology of copper particles has been studied. The effect of different additives on the electro-deposition of copper powder and its surface engineering has also been studied [**2-3**]. The effect of the anode material on the composition and dimensional characteristics of the nano-sized copper powder has been reported by Tesakova [**2**]. In addition, the effect of new additives such as lanolin on the electro-deposition of copper powder has been studied by Jafer [**4**] and co-workers. The effect of pH on the composition of copper oxide particles has been studied by Nikam [**5**]. The influence of the interaction between chloride and thiourea on copper electro-deposition has been reported by Tantavichet [**6**]. Unfortunately, different synthetic strategies under different experimental conditions are required to generate various shapes of Cu_2O NPs. Thus,

the developed a unified approach towards a facile and sustainable synthetic protocol for the controlled synthesis of Cu_2O with range of shapes is still a cha

This paper reports our successful attempt toward the facile and sustainable synthesis of copper/cuprous oxide NPs with a rod shape using a simple electrolysis technique. It was found that, tri-sodium citrate (TSC) plays an important role in the shape directive agent. The prepared materials were thoroughly characterized for their morphological, structural, and optical properties. To the best of our knowledge, the developed protocol for the synthesis of cuprous oxide NPs is unique and has not been reported before in the literature

Room Temperature Aerobic Copper–Catalysed Selective Oxidation of Primary Alcohols to Aldehydes has been reported by Patrick Gamez [**7**]**.** Electrodes functionalised with the organocatalyst 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) moiety hold great potential for the development of waste-free oxidation of alcohols has been investigated by Rosaria Ciriminna [**8**]. TEMPO-Copper(II) Diimine-catalysed oxidation of Benzylic alcohols in aqueous media has been studied by Paweł J. Figiel [**9**]. Waste-Free electrochemical oxidation of alcohols in water has been demonstrated by Giovanni Palmisano [**10**]. Recentaly mechanism of (bpy) Cu/TEMPO-mediated alcohol electrooxidation has been given by S. S. Stahl in 2016 [**11**]. Electrochemical Alcohol Oxidation Mediated by TEMPO like nitroxyl radicals has been reported by Rosaria Ciriminna in 2017 [**12**]. But by using copper NPs the electrochemical oxidation of alcohols has been not reported in the literature.

Herein we have investigated the effect of facets on their electrocatalytic activity, especially in the case of rod-shaped copper/cuprous oxide NPs. The electro-catalytic activity of these NPs has been studied in the oxidation of primary alcohol, i.e., methanol. Methanol oxidation on a surface of a catalyst is an important reaction, as it has the potential for fuel cell application (direct methanol fuel cell, [DMFC]). It has been noted that the facets of Cu/Cu_2O NPs make them better and more efficient electro-catalysts toward methanol oxidation.

Experimental

Materials/ Chemicals details

Analytical grade reagent (A.R.) TSC used as received commercially, a Cu rod used as a working electrode (99.99% pure), and a Pt wire (99.99%) as a reference electrode were used to synthesize the copper NPs. The solution of pH of 4. 22 has been maintained by adding in μL amount of concentrated A.R. HCl. All the solutions were prepared in double de-ionized water.

Material synthesis / Reactions

Preparation of Copper Nanostructures: TSC-capped copper nanostructures (Cu and Cu_2O NPs) were synthesized via electrochemical route at a 373K temperature and an applied potential of 15.0 V. The concentration of TSC was 2.55 mM and the pH of the solution was maintained at 4.22. An electrochemical cell was formed by immersing the copper electrode (anode) and platinum wire (cathode) in solutions of TSC that were kept at 100 mL in each set. Both electrodes were connected with a potentiostat and a desired potential (15 V) was applied for a fixed time interval of two hours. The electrolysis of copper was carried out either in air (for Cu_2O NPs) or under inert nitrogen-purged conditions (for Cu NPs) using an electrochemical cell equipped with a magnetic stirrer at 450 rpm. The solution turns brownish in color after ca. 30 min, indicating the formation of Cu/Cu_2O NPs in the electrolyte solution. The particles begin accumulating or adsorbing at the Pt cathode while the potential is being applied and as soon as the power supply is stopped, the Cu/Cu_2O NPs is stripped from the cathode in the form of precipitate and settle down the bottom of an electrochemical cell. Thus, the obtained precipitate is then filtered with Whatman filter paper number 42, washed several times with de-ionized water, and then dried under a vacuum oven. The reddish-brown powder was then collected and used for further characterization.

***Methanol Oxidation*:** The oxidation of methanol was conducted by drop-casting copper NPs on a gold disk electrode in the presence of 0.5M H_2SO_4 at a scan rate of 20 mV/s,50 mV/s,75 mV/s, 100 mV/s and 200 mV/s using cyclic voltammetry. An Ag-AgCl electrode was used as a reference electrode and platinum as a counter electrode. An amount (15μg) of copper NPs was loaded on to the circular portion of the gold of the electrode.

***Material Characterization*:** X-ray diffraction (XRD) measurements of the dried powder were taken been done by filling in the groove of a quartz glass sample holder using a Bruker D8 Advance diffractometer with Ni-filtered CuKα radiation. The data were collected in the 2θ range of 0–70^o with a step size of 0.02 and a step time of 1s. The surface morphology was studied by recording the transmission electron microscopy (TEM) images of the sample by using the Tecnai G^2 F 20 TWIN TMP series of the microscope, Model FEG 200KV. SEM images of the sample were obtained using Zeiss EVO 50 model (EHT 20 kV, WD 8 mm, Mag 25 K X). The electrocatalytic-oxidation of methanol was done using Auto Lab.

Results and discussion

Synthesis of Copper NPs an applied potential of 15.0 V at 373 K, pH 4.22

In this synthesis, Cu and Cu_2O NPs are formed following the nucleation of the NPs by an electrochemical reaction followed by the growth process. When the potential is applied, the copper anode first becomes oxidized into a +2-oxidation state (as per the following reaction), generating the Cu^{2+} species which in presence of citrate

capping ligands reduces to the Cu^{o} oxidation state (i.e. nucleation). Depending on the applied potential, the number of nuclei formed may vary and this leads to the different shapes of NPs. The Cu^{o} nuclei then undergo the growth process to generate NPs where the growth process is controlled by the diffusion of growth species, which in turn depends on the citrate additive concentration. Overall the nucleation and growth kinetics are controlled by the concentration of citrate additives, temperature and the applied potential. The experimental set-ups for the synthesis has been demonstrated in **Fig. S1** (See supportive informations).

$$Cu \rightarrow Cu^{2+} + 2e^{-} \quad (1)$$

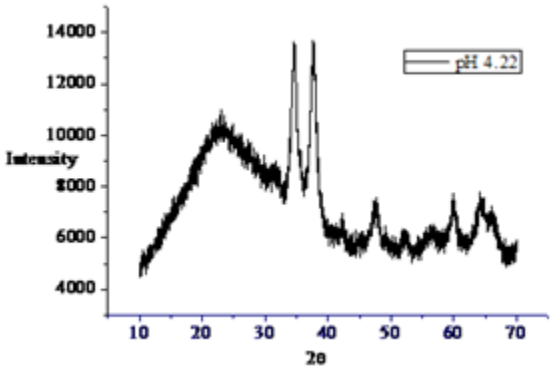

Fig. 1. Powder x-ray diffraction pattern of copper NPs with 2.55 mM TSC at pH 4.22, 15 V and 373 K.

The XRD pattern of mixed-phase copper and cuprous oxide NPs synthesized at 15 V, 373 K, and with 2.55 mM of TSC is shown in **Fig. 1.** The 2θ peaks at the 19.62° (111), 22.72° (200) ,32.42° (220), 38.32° (311), 39.85° (222), 46.39° (400), 50.57° (331), 51.91° (420) and 57.24° (422) planes belong to the FCC metallic Cu (JCPDS, PDF, File No. 01-1242). The other peaks in this diffraction pattern at 2θ values 29.58° (110), 36.44° (111), 42.32° (200),52.49° (211), 61.4° (220), 65.58º (211), 69.62º (310) and 73.55° (311) belong to Cu_2O (JCPDS, PDF, File No. 78-2076) indicating that Cu_2O also coexists together with copper particles. These results correlate with the results reported by Nikam [**5**]. The coexisting Cu_2O is considered due to some oxidation in the air environment during synthesis in the electrochemical cell. No impurity diffraction peaks have been detected confirming the high purity of the product obtained by this method. The observation of diffraction peak intensities for all the Cu NPs indicates these are crystalline in nature.

The SEM image and EDS of the synthesized Cu/Cu_2O (NPs) have been shown in **Figs. 2, 3**. It is clear from this micrograph that prepared copper NPs are approximately 50-60 nm in size. The EDS data shown in **Table1** confirm the formation of Cu and Cu_2O NPs. The elemental percentage ratios which show that in the synthesized sample the Cu NPs are presented double amount then the Cu2O NPs. To confirm the SEM analysis of Cu the NPs structure, a high-resolution TEM (HRTEM) analysis has been performed for to determine the exact size and shape of the particles. **Fig. 4.** shows the formation of rod shape of the nanostructure. The exact size of the copper rods have been found from 56.9 nm to 61.9 nm in length and from 8.11 nm to 9.57 nm in width. These particles are smaller than previously reported by Q. B. Zhang [**13**] and they have a different morphology as determined by the chemical reduction method [**14**]. The micrograph also demonstrates that some synthesized Cu NPs are well dispersed, and some are agglomerated.

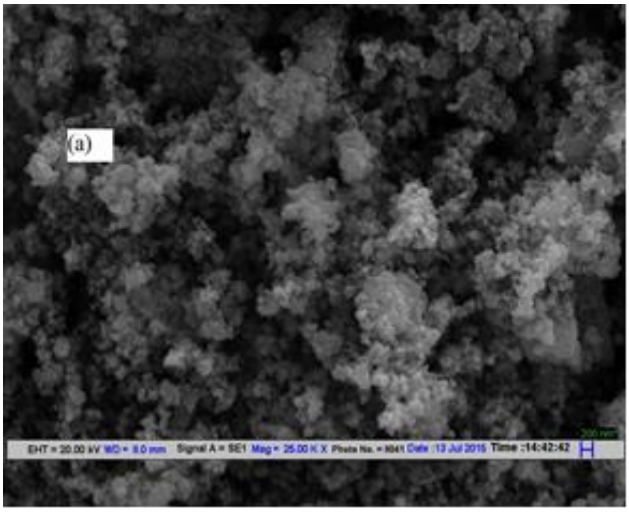

Fig. 2. SEM images of copper NPs with 2.55mM TSC at 15 V, pH 4. 22 and 373 K temperature, scale bar of the inset is 200 nm.

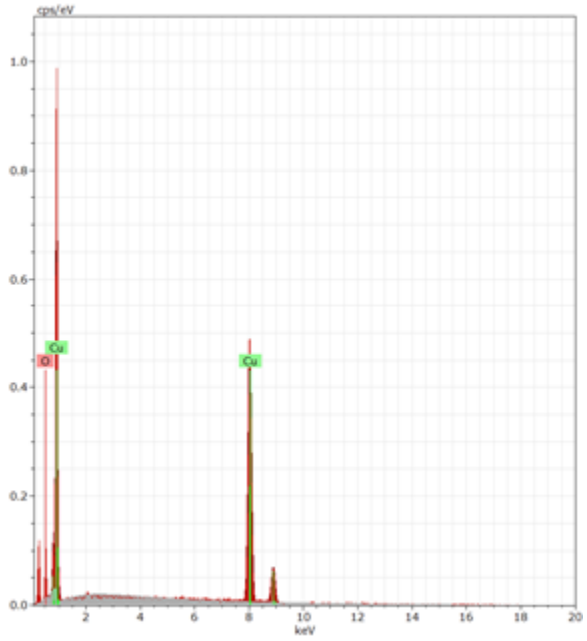

Fig. 3. EDS for rod-shaped Cu/Cu_2O NPs synthesized with tri-sodium citrate at pH 4.22.

Table 1. EDS data for rod-shaped Cu/Cu_2O NPs synthesized with tri-sodium citrate at pH 4.22

Element	series	[wt%]	[norm wt%]	[norm at %]	Error in wt % (3 Sigma)
Oxygen	K-series	7.8819	6.6349	22.0123	5.3349
Copper	K-series	110.9124	93.3650	77.9876	9.5545

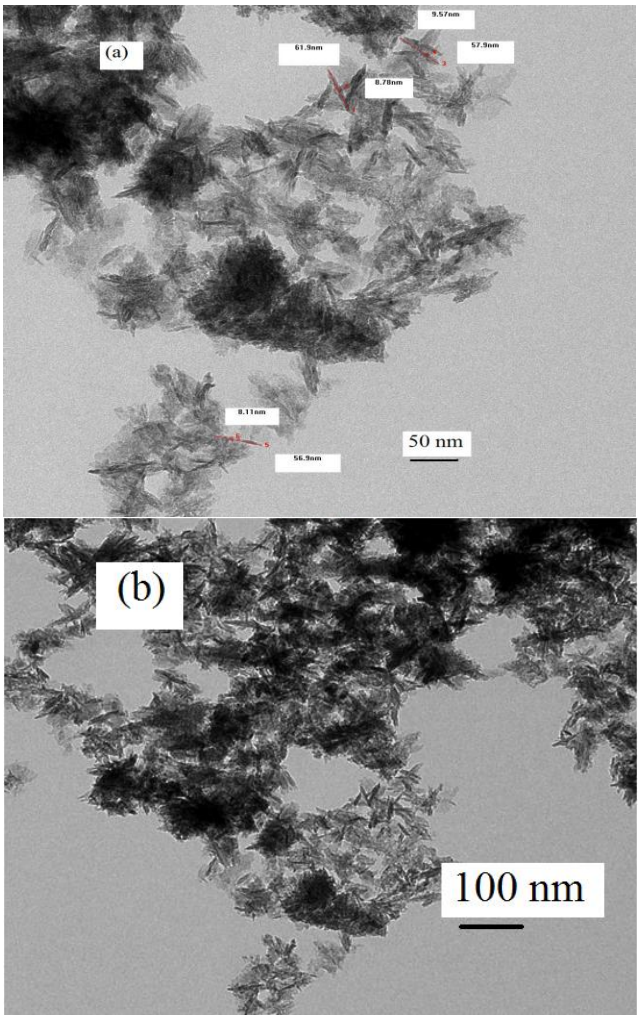

Fig. 4. TEM images of copper NPs with 2.55mM TSC at 15 V, pH 4.22, and 373 K temperature, scale bar of the inset is 50 nm in (a) and 100 nm in (b).

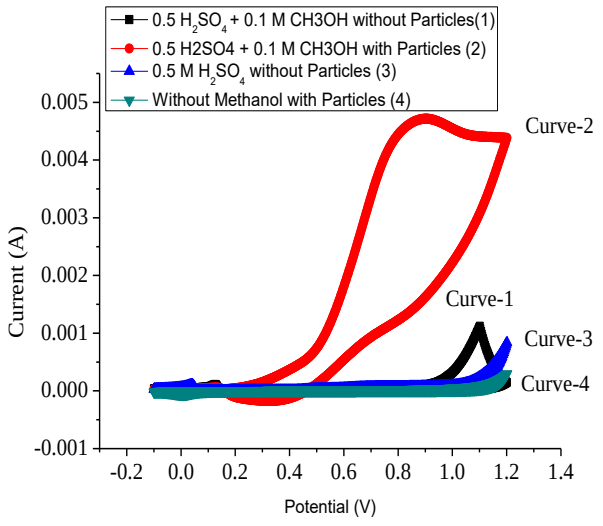

Fig. 5. Cyclic voltammograms (Curve-1) in (0.5 M H_2SO_4 + 0.1 M CH_3OH without particles, (Curve-2) in 0.1 M CH_3OH, 0.5 M H_2SO_4 with copper NPs drop-casted on a gold disk electrode, (Curve-3) in 0.5 M H_2SO_4 without particles, and (Curve-4) without methanol with particles, All Curves at a scan rate of 200 mV/s (scan 1- 4).

To explore the electrocatalytic applications of copper NPs, cyclic voltammetry measurements have been carried out. **Fig. 5**. (**Curve-2**) shows a cyclic voltammogram of methanol acquired using drop-casted copper NPs on a gold disk electrode as working electrode, Ag/AgCl as reference electrode and platinum wire as a counter electrode in 0.5M H_2SO_4 and in 0.1 M CH_3OH in the range of potential from -0.1 V to 1.2 V at a scan rate of 200mV/s. The oxidation peak has been appeared in the potential region from 0.4V-0.8V. The magnitude of current has been obtained in the range of 4.86×10^{-3} A (Ampere) as given in **Table. 3**. **Fig. 5** (**Curve-3**) shows a cyclic voltammogram acquired using a disk gold electrode as working electrode, Ag/AgCl as reference electrode and platinum wire as a counter electrode in 0.5M H_2SO_4 in the potential region from -0.1 V to 1.2 V at a scan rate of 200mV/s. All the peak potential has been given in **Table. 2** for different scan rates. The oxidation peak current for different scan rates have also given **Table 3**. The curves obtained at different scan rates10 mV/s, 20 mV/s, 50 mV/s, 75 mV/s and 100 mV/s have been given in **Figs. S 2, S 3, S 4** (See supportive informations). The oxidation peak has been not appeared in the potential region from 0.4V-0.8V in 0.5M H_2SO_4 and in 0.1 M CH_3OH in absence of Cu NPs particles (**Curve-1**). It means oxidation peak of methanol has not been obtained when the cyclic voltammogram has been obtained without Cu NPs. Or we can say in other words, the oxidation of methanol does not take place in absence of copper NPs on a gold disk electrode. The oxidation peak has not been obtained in 0.5M H_2SO_4 and in presence of copper NPs on a gold disk electrode (**Curve-4**, **without methanol**). It means the copper NPs have not been oxidized in these conditions. Or we can say copper NPs behaves as a electrocatalyst in oxidation of methanol (**Curve-2**). Ota *etal* [**15**] has shown oxidation of methanol at 0.6 V using platinized Pt electrode in 1M CH_3OH + 1M H_2SO_4.

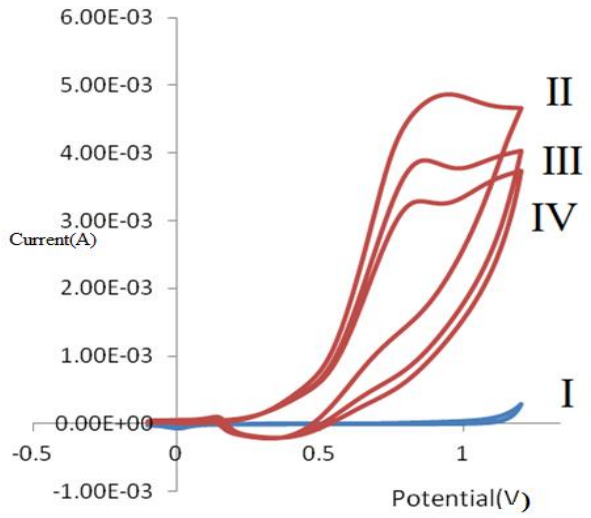

Fig. 6. Cyclic voltammograms (Curve-I) in (0.5 M H_2SO_4), (Curve-II-IV) in 0.1 M CH_3OH, 0.5 M H_2SO_4) with copper NPs drop-casted on a gold disk electrode at a scan rate of 200 mV/s (three cycles).

This oxidation peak is shifted toward the negative side with copper NPs with an increase in the number of cycles, as shown in **Fig. 6** (Curve II-IV). The oxidation peak current also decreases with increase in cycles at this scan rate. This shows that the electrocatalytic activity of methanol oxidation increases with the scan rate. The magnitude of current for oxidation peak has been decreased from 4.86×10^{-3} A to 3.27×10^{-3} A (Ampere) for three cycles. One oxidation peak has been obtained in this case that shows methanol oxidizes completely in CO_2 and H_2O which is an example of direct methanol fuel cell (DMFC).

Table 2. Data of potential (V) in Methanol Oxidation (0.1M) using Cyclic Voltammetry with Copper Nanoparticles drop – casted on disk gold electrode in 0.5 M H_2SO_4

Scan rate (mV/ s)	Voltage (V)		
	I	II	III
20	0.68	0.67	0.67
50	0.82	0.77	0.75
75	0.83	0.80	0.74
200	0.92	0.85	0.83

Table 3. Data of current in Methanol Oxidation (0.1M) using Cyclic Voltammetry with Copper Nanoparticles drop – casted on disk gold electrode in 0.5 M H_2SO_4

Scan rate (mV/ s)	Current : 1 X 10 $^{-3}$(A)(Ampere), In three Cycles		
	I	II	III
20	2.73	2.37	2.27
50	4.56	3.2	2.8
75	4.57	4.51	2.79
200	4.86	3.89	3.27

Conclusion

The electrochemical reduction behaviours of copper ions as well as their nucleation and growth on a platinum electrode have been studied in an aqueous solution of TSC. When potential of 15 V is applied copper + 2 ions have been obtained in the electrochemical cell from copper electrode and colour of solution becomes blue and subsequently these copper + 2 ions reduce in red-brownish colour of Cu and Cu_2O at platinum electrode. TSC works as a reducing as well as capping agent. Both the electrode potential and concentration play an important role in tuning the nucleation and growth kinetics as well as in controlling the final morphologies of copper NPs as reported in the literature [**16**]. It means nucleation and growth kinetics of copper NPs are affected by magnitude of applied potential and concentration of capping agent. This suggests uniform copper NPs with a small size distribution can be obtained at 2.55 mM of the TSC concentration at pH 4.22. Here, we also obtained copper particles along with copper oxide NPs which is not reported around pH 4 in the literature. Thus the rod-shaped particles can be obtained at low concentrations of a capping agent and at a higher potential and higher temperature. This electrochemical synthesis is a novel technique and it is simpler and environmentally friendly than the previously used conventional chemical reduction methods. Thus the electrolytic method is ideal because it involves a simple process, low energy consumption, high output, easy control and no environmental pollution. **Fig. 6** (Curve II-IV) shows the activity of methanol oxidation at copper and copper oxide NPs drop-casted on a disk gold electrode is markedly increased with a negative shift of the onset potential and a decrease in the oxidation current with an increase in the number of cycles. This means with an increase in number of cycles, the electrocatalytic activity of copper NPs decreases. The magnitude of oxidation peaks also decreases with an increase in the number of cycles. Only one oxidation peak is obtained in this case which shows methanol oxidizes completely in CO_2 and H_2O and very good magnitude of oxidation current this process behaves as a direct methanol fuel cell (DMFC). We have reported first time electrochemical synthesis of copper NPs without using the salt of copper and electrocatalytic oxidation of methanol by drop casting of Cu NPs on a gold disk electrode.

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Supporting information

Supporting informations are available from VBRI Press.

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