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Supporting Information

Composite electrodes with superior catalytic activity in methanol electro-oxidation process fabricated using ternary NiO-CuO-ZnO mixed metal oxides

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Table S1: Previously reported synthesis methods and applications of binary mixed metal oxide

Binary Oxides	Preparation Method	Precursor Materials	Applications	References
NiO-CuO	Sol-gel	Cu (CH_3COO). H_2O, CH_3OH, $NiCl_2$, C_2H_5OH, NaOH, butyl carbitol acetate (BCA), ethyl cellulose (EC)	Thick film sensor for the acute detection of hydrogen sulfide gas vapors	1
NiO/CuO	Hydrothermal method	CuO, diH_2O, Ni $(NO_3)_2$, NH_4F, Co $(NH_2)_2$	Use in supercapacitors	2
CuO/NiO	Biogenic synthesis	Azardica indica leaf extract, Ni $(NO_2)_3$.6H_2O, Cu $(NO_2)_3$.6H_2O	Degraded two hazardous water pollutants methylene blue and eosin yellow	3
NiO/CuO	Sol-gel	$CuSO_4 \cdot 5H_2O$, $NiSO_4$.6H_2O, NaOH, acetic acid glacial, Stock solution of Ho, Yb, and Sm	Efficient absorbent for rare earth elements (Ho, Yb, and Sm) from aqueous solutions	4

CuO-NiO	Facile wet-chemical method	Cu $(CH_3COO)_2 \cdot H_2O$ Ni $(CH_3COO)_2 \cdot 4H_2O$ diH_2O, glycol ($C_2H_6O_2$), ammonia water (25%) ($NH_3 \cdot H_2O$), NaOH, CuO or Ni $(OH)_2$	anode materials for lithium-ion batteries (LIBs)	5
CuO-ZnO	Hydrothermal technique	Alchornea cordifolia leaves, Zn $(CH_3COO)_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, Hela cells.	Use as an anticancer by generating reactive oxygen species capable of hampering the multiplication of tumor cells by apoptosis	6
CuO/ZnO	Green Biosynthesis	$Cu(CH_3COO)_2.H_2O$, Zn $(CH_3COO)_2.2H_2O$, MB ($C_{16}H_{18}ClN_3S$), *Penicillium corylophilum,* potato dextrose	Degradation of organic methylene blue dye	7
CuO/ZnO	co-precipitation method	$CuCl_2.2H_2O$, $ZnCl_2.2H_2O$, diH_2O, NaOH, absolute ethanol	Antifungal activity greater inhibition of strain Aspergillus flavus Trichoderma compared to respective mono oxides	8
ZnO/CuO	sol-gel	Zn $(NO_3)_2.6H_2O$, Cu $(NO_3)_2.3H_2O$, polyvinyl alcohol (PVA), absolute ethanol, diH_2O	photodegradation of methylene blue (MB) increased three times	9
ZnO-CuO	simple chemical co-precipitation method	$ZnCl_2$, $CuCl_2$, CTAB, NaOH, dH_2O	The superior antibacterial activity of binary oxide nanocomposite is attributed to oxidative stress generated by the electron transfer pathway and reactive oxygen species (ROS) generation.	10
ZnO/CuO	co-precipitation method	Zn $(CH_3CHOO)_2.2H_2O$, NaOH, Cu $(CH_3CHOO)_2.2H_2O$, water, water/monohydric alcohol (ethanol),	Use in coupled semiconductors	11

		water/dihydric alcohol (ethane-1, 2-diol)		
ZnO/CuO	hydrothermal method.	zinc acetate and copper nitrate, deionized water as a solvent, hexamethylenetetramine (HMT) as an alkali source	Magnetic measurements showed composites possessed room-temperature ferromagnetism with the increase of CuO content in the composites. ZnO/CuO displayed the coexistence of ferromagnetism and para-magnetism.	[12]
ZnO-NiO	Sol-gel and spin-coating methods	Zn $(CH_3COO)_2{\cdot}2H_2O$, 2-methoxy ethanol ($C_3H_8O_2$), diethanolamine (MEA), nickel acetate tetrahydrate ($C_4H_6NiO_4{\cdot}4H_2O$), 2-methoxy ethanol ($C_3H_8O_2$)	Gas detection, UV detectors, photodiodes	[13]
NiO-ZnO	co-precipitation/co-gel formation	KOH, $H_2C_2O_4$, Na_2CO_3, Ni $(NO_3)_2{\cdot}6H_2O$, Zn $(NO_3)_2{\cdot}6H_2O$, H_2O	maximum activity for the decolorization of both the dyes and the decolorization rate of methylene blue and methyl orange	[14]
NiO/ZnO	Hydrothermal synthesis	Zn $(NO_3)_2{\cdot}6H_2O$, Ni $(NO_3)_2{\cdot}6H_2O$, urea ($CO(NH_2)_2$), KOH	electrode material for supercapacitors with the highest specific capacitance	[15]
NiO-ZnO	chemical co-precipitation	$Zn(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, NaOH, diH_2O,ethanol	bactericidal agents against pathogenic bacterial species	[16]
NiO/ZnO	aqueous chemical growth method	Nickel acetate tetrahydrate, methanol, zinc acetate dihydrate, ethanol, boric acid, sodium dihydrogen phosphate, NaCl, KCl, stock solution of CBZ, Britton-Robinson buffer (BRB)	electrochemical sensor in different pharmaceutical formulations with acceptable percent recoveries	[17]

ZnO-NiO	Homogeneous precipitation	$Zn(NO_3)_2.6H_2O$,$Ni(NO_3)_2.6H_2O$, SDS, HMT, dH_2O, NaOH	nanocomposites provide an opportunity for band tuning for better functional performance for device fabrication compared to the basic metal oxides	18

Table S2: Previously reported synthesis methods and applications of ternary mixed metal oxide

Ternary Oxides	Preparation Method	Precursor Materials	Applications	References
NiO/CuO/ZnO	Hydrothermal	Zn $(CH_3COO)_2{\cdot}2H_2O$, $NiSO_4{\cdot}6H_2O$, Cu $(NO_3)_2$	photovoltaic use	19
NiO/CuO/ZnO	Co-precipitation & hydrothermal	$CuCl_2.2H_2O$, $ZnCl_2$, $NiCl_2.6H_2O$	Use in semiconducting devices	20
CuO-NiO-ZnO	Co-precipitation	Zn $(NO_3)_2.6H_2O$, Ni $(NO_3)_2.6H_2O$, $CuCl_2.2H_2O$	sensor, photonic, and optoelectronic applications	21
CuO-NiO-ZnO	Green synthesis	Aqueous leaf extract of the Rheum ribes	Catalytic activity and selectivity	22
ZnO-NiO-CuO	Gel combustion process	Zn $(NO_3)_2.6H_2O$, Ni $(NO_3)_2.6H_2O$, Cu $(NO_3)_2.6H_2O$	Electrode synthesis	23
ZnO-NiO/graphene	hydrothermal synthesis	GO, $Zn(Ac)_2{\cdot}2H_2O$, $Ni(Ac)_2{\cdot}4H_2O$,glycine, NH_4HCO_3	anode materials for lithium-ion battery	24
CuO–MnO–$2TiO_2$	Aerosol-assisted chemical vapor deposition (AACVD) method	Cu (CH3COO) 2.H2O, Mn (CH3COO)2, Ti(O(CH2)3CH3)4, trifluoroacetic acid	photoelectrochemical studies	25

		(TFA).		
$Co_3O_4/NiO/MnO_2$	hydrothermal & precipitation	$CoCl_2 \cdot 6H_2O$, NaCl, HMT, ethanol, $KMnO_4$, HCl	Decrease resistance and enhance capacitance	26
CuPtPd (Dentritic)	Directly reducing metal ions	Metals	electrocatalytic & anti-poisoning activity towards the oxidation of methanol	27
CuO-ZnO/rGO	Precipitation	H_2SO_4, graphite flakes, H_3PO_4, $KMnO_4$, HCl, H_2O_2, NaOH, & ammonia solution, (Zn $(NO_3)_2.6H_2O$, Cu $(NO_3)_2.3H_2O$	NO_2 gas sensors	28
CuO/Co_3O_4-CeO_2	Co-precipitation	$Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, Co_3O_4-CeO_2	enhance the H_2 Oxidation	29
Au-Cu-Pt	Electrodeposition	$HAuCl_4$, H_2PtCl_6 CH_3OH, H_2SO_4, $CuSO_4$	Methanol fuel cell (DMFC)	30
$Cu_2O/ZnO/Ag_3PO_4$	Co-precipitation	$CuCl_2.2H_2O$, NaOH, (Ag_3PO_4), $Na_2HPO_4.12H_2O$, $ZnSO_4.7H_2O$	Enhance photocatalytic activity	31
Pt-ZnO-Bi_2O_3	Hydrothermal Method	Bi $(NO_3)_3.5H_2O$, $Zn(CH_3COO)_2.6H_2O$, Glycerol	Anode-catalytic oxidation of methanol in alkali	32
CuO-SnO_2-ZnO	RF magnetron sputtering technique	pure CuO, SnO_2 & ZnO powders, polyvinyl alcohol,	films used in the detection of NH_3 at room temperature	33

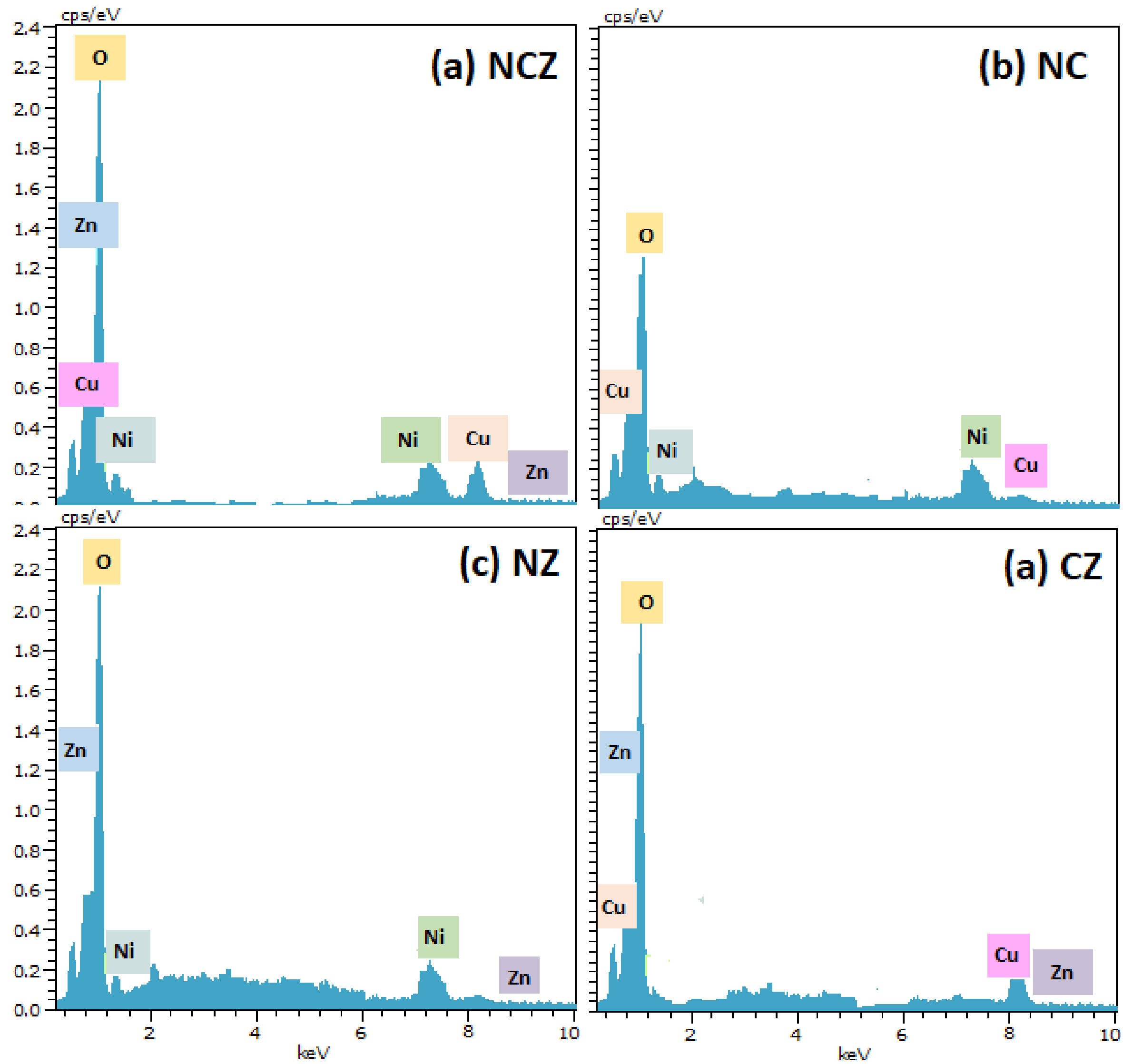


Figure S1: EDX spectra of NCZ, NZ, CZ, and NC mixed metal oxides composites.

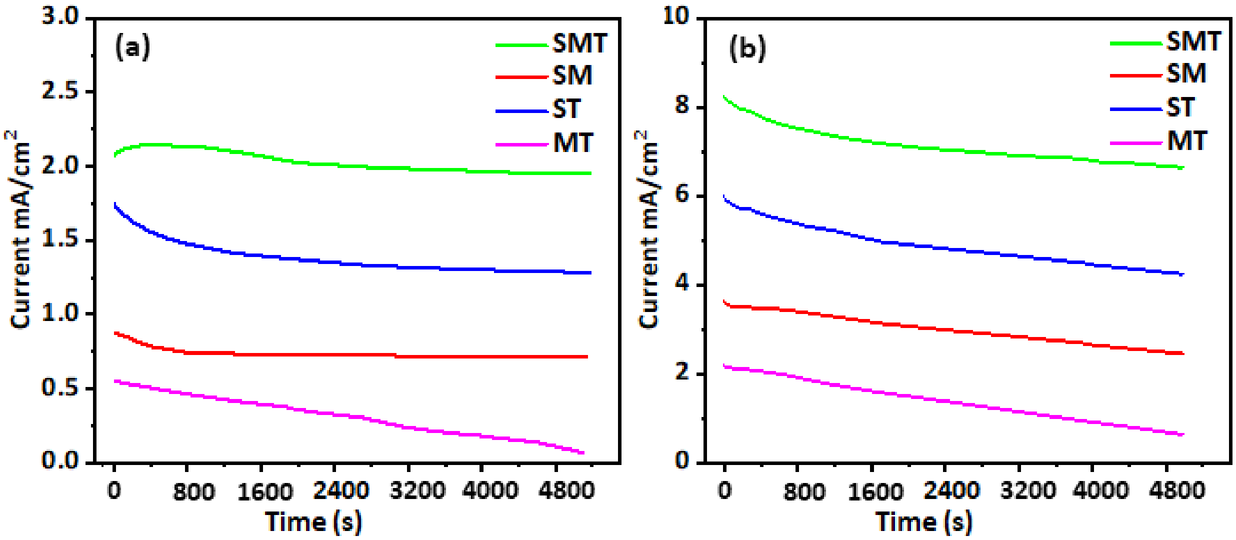
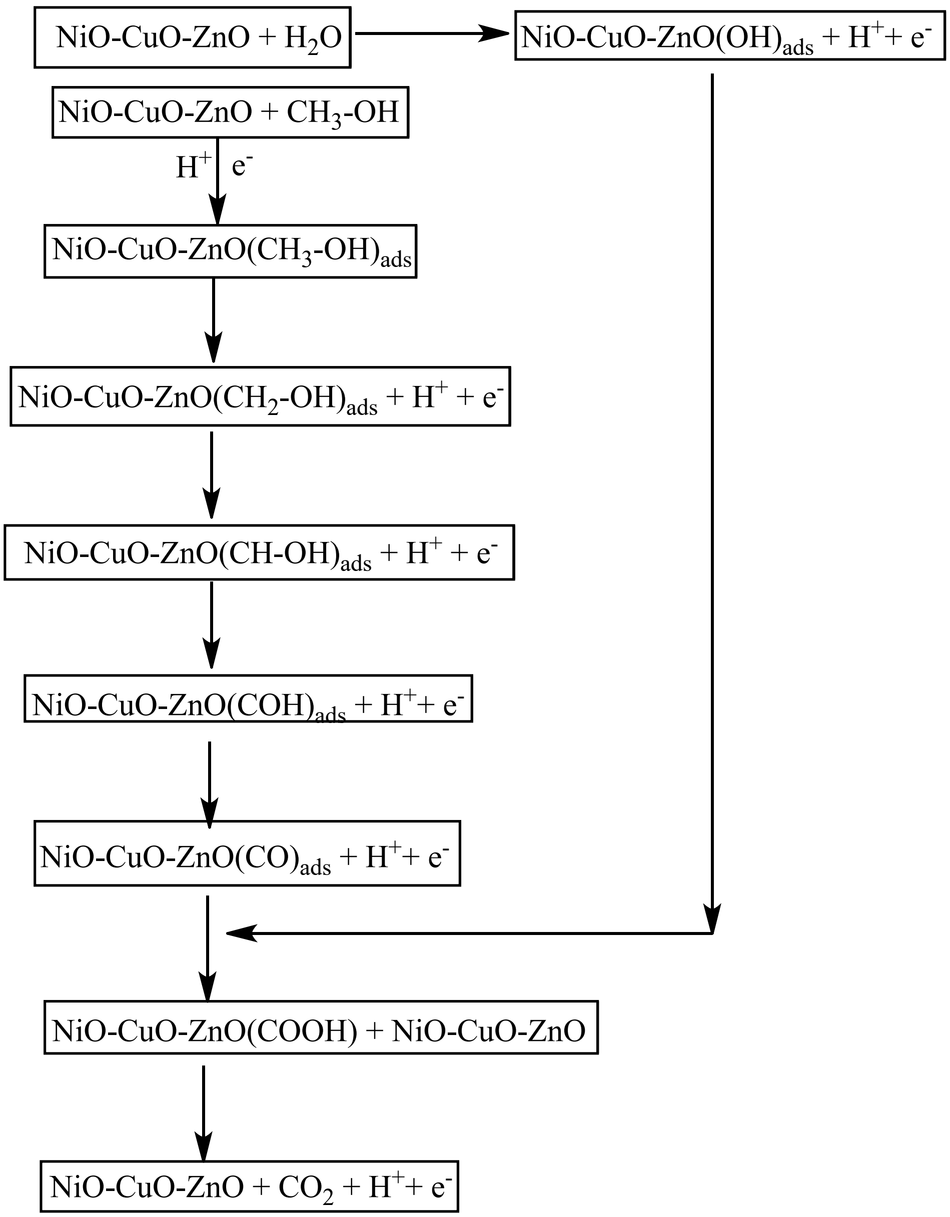


Figure S2: Chronoamperometric plot of Binary and ternary composite electrodes for 80 minutes in (a) acidic and (b) basic medium

Methanol Oxidation Reaction (MOR) mechanism in acidic media



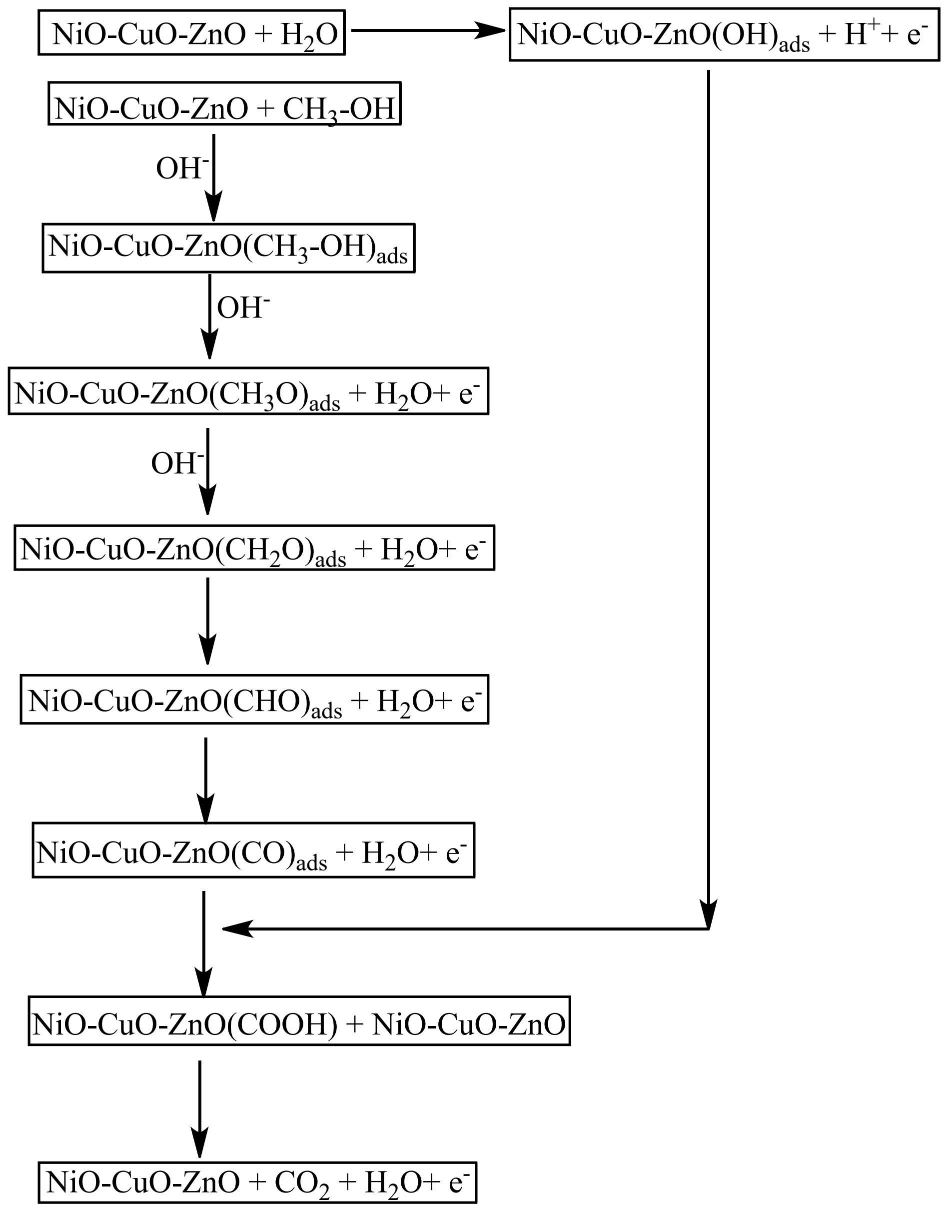
Acidic media

Anode: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $3/2O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

Cell reaction: $CH_3OH + 3/2O_2 \longrightarrow CO_2 + 2H_2O$

Methanol Oxidation Reaction (MOR) mechanism in basic media



Basic media

Anode: $CH_3OH + OH^- \longrightarrow CO_2 + 6e^- + 5H_2O$

Cathode: $3/2O_2 + 6e^- + 3H_2O \longrightarrow 6OH^-$

Cell reaction: $CH_3OH + 3/2O_2 \longrightarrow CO_2 + 2H_2O$

Methanol oxidation reaction (MOR) mechanism[34, 35]

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