



Copper selenide nanobelts as an electrocatalyst for methanol electro-oxidation reaction

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Abstract

Energy crisis of the current society have attract the research attention for alternative energy sources. Methanol oxidation is source of energy but need efficient electrocatalyst like Pt. However, their practical ability is hinder due to cost and poisoning effect. In this regard, efficient catalyst is required for methanol oxidation. Herein, high temperature, pressure, and diethylenetriamine (DETA) as reaction medium/structure directing agent during solvothermal method are used for nanobelt $\text{Cu}_3\text{Se}_2\text{Cu}_{1.8}\text{Se}$ (mostly hexagonal appearance) formation. The electrocatalyst shows optimized methanol electrooxidation reaction (MOR) response in 1 M KOH and 0.5 M methanol at scan rate of 50 mV/s and delivers a current density 7.12 mA/mg at potential of 0.65 V (vs Ag/AgCl). The catalyst exhibits high electrochemical active surface area (ECSA) (0.088 mF/cm²) and low R_{ct} with good stability for 3600 s which favor its high MOR performance. This high response is due to its 2D hexagonal nanobelt morphology, which provides large surface area for reaction. The space among nanobelt reduce diffusion kinetics and rough/irregular edge increase reaction site to overall improve the methanol oxidation reaction.

Keywords Copper selenides · Electrocatalyst · Nanobelt · Methanol oxidation

Introduction

The current day research focuses sustainability in order to stimulate the engineering of more feasible energy storage and conversion alternatives prioritizing energy crises and environmental pollution [1, 2]. In this context, diverse energy storage and conversion devices have been proposed owing promising outcomes for instance batteries, supercapacitors, and diverse fuel cells have been claimed for exhibiting higher electrocatalytic abilities [3]. Still, the room for improvement is open for new developments in this

area and the researchers are always in progressive development for the quest of more prospective power substitutes that are more reliable, affordable, and eco-friendly [4]. In this regard, recently direct methanol fuel cells (DMFCs) have been proposed as the best substitutes in the meantime with the capability to produce electricity from the chemical energy of small organic molecules by virtue of electrochemical processes [5].

These (DMFCs) are considered future energy sources for vehicles and portable electronic devices due to their high energy density, low pollution emission, low working temperature, and high availability of methanol [6, 7]. The primary obstacle is the synthesis of optimal materials capable of undergoing electrocatalytic reactions for the advancement of DMFCs. For acquiring extra-economical electrocatalyst deprived of upsetting the durability and electrocatalytic activity is practically a real research challenge [4]. Noble metals and Platinum group metals such as Ir, Os, Pt, Pd, Ru, Rh, Ag, and Au are comparatively stable with high catalytic performance [8]. For instance, Pt is the most efficient electrocatalyst but its high price and poisoning effect due to CO, are main limiting factors that causes a loss in cell voltage for its practical application and results the long term instability due to agglomeration [9, 10]. Additionally, alkaline methanol

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electro-oxidation reaction (MOR) exhibits faster reaction kinetics, negligible poisoning, reduce corrosion and high efficiency compared to acidic MOR [11]. Thus, it is intensively required to develop non-precious metal-based electrocatalyst for alkaline medium with high efficiency for MOR.

Although these discussed materials have shown promising outcomes but the high costs, catalyst poisoning, long-term instability, and inappropriate methanol crossover are inevitable with losses in cell voltage. In a very quick succession during last decades, keen attentions have been given to commercialize more innovative electrocatalysts by tuning various features such as topography, morphology, and surface architecture of diverse electrocatalytic materials with efficient mass transport efficiency, crystal facets, and more redox interactions [10]. In this regard, transition metal-based electrocatalyst especially copper selenides got special attention due to their multiple crystal phases and oxidation state. These multiple oxidation state and multiple crystal phase will facilitate its catalytic application [12]. And the Cu at edge of catalysts is unsaturated which provide more active points for the reaction to occur [13]. Additionally, the presence of Se in the sample will further improve its activity due to its unique metallic features [14]. However, to the best of our knowledge, there is no study on copper selenide-based methanol electrooxidation reaction.

With these motivations, $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$ composite material has been developed here via simple and single-step solvothermal process. The $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$ showed nanobelt morphology which is due to diethylenetriamine (DETA) as solvent and structure directing agent. The $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$ is used for the first time and showed excellent performance for MOR application, due to multiple oxidation states of Cu in the catalytic materials and large surface area due to nanobelt morphology.

Experimental

Materials

Absolute ethanol [$\text{C}_2\text{H}_5\text{OH} \geq 99.7\%$], methanol [$\text{CH}_3\text{OH} \geq 99.5\%$], potassium hydroxide [$\text{KOH} \geq 85\%$], sodium selenite [$\text{Na}_2\text{SeO}_3 \geq 99\%$], copper nitrate hexahydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \geq 98.5\%$], and diethylenetriamine (DETA) $\geq 99\%$ were purchased from Sigma-Aldrich and were of analytical grade. Deionized water was used throughout the experiments.

Synthesis of copper selenide nanobelts

A simple solvothermal method was applied for mix-copper selenide synthesis. Typically $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (1.2 mmol) and Na_2SeO_3 (0.8 mmol) were added simultaneously to

DETA (30 mL) under stirring to get a homogeneous mixture. The final mixture was transfer to stainless steel Teflon autoclave (50 mL), and heat for 16 h at 180 °C. The sample was cooled down to room temperature and collected via centrifuge. The sample was washed with water and ethanol subsequently to remove impurities. The final catalyst was dried and stored for further investigation and application.

Electrochemical application

Electrochemical application of catalyst is study by mAulolab potentiostat connected with three electrode system. Glassy carbon electrode (GCE), Ag/AgCl (3 M KCl), and Pt rod are used as working, reference, and auxiliary electrode respectively. The sample (5 mg) was added to mixture of 250 μL of ethanol and 750 μL of water and ultrasonicate for 30 min to obtain a homogeneous suspension. $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$ suspension (2 μL) was drop-casted on freshly clean GCE surface and let to dry, and then, 2 μL of Nafion was dropped on GCE/ $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$, and made it dried again. The GCE/ $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$ was applied for electrochemical studies of methanol (0.0 to 1.0 M) in alkaline (1 M KOH) medium at different scan rate (25–100 mV/s) via cyclic voltammetry (CV). Electrochemical impedance spectroscopy (EIS) was studied at frequency of 0.1– 10^5 Hz, amplitude of 5mV, and with open circuit potential. Chronoamperometry was study for continuous 3600 s at potential of 0.65 V vs Ag/AgCl. The electrochemical active surface area (ECSA) was calculated from CV collect in non-faradic region at scan rate of 20–100 mV/s follow by C_{dl} .

Results and discussion

Characterization

SEM, TEM, and EDX were studied with STEM (NOVA 450) to characterize the morphology and purity of the sample. SEM data (Fig. 1a, b) shows that the material is composed of nanobelts which are stack on each other. The nanobelt are mostly in hexagonal shape (Fig. 1a), which are in different size. Irregular shape materials are also shown which may be initials of nanobelt formation or it represents two different states of copper selenides in mix-copper selenide sample. The data shows space in between nanoblet, this space and 2D appearance of nanobelt with small size increase its surface area, while the irregularity at the edge of the sample also increases the number of active spots for reaction, which ultimately improved its electrochemical application.

TEM data (Fig. 1c, d) confirmed the hexagonal shape nanobelt morphology of the sample. Gray appearance demonstrates low thickness of the nanobelt which also a proof for its high surface area. However, the dark black

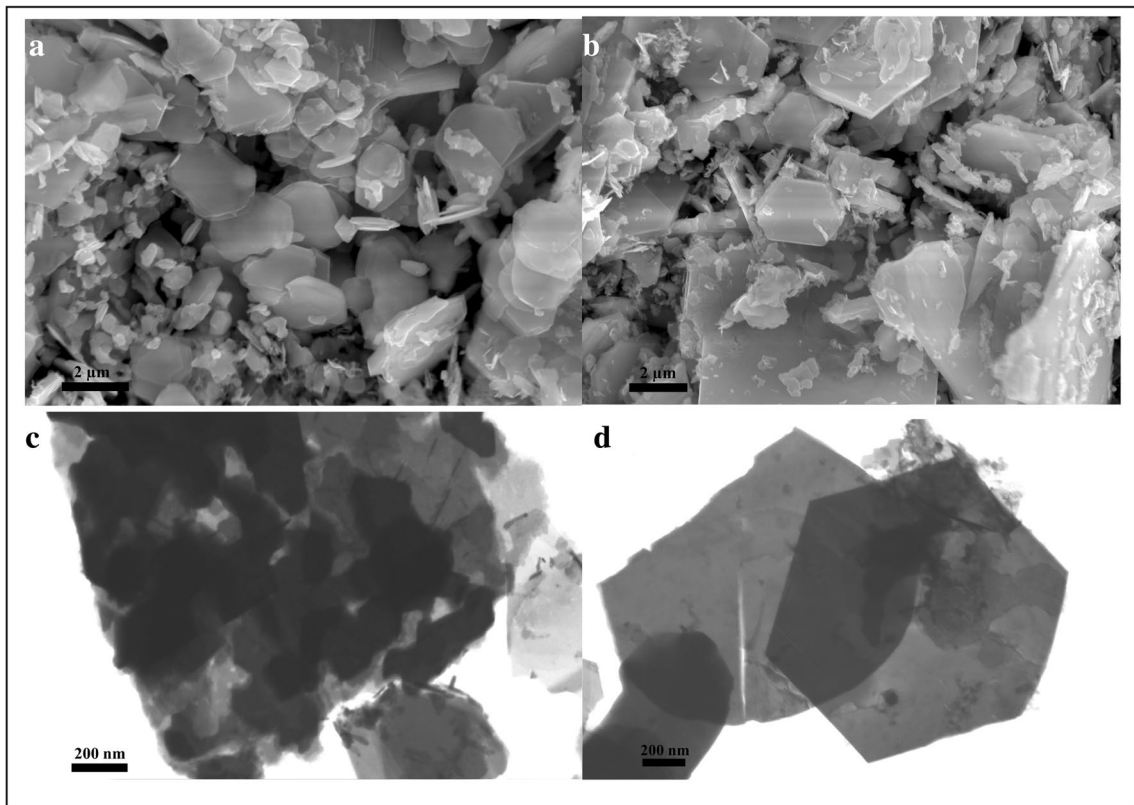


Fig. 1 **a, b** SEM and **c, d** TEM images of $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$

appearance is due to stacking of materials due to their 2D morphology. The presence of space in material provides a channel for electrolyte to go inside and develop short distance interaction with active materials which resulted in high performance. The morphological data confirmed the space in between the nanobelts for its high surface area and activity. The irregularity in the appearance and at the edge of nanobelts is further confirm and is a reaction for

high response of the materials. The EDX data (Fig. 2a) shows that materials only consist of Se and Cu which is corresponding to XRD data.

However, it is very important to determine the composition of materials, purity, and crystal structure of the material. In this regard, X-Ray diffractometer (XRD) (Aeris 1.2.0 (PAN analytical) diffractometer with Cu radiation and PIXcel 1D detector) was used to determine crystal phases of

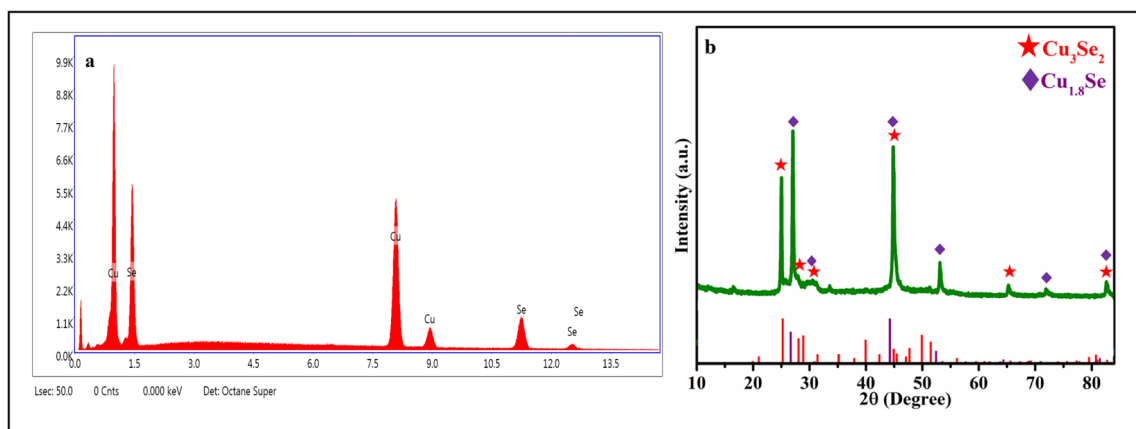


Fig. 2 **a** EDX and **b** XRD data of $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$

the sample. XRD (Fig. 2b) data confirmed that the material is a composite composed of two different phase of copper selenides. The most prominent peaks at 2θ degree of 27.06° , 30.99° , 44.83° , 53.06° , 65.24° , 71.89° , and 82.55° are corresponding to fringes value of (111), (200), (220), (311), (400), (331), and (422) are very well-match with cubic unit cell of $\text{Cu}_{1.8}\text{Se}$ according to ICDD # 71-0044. The other peaks at 2θ degree of 25.07° , 27.25° , 31.12° , 44.83° , 65.32° , and 82.73° are corresponded to fringes value of (101), (200), (210), (310), (331), and (313) are well matched with tetragonal unit cell of Cu_3Se_2 according ICDD # 47-1745. There are some other very small peaks in the XRD graph with low intensity that are also well match with other fringes of value Cu_3Se_2 . The data confirmed that material is highly crystalline and single phase with high purity.

MOR application

The GCE modified with $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$ an electrocatalyst was studied in 1 M KOH solution without methanol via CV at scan rate of 50 mV/s. The CV shows in Fig. 3a confirmed

an oxidation peak at 0.48 V (vs Ag/AgCl), for the oxidation of copper to higher state and this oxidation is favorable for MOR. Similarly, a reduction peak can be seen at about 0.37 V for conversion of copper to original state of the materials. When methanol 0.25 M was added to solution under same condition, the oxidation peak immediately followed by MOR and get increased to higher current density. The peak shifts to a higher current density and potential which confirmed that the material is active for MOR and provides excellent response. It is worth-noting that the current density in oxidation reaction of MOR is high at 0.65 V and makes a peak slightly broad, which confirmed partial oxidation of methanol during the reaction. However, as the reduction reaction proceeds, the peak again increased at 0.65 V and the graph became inverted as studied previously [15]. This inverted behavior and high current density in reduction direction can be attributed to oxidation of intermediates formed during oxidation. The system gave optimized response in 0.5 M methanol to deliver a current density of 7.12 mA/mg at a potential of 0.65 V (vs Ag/AgCl) at the scan rate of 50 mV/s. Because, as the concentration further increases to 0.75 M of

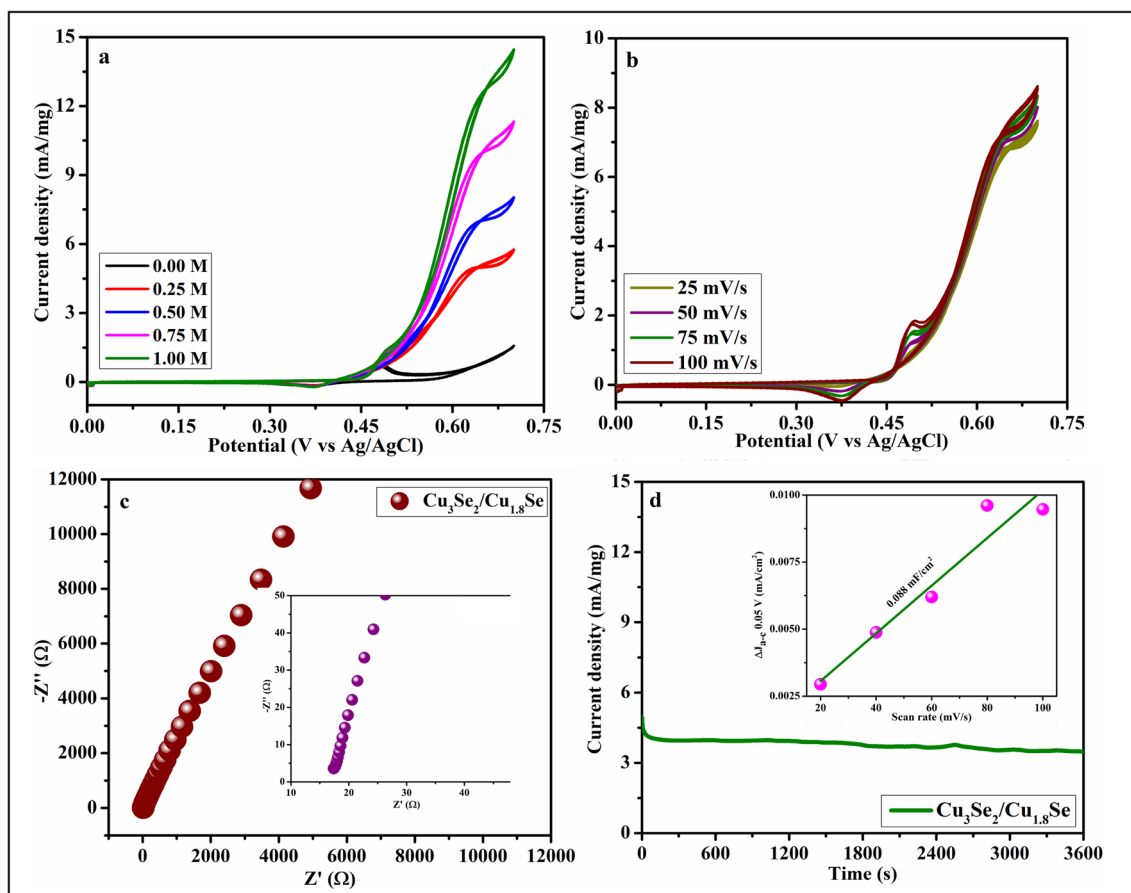


Fig. 3 CV cycles for MOR application in **a** 1 M KOH, 0.25–1M methanol at scan rate of 50 mV/s, **b** effect of scan rate in 1 M KOH and 0.75 M methanol, **c** EIS (inset EIS at high frequency) of $\text{Cu}_3\text{Se}_2/\text{Cu}_{1.8}\text{Se}$ electrocatalyst, **d** chronoamperometry test for stability of 3600s, (inset ECSA)

Table 1 Comparison of active materials for MOR

S. no.	Catalysts	Overpotential	Current density	Ref.
1	Ni/P(1,5-DAN)/MCPE	0.68 V vs Ag/AgCl	1.4 mA/cm ²	[16]
2	Pt/Pani/Pt	0.62 V vs SCE	5 mA/cm ²	[17]
3	Pt–Ru/C	0.9 V vs RHE	7.2 mA/cm ²	[18]
4	Cu/P(2ADPA)/MCPE	0.85 V vs Ag/AgCl	46 mA/cm ²	[19]
5	PtNiPb/WC	0.85 V vs RHE	2.67 mA/cm ²	[20]
6	Pt/Ni–WC	0.4 V vs Ag/AgCl	0.51 mA/cm ²	[21]
7	CuCo ₂ Se ₄	250 mV vs RHE	15 mA/cm ²	[22]
8	CuCoSe–HNCs	1.1 V vs RHE	10 mA/cm ²	[23]
9	10Pt/Ni–MoC _x /C	0.9 V vs RHE	260.5 mA/mg	[24]
10	Cu ₃ Se ₂ /Cu _{1.8} Se	0.65 V vs Ag/AgCl	7.12 mA/mg	This work

methanol, the peak corresponded to oxidation of methanol and intermediate decreases and become completely flatted in 1 M methanol, which demonstrates that in such a high concentration, incomplete oxidation occur and produce intermediates as pollutants. In this regard, it is important to avoid the formation of intermediate pollutant, it is necessary to follow the reaction condition where it gives high current density as energy so that minimum pollutants are produce. Thus, the optimize concentration (1 M KOH, 0.5 M methanol) was further studied with scan rate of 25–100 mV/s to determine the optimized scan rate for the reaction. In scan rate study, it is also observed that at the scan rate of 25 and 50 mV/s, the oxidation is immediately followed by MOR and delivered good response for the reaction. In reduction reaction the current signal inverted as discuss above in order to oxidize the remaining intermediates. However, at high scan rate like 75 and 100 mV/s, the oxidation peak became disappeared which might be attributed to incomplete oxidation due to fast reaction rate. With the increase of scan rate, the current increase which confirmed that the reaction is completely electrochemical and depended on potential and no side reaction takes place. EIS was collected in 1 M KOH, 0.5 M methanol at frequency range of 0.1–10⁵ Hz, 5 mV amplitude, and open circuit potential to determine charge transfer resistance (R_{ct}).

The negligible semi-circle (Fig. 3c inset) at high-frequency range determined its low R_{ct} value which favors its high performance. Almost horizontal response (Fig. 3c) of EIS in low-frequency range determined its high capacitance. The low R_{ct} value is due to its morphology where the large surface area and the presence of pores in between the nanobelt facilitates the transport of target materials (methanol) for reaction and reduce the resistance. Additionally, the irregular shape and edge of the materials also provide high number of active spots for the reaction and fast adsorption/desorption, which also reduces resistance and facilitate the reaction for high performance. Similarly, the high capacitive behavior is also related to its 2D appearance. Stability is the basic requirement for any

efficient electrocatalyst. Cu₃Se₂/Cu_{1.8}Se showed a very promising stability with negligible change in current density for continue 3600 s in electrolyte of 1 M KOH and 0.5 M methanol at potential of 0.65 V (vs Ag/AgCl) as shown in Fig. 3d. ECSA was collected in 1 M KOH and 0.5 M methanol from the CV in non-faradaic region (0.0–0.1 V vs Ag/AgCl) at scan rate of 20–100 mV/s. ECSA value is obtained from double layer capacitance calculation, when current density difference of anodic and cathodic reaction is plotted against scan rate. Half of the slop is equal to ECSA value which is equal to 0.088 mF/cm² (Fig. 3d inset). The high value of ECSA can be attributed to its flatted morphology which provides large surface area, and the edge of thin materials further improves the number of active spots. The excellency of this material in comparison with other materials is shown in Table 1.

Conclusion

Cu₃Se₂/Cu_{1.8}Se electrocatalyst was developed via single-step solvothermal method. DETA act as reaction medium and structure directing agent and as result nanobelt Cu₃Se₂/Cu_{1.8}Se are developed with mostly hexagonal appearance. The spectroscopic characterization of catalyst confirmed single phase, high purity, and crystallinity. The electrocatalyst showed optimized MOR response in 1 M KOH and 0.5 M methanol at scan rate of 50 mV/s. In optimized condition of electrolyte and scan rate, the catalyst delivered a current density 7.12 mA/mg at potential of 0.65 V (vs Ag/AgCl). The catalyst exhibited low R_{ct} and high ECSA (0.088 mF/cm²) with good stability for 3600 s.

Author contribution N. U.: supervision, conceptualization, writing—original draft, investigation. S. C.: investigation. D. G.: supervision, writing—review and editing, resources. S. K.: review and editing. S. H.: formal analysis, methodology, supervision. M. M.: investigation.

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Data availability Data is available on request.

Declarations

Ethical approval Not applicable.

Competing interests The authors declare no competing interests.

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References

- Gao H, Cao Y, Chen Y, Lai X, Ding S, Tu J, Qi J (2018) Au nanoparticle-decorated NiCo₂O₄ nanoflower with enhanced electrocatalytic activity toward methanol oxidation. *J Alloys Compd* 732:460–469
- Gu L, Qian L, Lei Y, Wang Y, Li J, Yuan H, Xiao D (2014) Microwave-assisted synthesis of nanosphere-like NiCo₂O₄ consisting of porous nanosheets and its application in electro-catalytic oxidation of methanol. *J Power Sources* 261:317–323
- Zuo Y, Sheng W, Tao W, Li Z (2022) Direct methanol fuel cells system—a review of dual-role electrocatalysts for oxygen reduction and methanol oxidation. *J Mater Sci Technol* 114:29–41
- Borghei M, Lehtonen J, Liu L, Rojas OJ (2018) Advanced biomass-derived electrocatalysts for the oxygen reduction reaction. *Adv Mater* 30:1703691
- Ren X, Wilson MS, Gottesfeld S (1996) High performance direct methanol polymer electrolyte fuel cells. *J Electrochem Soc* 143:L12
- Hsieh M-W, Whang T-J (2013) Electrodeposition of PdCu alloy and its application in methanol electro-oxidation. *Appl Surf Sci* 270:252–259
- Peng H, Ren J, Wang Y, Xiong Y, Wang Q, Li Q, Zhao X, Zhan L, Zheng L, Tang Y, Lei Y (2021) One-stone, two birds: alloying effect and surface defects induced by Pt on Cu₂-xSe nanowires to boost C-C bond cleavage for electrocatalytic ethanol oxidation. *Nano Energy* 88:106307
- Fang H, Yang J, Wen M, Wu Q (2018) Nanoalloy materials for chemical catalysis. *Adv Mater* 30:1705698
- Hassan D, El-Safty S, Khalil KA, Dewidar M, Abu El-Maged G (2016) Mesoporous carbon/Co₃O₄ hybrid as efficient electrode for methanol electrooxidation in alkaline conditions. *Int J Electrochem Sci* 11:8374–8390
- Huang W, Wang H, Zhou J, Wang J, Duchesne PN, Muir D, Zhang P, Han N, Zhao F, Zeng M (2015) Highly active and durable methanol oxidation electrocatalyst based on the synergy of platinum–nickel hydroxide–graphene. *Nat Commun* 6:1–8
- Luo Q, Peng M, Sun X, Asiri AM (2015) In situ growth of nickel selenide nanowire arrays on nickel foil for methanol electro-oxidation in alkaline media. *RSC Adv* 5:87051–87054
- Kim U, Mun J, Koo D, Seo J, Choi Y, Lee G, Park H (2022) Catalytic centers with multiple oxidation states: a strategy for breaking the overpotential ceiling from the linear scaling relation in oxygen evolution. *J Mater Chem A* 10:23079–23086
- Ali Z, Asif M, Zhang T, Huang X, Hou Y (2019) General approach to produce nanostructured binary transition metal selenides as high-performance sodium ion battery anodes. *Small* 15:1901995
- Shi Y, Li H, Ao D, Chang Y, Xu A, Jia M, Jia J (2021) 3D nickel diselenide architecture on nitrogen-doped carbon as a highly efficient electrode for the electrooxidation of methanol and urea. *J Alloys Compd* 885:160919
- Ullah N, Xie M, Oluigbo CJ, Xu Y, Xie J, Rasheed HU, Zhang M (2019) Nickel and cobalt in situ grown in 3-dimensional hierarchical porous graphene for effective methanol electro-oxidation reaction. *J Electroanal Chem* 838:7–15
- Ojani R, Raouf J-B, Zavvarmahalleh SRH (2008) Electrocatalytic oxidation of methanol on carbon paste electrode modified by nickel ions dispersed into poly (1, 5-diaminonaphthalene) film. *Electrochim Acta* 53:2402–2407
- Niu L, Li Q, Wei F, Wu S, Liu P, Cao X (2005) Electrocatalytic behavior of Pt-modified polyaniline electrode for methanol oxidation: effect of Pt deposition modes. *J Electroanal Chem* 578:331–337
- Wang Z, Yin G, Zhang J, Sun Y, Shi P (2006) Co-catalytic effect of Ni in the methanol electro-oxidation on Pt–Ru/C catalyst for direct methanol fuel cell. *Electrochim Acta* 51:5691–5697
- Ojani R, Raouf J-B, Ahmady-Khanghah Y (2011) Copper-poly (2-aminodiphenylamine) as a novel and low cost electrocatalyst for electrocatalytic oxidation of methanol in alkaline solution. *Electrochim Acta* 56:3380–3386
- Wang Z-B, Zuo P-J, Liu B-S, Yin G-P, Shi P-F (2009) Stable PtNiPb/WC catalyst for direct methanol fuel cells. *Electrochem Solid-State Lett* 12:A13
- Wang Y, Su J, Dong L, Zhao P, Zhang Y, Wang W, Jia S, Zang J (2017) Platinum supported on a hybrid of nickel and tungsten carbide on new-diamond electrocatalyst for methanol oxidation and oxygen reduction reactions. *ChemCatChem* 9:3982–3988
- Saxena A, Kapila S, Medvedeva JE, Nath M (2023) Copper cobalt selenide as a bifunctional electrocatalyst for the selective reduction of CO₂ to carbon-rich products and alcohol oxidation. *ACS Appl Mater Interfaces* 15:14433–14446
- Zhao B, Liu J, Xu C, Feng R, Sui P, Luo J-X, Wang L, Zhang J, Luo J-L, Fu X-Z (2021) Interfacial engineering of Cu₂Se/Co₃Se₄ multivalent hetero-nanocrystals for energy-efficient electrocatalytic co-generation of value-added chemicals and hydrogen. *Appl Catalysis B: Environ* 285:119800
- Zhang Y, Zang J, Jia S, Tian P, Han C, Wang Y (2017) Low content of Pt supported on Ni–MoC_x/carbon black as a highly durable and active electrocatalyst for methanol oxidation, oxygen reduction and hydrogen evolution reactions in acidic condition. *Appl Surf Sci* 412:327–334

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