

Formation mechanism of mesoporous Cu/CuSe and its application as electrocatalyst for methanol oxidation reaction

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Abstract

Single step solvothermal method is used to prepare Cu/CuSe as an electrocatalyst for methanol electro-oxidation reaction (MOR). 1,3-butan-diol is selected as a reaction medium, whose viscosity and complex formation with Cu(II) ions, dictate the catalyst morphology. The catalyst has a mesoporous structure, which is composed of nanoballs with a high purity, crystallinity, and uniform morphology. The electrocatalyst is excellent for MOR, as it delivers current density of 37.28 mA/mg at potential of 0.6 V (vs Ag/AgCl) in the electrolyte of 1 M KOH and 0.75 M methanol at a 50 mV/s scan rate under conditions of cyclic voltammetry. The catalyst also shows good stability for 3600 s with negligible charge transfer resistance and high electrochemical active surface area (ECSA) value of 0.100 mF/cm².

Key words: Cu/CuSe; nanoballs; formation mechanism; MOR; Nanocomposite;

Introduction

Technology advancement has triggered fast depletion of fossil fuels, which resulted in energy crisis and environmental protection. These issues attract researcher's attention, to develop renewable energy sources such as direct methanol fuel cells (DMFCs) [1, 2]. DMFCs produce energy from MOR, which exhibits superior activity, rich source (methanol) and high energy density [3, 4]. Additionally, MOR can reduce carbon emission as well as methanol content in industrial technical waste [5, 6]. Platinum is an excellent catalyst for MOR but the high price, low abundance, and CO poisoning hinder its application [7, 8].

In this regards, transition-metal based electrocatalysts, such as copper selenides are consider to be promising material for MOR, due to high activity, multiple crystal phases, and multiple oxidation states of Cu in selenides [9]. Copper strongly facilitates alcohol oxidation, in particular in an alkaline medium [10]. Combining copper with selenium e.g., copper selenides with the unique metallic properties [1], may further improve the applications in the direction of electrocatalysis. The available work about copper selenides is related to PtCu/Cu_{2-x}Se nanowires, which deliver a total current density of 5.29 A/mg for methanol oxidation, which is 5.3-fold higher than commercially available Pt/C [9].

With this motivation, a single phase Cu/CuSe was synthesised via simple, one-step solvothermal reaction for MOR application. The catalyst morphology consists of small nanoballs which aggregate to develop mesoporous morphology with excellent performances toward MOR.

Materials and methods

One step simple solvothermal method was used for synthesis of Cu/CuSe. Typically 1.2 mmol of Cu(NO₃)₂•2H₂O and 0.8 mmol of Na₂SeO₃ were mixed simultaneously in 30 mL of 1,3-butane-diol and stirred to form a homogeneous mixture. The mixture was transferred into 50 mL stainless steel Teflon autoclave and heated at 180 °C for 16 h. Then, the sample was cooled down to room temperature to collect sample after centrifuging. The sample was washed with water and

ethanol to remove impurities and finally dried and stored in ambient conditions to be used for further application.

Electrochemical application

A three-electrode system connected with μ Autolab potentiostat was used for electrochemical applications. Pt rod, Ag/AgCl (3 M KCl) and glassy carbon electrode (GCE) were used as auxiliary, reference and working electrode, respectively. 5 mg of the sample was added to a mixture of 750 μ L of water and 250 μ L of ethanol, and ultrasonicated for 20 min until full homogenization. The as-prepared suspension (2 μ L) was drop-casted on a freshly cleaned GCE surface and drying at room temperature; subsequently, 2 μ L of Nafion was dropped on the modified GCE surface and dried. The finally modified GCE was used for electrochemical application in an alkaline solution (1 M KOH) with different concentrations of methanol (0.25 - 1 M) at different scan rates (25 - 100 mV/s) via cyclic voltammetry (CV). Electrochemical impedance spectroscopy (EIS) was studied at open circuit potential, at frequency range of 0.1 - 10^5 Hz with AC amplitude of 5 mV. Chronoamperometry was conducted at potential of 0.6 V vs. Ag/AgCl for continuous 3600 s. The electrochemical active surface area (ECSA) was calculated from CVs collected in the non-faradic region at scan rates of 20 to 100 mV/s.

Characterization

The electrocatalyst is characterized with STEM (HR-SEM, Nova NanoSEM 450, FEI, Hillsboro, OR, USA, equipped with STEM II detector) to determine its morphology via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The presence of metal and the purity of sample was determined by energy dispersive spectroscopy (EDS, EDAX/AMETEK, Materials Analysis Division, Model Octane Super, Mahwah, NJ, USA). The purity and phase composition of the sample was determined with XRD (Aeris 1.2.0 (PAN analytical) diffractometer with Cu radiation and PIXcel 1D detector).

Result and discussion

Formation mechanism

The material is synthesized in 1,3-butane-diol solvent, which is critically important for the final morphology of the material, as it forms copper complexes with Cu^{2+} ions, added in form of $\text{Cu}(\text{NO}_3)_2$. In the course of the reaction with selenite ions the slow release of copper ions from the organic complexes leads to formation of a large number of nucleation centers, resulting in nanosized CuSe deposit. At the same time, relatively high viscosity of the organic medium slows down the kinetics of the reaction, which also contribute to more nucleation centers, resulting in a ball-like morphology of the synthesized material [11]. Some of the Cu set in the vicinity of crystal or in between the ball morphology of the sample to give Cu/CuSe composite. It is most likely that nanoballs are initially formed, which bind to each other in the course of the reaction yielding finally a mesoporous morphology.

Morphology and composition

The SEM images (Fig. 1a, b) confirmed that the material is composed of nano sized spherical particles. The nanoballs are bound together to develop mesoporous morphology of the materials. The binding of nanoballs yields rough/irregular surface of the material which is responsible for maximizing active spots for electrocatalytic reaction. SEM data also confirmed that material is uniformly developed. TEM study (Fig. 1c, d), supported SEM data and revealed that the material is composed of nanoballs with different size; presumably, initially formed nanoballs aggregate, leading to irregular mesoporous morphology. Energy dispersive X-rays (EDX) data (Fig. 2a) revealed that the synthesized material is mainly composed of Cu and Se, which confirmed the purity of the sample. The porosity of the material increases the surface area, providing a short distance for electrolyte to interact with active materials, which is critical for Intensive MOR activity.

The XRD graph shown in Fig. 2b consists of sharp peaks at 35.5° , 42° , 49.2° , and 80.8° ascribed fringes values of (013), (014), (100), and (019) corresponding to COD # 04-014-1982 of the hexagonal crystal of CuSe. The peaks present at 43.3° , 51.2° , and 73° are corresponded to

fringes value of (111), (200), and (220) of cubic copper crystal according to COD # 01-088-3992. The XRD data confirmed that the electrocatalyst is highly pure, crystalline and composed of copper and copper selenide.

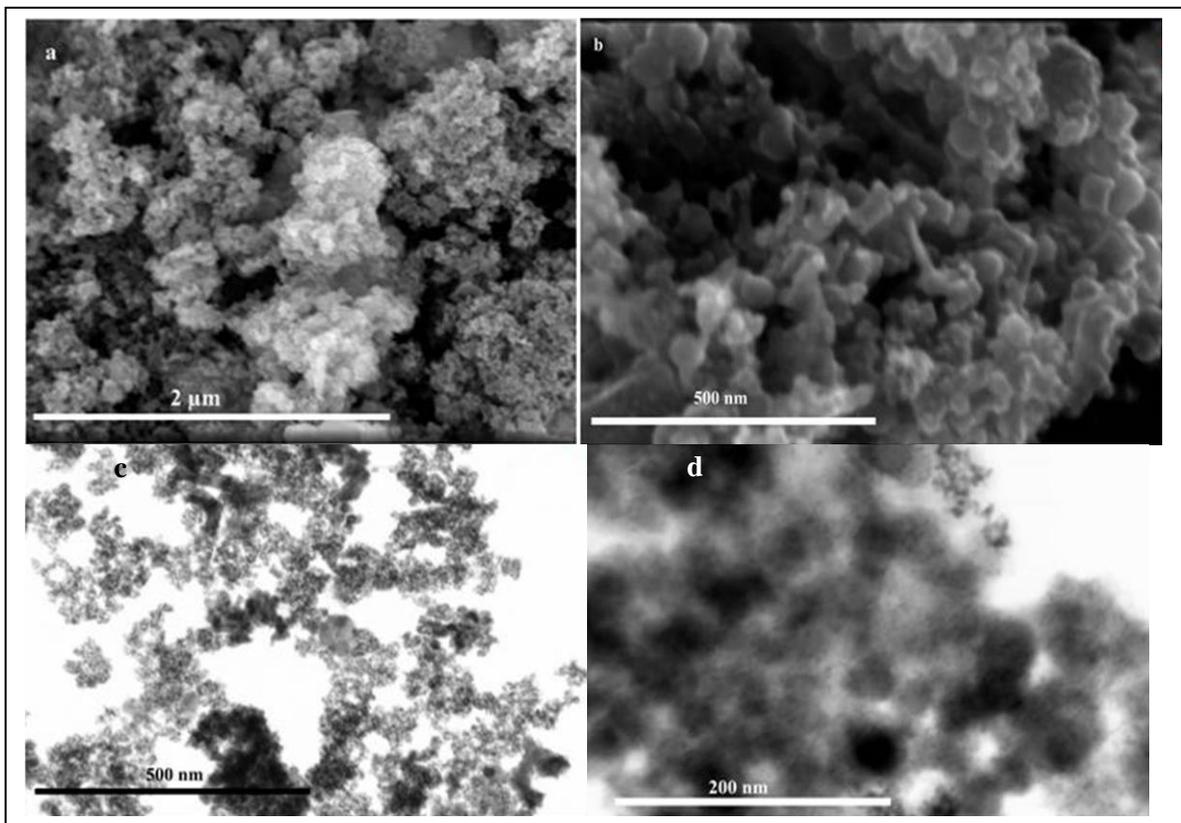


Fig. 1 (a,b) SEM (c,d) TEM images of Cu/CuSe

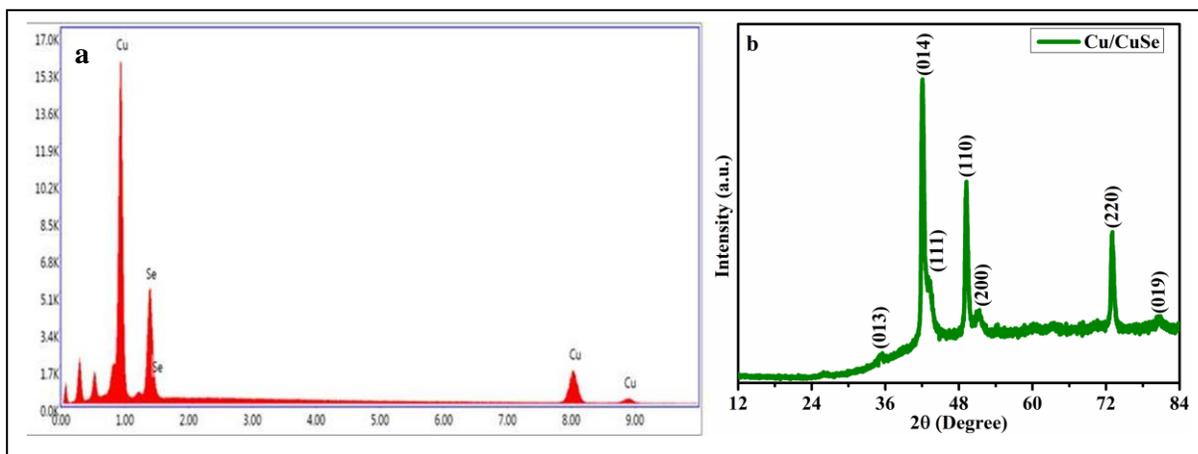


Fig. 2. (a) EDx and (b) XRD data of Cu/CuSe

MOR application

MOR application of Cu/CuSe is studied in an alkaline solution (1 M KOH) with different concentrations (0 - 1 M) of methanol, at scan rates from 25 to 100 mV/s in CV (Fig. 3a). The cyclic voltammetry was first applied in 1 M KOH solution without methanol with repetitive potential cycling until obtaining a stable voltammetric response, at scan rate of 50 mV/s. The CV shows a small anodic current tail in the supporting electrolyte (1 M KOH) with an onset potential of 0.65 V (vs. Ag/AgCl). As methanol was added in the electrolyte solution (0.25 M), the current increased dramatically and the onset potential of the anodic current diminished to 0.45 V (vs. Ag/AgCl), which is 200 mV lower than in the absence of methanol. Such a decrease in the onset potential and increase of the current density are attributed to MOR. As concentration of methanol increases the onset potential decrease slightly, but the current enhances greatly. At methanol concentration of 0.75 M the system shows the best performance, as the further increase to 1 M methanol does not produce significant current change. It confirmed that the 1 M KOH and 0.75 M methanol is suitable combination for best MOR application, as it provides the highest current density of 37.28 mA/mg at potential of 0.60 V (vs Ag/AgCl) and low Tafel slope of 128.1 mV/dec, as shown in Fig. 3a and 3b respectively. Detail current density and Tafel slope with respect to methanol concentrations are shown in Table 1. The system is also studied at a varying scan rate over the interval 25 - 100 mV/s. As the scan rate enhances the onset potential decreases concomitantly; in addition, the current density increases due to diffusional transfer effect of the methanol towards the electrode surface (Fig. 3c). Thus, the scan rate of 50 mV/s is considered as an optimal value, taking into account the electrocatalytic rate of the electrode reaction of methanol.

Table 1. Current density and Tafel slope of Cu/CuSe electrocatalyst at scan rate of 50 mV/s and in 1 M KOH electrolyte with respect to methanol concentration

Methanol concentration M	Current density mA/mg	Tafel slope mV/dec
0.0	3.20	212.6
0.25	20.82	145.1
0.50	27.45	141.1

0.75	37.28	128.1
1.00	39.60	128.0

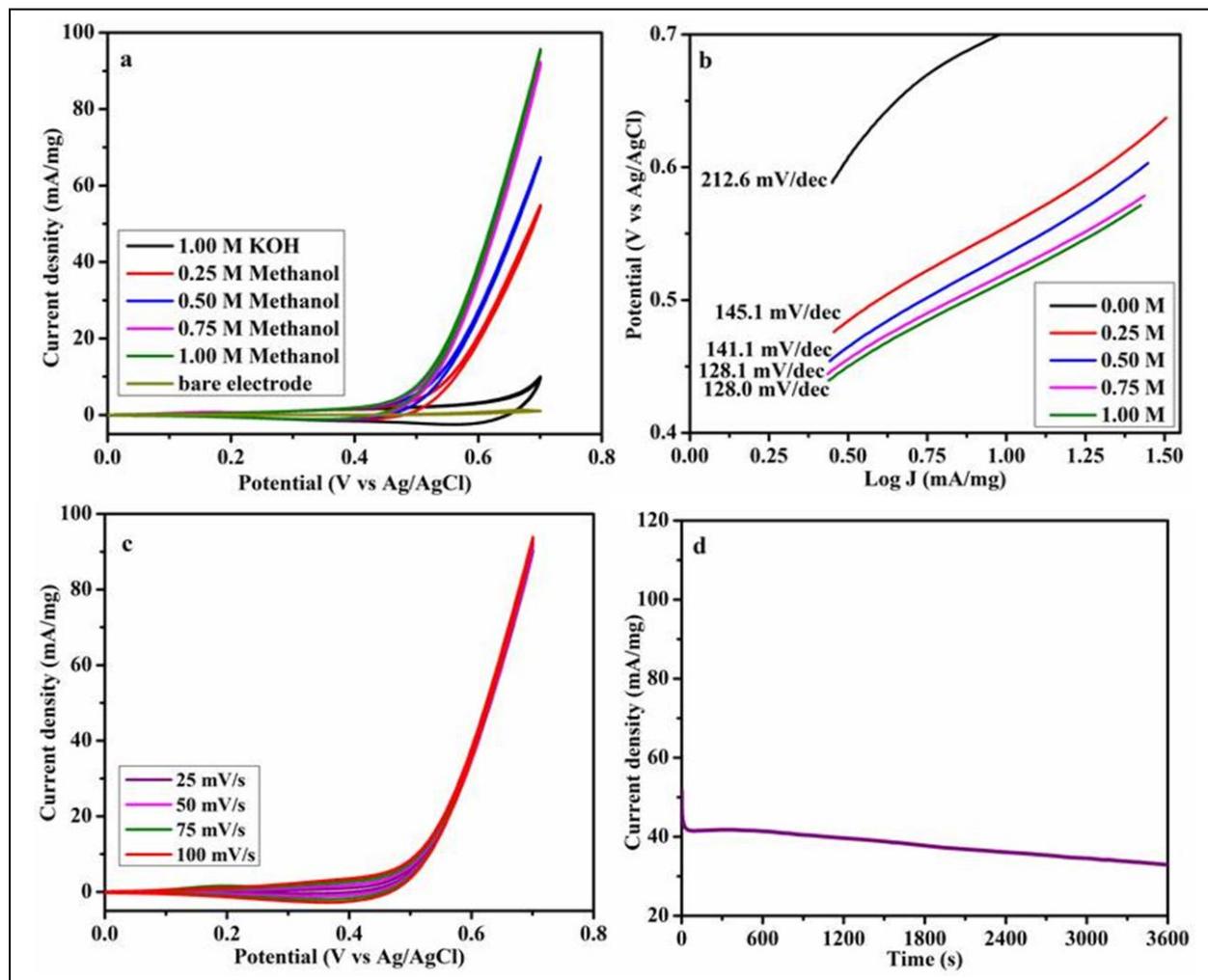


Fig. 3. CV cycles for MOR application in (a) 1 M KOH, 0.25 - 1M methanol at scan rate of 50 mV/s, (b) Tafel slope at different methanol concentration (c) effect of scan rate and (d) chronoamperometry test for stability of 3600s, in 1 M KOH and 0.75 M methanol for Cu/CuSe

Stability is a vital feature of any catalyst for its practical application. Cu/CuSe shows a very good stability for 3600 s in the course of chronoamperometric experiment at potential of 0.60 V in 1 M KOH, containing 0.75 M methanol (Fig. 3d). The electrochemical active surface area (ECSA) is calculated from the double layered capacitance (C_{dl}) obtained from CV (-0.20 to -0.10

V, non-faradaic potential range) at scan rates varying from 20 to 100 mV/s [12]. The current density J_{a-c} (a = anodic, c = cathodic at potential at -0.15 V vs (Ag/AgCl) is plotted against scan rate and get linear slope. Half of the slope is equal to ECSA, which is equal to 0.100 mF/cm^2 for Cu/CuSe as shown in Fig. 4a. The EIS is collected in 1 M KOH containing 0.75 M methanol over the frequency interval $0.1 - 10^5 \text{ Hz}$, with the AC amplitude of 5 mV, at open circuit potential. EIS (Fig. 4b) shows almost negligible semi-circle at high frequency which confirmed negligible charge transfer (R_{ct}). The graph (Fig. 4c) also shows almost horizontal line at low frequency which confirmed its good capacitance due to large surface [12].

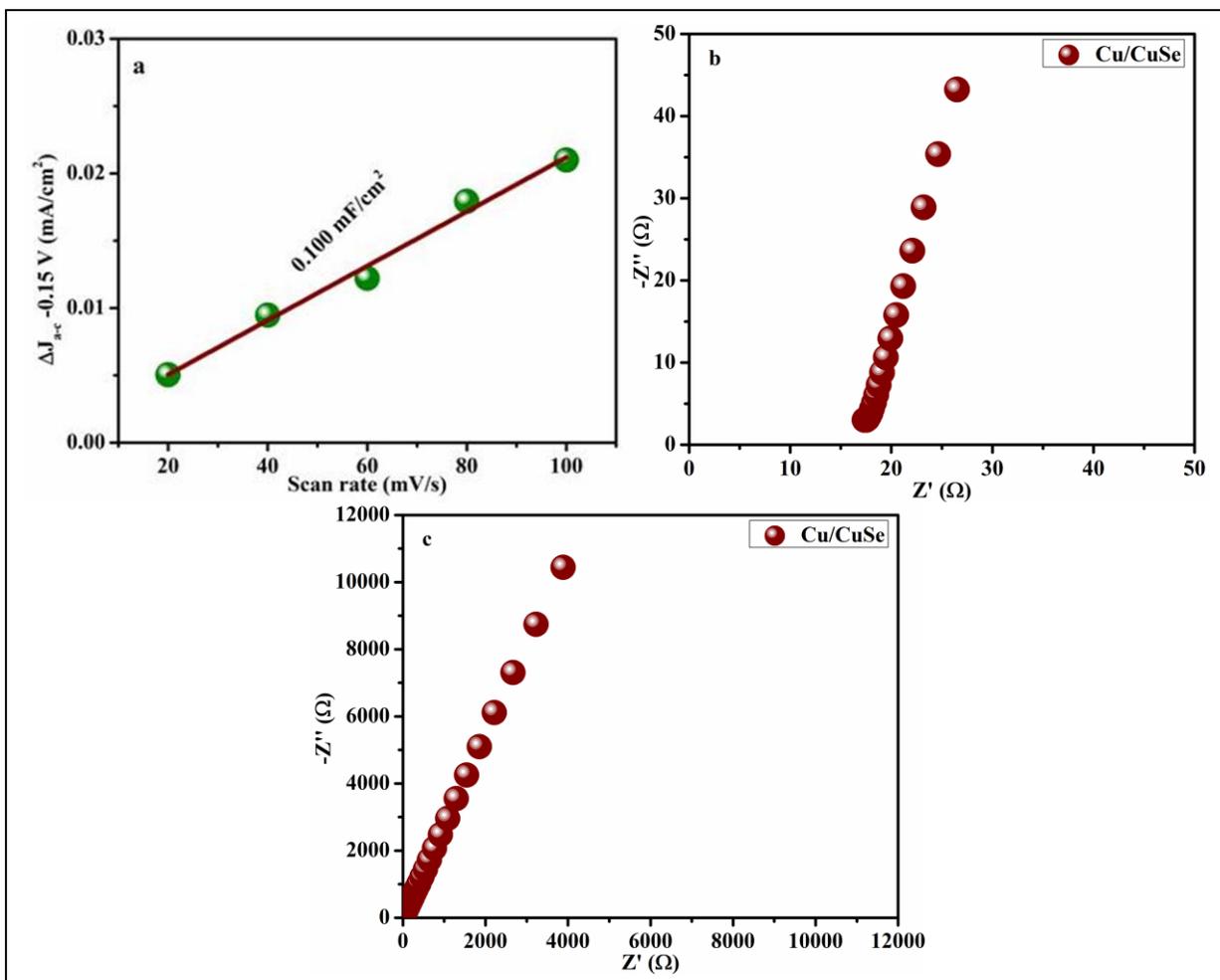


Fig. 4 (a) ECSA calculated by Cdl from CV cycles (a) EIS in high frequency with negligible semi-circle (c) EIS in low frequency with horizontal line For Cu/CuSe electrocatalyst.

Conclusion

The electrocatalyst is prepared via simple solvothermal method. The catalyst exhibits mesoporous morphology which is composed of nanoballs. This unique morphology of the sample is consequence of the usage of 1,3-butane-diol as a reaction medium. The electrocatalyst shows good performance for methanol oxidation. The best performance is obtained in 1 M KOH and 0.75 M methanol at scan rate of 50 mV/s. Electrocatalyst shows current density of 37.28 mA/mg, with low charge transfer resistance, and a long-term stability of 3600 s at potential of 0.6 V (vs Ag/AgCl). The catalyst exhibits ECSA value of 0.100 mF/cm².

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Conflict of interest

The authors have no conflict of interest

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