Fabrication of NiCu interconnected porous nanostructures for highly selective methanol oxidation coupled with hydrogen evolution reaction

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Abstract

Electrocatalytic water electrolysis is the most promising clean and efficient process for pure and clean generation of hydrogen. However, water oxidation reaction requires a large overpotential owing to its slow kinetics, causing a lower efficiency of hydrogen production and high energy consumption. Herein, we report the bimetallic NiCu interconnected porous nanostructures on copper foil (NiCu@Cu) prepared by hydrogen bubbles templating electrodeposition technique for methanol oxidation reaction (MOR), which replaces the kinetically sluggish water oxidation reaction and enhances the hydrogen production with lower energy input. With their high macroporosity, interconnected growth on copper foil with excellent conductivity and easy flow of electrolyte on electrode interface, and stabilization of active sites due to bimetallic synergistic effects, the NiCu@Cu electrocatalysts exhibit outstanding activities for HER and MOR. The NiCu@Cu requiring just 1.32 V anodic potential vs RHE at 10 mA cm\textsuperscript{-2} overall input voltage for HER and MOR.

Highlights

- The electrochemical properties of 3D bimetallic NiCu@Cu electrodes are investigated.
- The effect of Cl\textsuperscript{-} ions on the electrodeposition of catalysts is explored.
- MOR required 170 mV less potential than OER to attain the same current density.
- NiCu@Cu required only 1.45 V at 10 mA cm\textsuperscript{-2} overall input voltage for HER and MOR.
- The catalyst demonstrated good selectivity for methanol upgrading to yield formate.
Methanol-assisted hydrogen production
Energy-saving hydrogen production

Introduction

It is of vital importance to move from fossil fuels to renewable energy resources to address the rising problems of environmental pollution and severe climatic changes [1]. Electro-catalytic water splitting is a promising clean strategy for the pure hydrogen generation [2,3]. Conventional electrolysers for water electrolysis simultaneously generate oxygen at the anode through oxygen evolution reaction (OER) and hydrogen at the cathode through hydrogen evolution reaction (HER) [4,5]. Among the two half-cell reaction, OER has sluggish kinetics and unfavorable thermodynamics owing to multi-step multi-electron process and it impedes the efficiency of overall water electrolysis [6]. Hence, OER has been regarded as the bottleneck restricting the efficiency of hydrogen production in the overall water splitting. Recently researchers have introduced different electronic and structural modulation strategies for the rational design of anode to deliver high output at low input voltage and make it sustainable at high current density [7–9]. However, high thermodynamic barrier for O–O coupling and the structural and chemical instability of anode at high anodic bias retard its commercialization for a large-scale hydrogen production [10]. An attractive strategy in this regard is to replace OER reaction with thermodynamically promising and economically-attractive oxidation reactions [11]. To avoid unfeasible and high OER overpotential, more efficiently oxidizable molecules like alcohols [12], hydrazine [13], urea [14], and 5-hydroxymethylfurural [15] have been employed for electrocatalytic oxidation reaction, replacing OER for achieving cost effective H2 generation. Among rapidly oxidized molecules, methanol is considered as the simplest alcohol which is not only cheaper, but it also has huge production capability [16]. Compared to OER equilibrium potential (1.23 V), the methanol has lower oxidation potential (0.58 V). It is possible to couple HER with the methanol oxidation reaction (MOR) to realize the large-scale production of green hydrogen at lower input voltage.

Pt decorated carbon-based electrocatalysts are still known to be the most efficient, and widely applied to the electro-chemical processes such as MOR, HER and ORR. However, high cost, scarcity, and poor stability are the main bottlenecks which hamper their commercial applications [17–20]. With the advancement of nanomaterials, various non-noble metals including Ni-, Fe-, Co-, Cu-, W-, and Mo-based electrocatalysts have been developed for HER performance as promising alternatives to noble metal-based electrocatalysts [21,22]. Among these, Ni-based electrocatalysts demonstrated the best activity, selectivity, and stability for both HER and MOR in strongly alkaline media at high current densities [23–25]. Bimetallic NiCu-based nanostructures have been reported as excellent electrocatalysts for HER and MOR, but a major issue is that these nanostructures have a low current density and are not durable in alkaline media [26–28]. Low stability in copper-based electrocatalysts is caused by oxidation of Cu in alkaline electrolytes, which causes catalyst degradation. Recently, many efforts have been made to develop the innovative strategies to design cost effective and highly efficient electrodes for MOR. The theoretical and experimental investigations have revealed that metal d orbital energy relative to the Fermi energy level define chemisorption energy of reaction intermediates and is considered as the key factor to control active centers and their reactivity. The intermetallic bond formation alters the coordination chemistry of active sites, modulates the electronic structures due to the overlap of d bands and is considered as the effective approach to modify intrinsic activity of active centers. The partial transfer of electrons occurs towards lower orbital energy, shifting d band center, creating electrophilic active centers, and adsorbing the OH intermediates preferably. In this system, MOR reaction proceeds via plausible ‘bifunctional mechanism, where removal of CO intermediates and oxidation is facilitated by adsorbed hydroxide (OH) species. This assists in creating greater active centers for methanol oxidation at very low overpotential thereby improving the catalytic performance.

In this context, herein we present the development of porous 3D bimetallic NiCu electrode by facile hydrogen bubble templating electrodeposition process. The interconnected porous NiCu electrode showed highly selective methanol oxidation along with hydrogen evolution. More importantly, with anodic methanol oxidation replacing conventional oxygen evolution reaction reaction, potential required at 10 mA cm–2 was negatively shifted by ~170 mV, resulting in reduced consumption of energy to get a similar turn over number of H2. This study revealed the structural and electronic modification of a bimetallic NiCu nanostructure by optimizing the electrodeposition parameters and tuning the electrolytic engineering, resulting in high current density methanol oxidation with high selectivity and durability in alkaline media. The following advantages have been revealed by the NiCu bimetallic interconnected networks: (1) The metallic porous infrastructure with wide nanochannels, interconnected dendrites and macropores with well-designed and decorated nanoparticles offered short diffusion channels, increasing the contact between electrode and electrolyte and thus enabling efficient mass transfer at the electrode/electrolyte interfaces; (2) Cu insertion into Ni framework enhances the electronic conduction because of its distinctive electronic confinement and accelerates the charge transfer kinetics in electrocatalyst pores and at electrode-electrolyte interface; (3) The bubbles templating electrodeposition offers a robust interaction between catalyst and support and sustained the mechanical, structural and chemical
durability of electrocatalyst especially at high current density where huge gases production occurs. Consequently, this work demonstrates selective and specific oxidation of methanol as an attractive alternative anodic reaction in chemical up-gradation and energy-efficient hydrogen evolution reaction.

**Experimental work**

**Materials**

The copper foil was purchased from Alfa Aesar with a thickness of ~0.075 mm (99.999% purity). Nickel sulfate (NiSO₄·6H₂O, 99.99%), copper sulfate (CuSO₄, 99.99%), ethanol (95%), methanol (99.85%), potassium hydroxide (KOH, 90%), hydrochloric acid (HCl, 37%), and sulfuric acid (H₂SO₄, 98%) were purchased from Sigma-Aldrich.

Electrodeposition of Ni, Cu, and NiCu on copper foil

All metal depositions were performed in a three-electrode/single-compartment electrochemical glass cell using Gamry Potentiostat-600. All electrodeposition experiments were accomplished in three-electrode set-up using Cu foil (0.25 cm² working area) (working electrode), Pt wire (counter electrode) and Hg/Hg₂SO₄ (reference electrode), respectively. Before deposition, copper substrates were ultrasonically washed in 3 M aqueous HCl solution for 10 min followed by absolute ethanol and deionized water. Electrodeposition was performed at 2.4 A/cm² constant current density for 200 s at 25 °C in an electrolyte solution of NiSO₄, 6H₂O (0.2 M), CuSO₄ (0.2 M), and H₂SO₄ (1.5 M) with varying concentrations of HCl (0, 0.1 M, 0.5 M and 1 M HCl) and the corresponding samples were labeled as NiCu.a@Cu, NiCu.b1@Cu, NiCu.b2@Cu and NiCu.b3@Cu, respectively. During the synthesis of NiCu@Cu electrocatalysts, the same Ni/Cu (3:1) ratio was used in the electrolyte for electrodeposition of all catalysts.

Characterizations

The surface structure and morphology of catalysts were examined by scanning electron microscope (FEI NOVA FESEM-450, EDX detector). The crystallinity and phase purity of materials were identified with X-Ray diffractometer (Bruker D2 Phaser with Cu Kα radiation). The electronic structure and chemical environment of electrocatalysts were examined by Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) sourced from Mg Kα (1253.6 eV) at 300 W and 117.40 eV transition energy. The spectra were recorded using a 60° take off angle relative to the surface normal. Electrocatalysts surface composition after HER and MOR stability tests were calculated from full spectrum binding energy ranging from 0 to 1000 eV. High resolution scans for Ni, Cu and O were also performed.

Electrochemical measurements

All electrocatalytic activities were measured using Gamry-600 potentiostat with three electrode setup (Hg/HgO and Pt as reference and counter electrodes, respectively) in two types of electrolytic solution (1 M KOH and 1 M KOH + 2 M Methanol). The polarization curves of linear sweep voltammetry (LSV) and cyclic voltammetry (CV) (5 mV/s scan rate) were performed at 0 V to −1.5 V (potential window) for HER and 0 V–1 V vs. Hg/HgO for MOR and OER. Using relevant equation-S1, all potentials measured vs. Hg/HgO were converted to potential vs. RHE. The Rct (charge transfer resistance), of all catalysts was estimated by performing the Electrochemical Impedance Spectroscopy (EIS) in the frequency range of 0.1–100,000 Hz. Chronopotentiometry experiments were performed at contact current density to evaluate the catalyst stability. The measurement of electrochemical active surface area (ECSA) was performed through double layer capacitance by recording the cyclic polarization curve with various scan rates in non-Faradic region. The Faradaic efficiency of cathodic reaction (HER) was calculated using water displacement technique. The Overall methanol oxidation assisted hydrogen evolution and water splitting activities were performed in two electrode setup, by NiCu.b2@Cu electrodes as cathode as well as anode.

**Results and discussion**

Electrodeposition of porous NiCu electrodes

Fig. 1 shows schematic illustration of the fabrication process of dynamic hydrogen bubbles templating electrodeposition for the development of monometallic (Cu@Cu and Ni@Cu) and bimetallic (NiCu.a@Cu, NiCu.b1@Cu, NiCu.b2@Cu and NiCu.b3@Cu), which is a time and energy saving process as compared to the hydrothermal and other traditional calcination methods. During cathodic deposition process, reduction of metal ions occurs generating OH⁻ ions that react immediately with the exposed metal. At the same time, high-rate evolution of hydrogen bubbles occurs from water splitting creating dynamic bubble templates with the electrodeposition of Ni and Cu metals. The detachment of hydrogen molecules occurs automatically from the pores and growing layer, which act as dynamic templates in electrodeposition.

The three dimensional and porous structure of electrocatalyst was characterized using FESEM analysis. The SEM images of monometallic porous Cu@Cu exhibited three-dimensional and porous interconnected infrastructure having pore size in the range of 20–50 μm (Figs. S1a–b). Moreover, the higher magnification SEM images demonstrate that three-dimensional porous infrastructure was also assembled by a large number of metal nanoparticles (Fig. S1c). The monometallic Ni@Cu nanostructure grown under the identical conditions resulted in the formation of a smooth film without any porous metallic framework (Figs. S1d–f).Fig. 2a-c shows SEM images of NiCu.a@Cu (without addition of HCl during synthesis) electrocatalyst indicating that the surface of catalyst exhibits consistent growth of NiCu nanoparticles but do not exhibit the porosity as observed in the case of monometallic porous Cu@Cu catalyst. Recent investigations revealed that the additives have substantial impact on the growth and nucleation of nanostructures and thus play very significant role in defining the shape and critical size of the structures. Among the various additives studied, chloride ions...
Fig. 1 – Schematic illustration for electrodeposition of nanostructured porous NiCu@Cu electrocatalysts by DHBT technique.

Fig. 2 – SEM images of NiCu.a@Cu (a–c) and NiCu.b2@Cu (d–f) samples at different magnifications. Elemental mapping scan profiles of NiCu.b2@Cu electrode (g–j).
have gained more attention as a single additive because of its strong depolarization power. Many reports have demonstrated that chloride ions help in the acceleration of nucleation and controlling the growth process [29]. The addition of HCl (0.1 M, 0.5 M and 1 M) labeled as NiCu.b1@Cu, NiCu.b2@Cu and NiCu.b3@Cu, respectively) in electrolyte bath speeding-up the porous framework growth; hence walls of interconnected infrastructure are filled efficiently with copper sites. Fig. 2d-e shows SEM images of NiCu.b2@Cu (optimized concentration) that exhibit three-dimensional and porous interconnected infrastructures. It can also be observed clearly that the NiCu is assembled by interconnected growth of nanoparticles and nanowires as shown in high resolution SEM image (Fig. 2f).

The EDX spectra of Cu@Cu, Ni@Cu, NiCu.a@Cu and NiCu.b2@Cu electrocatalysts are presented in Figs. S2(a–d). Elemental mapping revealed that Cu and Ni elements are homogeneously distributed across nanowires and nanoparticles (Fig. 2 g-j). The phase purity and crystallinity of the composites was investigated with X-ray diffraction analysis (Fig. 3a and b). Three characteristic diffraction peaks identified at 2θ value of 43.62°, 50.75° and 74.2° correspond to Cu (111), Cu (200) and Cu (220), which indicate the face centered cubic (fcc) structure, while two diffraction peaks at 36.79°, 42.65° and 61.2° correspond to (200), (111) and (220) reflections of crystalline Cu2O [30,31]. NiCu phase separation and formation of two-phase NiCu microstructures was investigated with X-ray diffraction analysis for peaks position comparison.

Initially, the HER activity of as-prepared electrocatalysts was assessed in basic electrolyte using 3-electrodes electrochemical cell. As shown in Fig. 5a, the porous NiCu.b2@Cu electrocatalyst (optimized catalyst with the addition of 0.5 M HCl during synthesis) exhibited improved hydrogen evolution activity and attained the largest current density compared to that of NiCu.a@Cu, Ni@Cu, and Cu@Cu. The 3D porous NiCu.b2@Cu catalyst required a small input voltage of 40 mV to initiate the HER process, which was 8 mV, 94 mV, and 400 mV lower compared to that required by NiCu.a@Cu, Ni@Cu, and Cu@Cu (Fig. 5c). The HER activity comparison of NiCu.b1@Ni, NiCu.b2@Ni, and NiCu.b3@Ni revealed that the optimized NiCu.b2@Cu demonstrated the highest activity when compared to the others (Figs. S3 and 5b). The X-ray photoelectron spectroscopy (XPS) was performed to explore valence state, chemical environment and elemental composition of NiCu.b2@Cu catalyst (Fig. 4). The conventional peaks of Ni, Cu, and O elements are visible in XPS survey scan spectrum (Fig. 4a), which is consistent with EDX results. The Ni core level 2p spectrum shows two spin orbit doublet at binding energy (BE) of 855 eV and 873 eV, which correspond to Ni 2p3/2 and Ni 2p1/2, with two satellite peaks around 862 eV and 880 eV, confirming the presence of Ni2+ state on the surface of the material (Fig. 4b) [34]. The XPS spectra of Cu at its core level shows two spin orbital doublets at BE of 932 eV corresponding to Cu 2p3/2 and 952 eV for Cu 2p1/2 respectively (Fig. 4c). After deconvolution, Cu 2p3/2 exhibits two peaks at 923.2 eV and 933.6 eV, while Cu 2p1/2 exhibits two peaks at 952.1 eV and 953.2 eV, confirming the existence of metallic copper Cu0 and Cu1+ in the form Cu2O [35]. The appearance of smaller satellite shakeup peaks around binding energy of 943 eV and 962 eV further indicate the uniform surface oxidation of Cu nanostructures exposed in air under ambient conditions. The oxygen core level spectrum shows two peaks at binding energy (BE) of 530.6 eV and 531.3 eV, which correspond to lattice oxygen (attached with metals) and adsorbed oxygen (adsorbed water), respectively (Fig. 4d).
electrocatalysts showed very high increment within small potential window due to maximum charge transfer kinetics at the interface of electrolyte and electrode. The Tafel slopes were measured to find the kinetics favorability of electrochemical reaction at different electrodes’ surfaces (Fig. 5d). Tafel slope of NiCu.b2@Cu was calculated to be $143 \text{ mV dec}^{-1}$, which is much lower than that of NiCu.a@Cu ($270 \text{ mV dec}^{-1}$) and Cu@Cu ($420 \text{ mV dec}^{-1}$), but comparable with Ni@Cu ($141 \text{ mV dec}^{-1}$) suggesting that the intermetallic bonding between Ni and Cu tunes the electronic properties and structure of active centers, and facilitates active sites with optimum chemisorption energy and reduces the activation barrier for HER. In alkaline solution, HER frequently follows hydrogen adsorption and desorption processes. The calculated Tafel slope value revealed that Volmer reaction is the rate determining step.

The charge transfer kinetics was calculated by electrochemical impedance spectroscopy (EIS). The semicircle diameter indicates that charge transfer resistance ($R_{ct}$) corresponds to resistance at the electrode pores and electrode-electrolyte interfaces. The Nyquist plots were fitted and the equivalent circuit diagrams are given in Figure S4. As described in Fig. 5e, $R_{ct}$ charge transfer resistance of Ni@Cu (25.86 Ω), Cu@Cu (10.57 Ω) and NiCu.a@Cu (7.4 Ω) are greater than that of NiCu.b2@Cu foam (4.0 Ω), indicating enhanced conductivity and faster interfacial electronic transfer of NiCu.b2@Cu during the hydrogen evolution process. To attain intrinsic electrocatalytic activity of electrocatalysts, double layer capacitance ($C_{dl}$) was estimated for the electrocatalyst in non-Faradic region, where the capacitive current and scan rate have direct relation (Fig. S5). As presented in Fig. 5f, the NiCu.b2@Cu exhibits the highest $C_{dl}$ value (11.7 mF cm$^{-2}$; ECSA = 292.5 cm$^2$) among all the catalysts that is attributed to its porous structure. Thus, NiCu.b2@Cu with nanowires/nanoparticles may not only carry large number of active sites but it also assists the electrolyte penetration into interior infrastructure that is beneficial for water splitting.

The durability, mainly at high current density where intense gas generation occurs, is one of the important parameters for practical viability evaluation of any electrocatalyst. The chronopotentiometry (CPE) revealed that the catalyst can sustain high 50 mA cm$^{-2}$ current density for 16 h without noticeable degradation (Fig. 5g). The LSV polarization curve of NiCu.b2@Cu recorded after 16 h stability experiment demonstrated a minor positive shift in the onset which may be due to the irreversible adsorption of intermediates or bubble accumulations (Fig. S6c). To investigate the kinetic favorability and selectivity of the synthesized electrode for HER, Faradaic efficiency was measured via water displacement method. The NiCu.b2@Cu cathode showed the Faradaic
Efficiency of 96.5% (Fig. 5h) demonstrating high selectivity of active sites for HER. The SEM, XPS and XRD analysis was performed to explore the structural, and compositional changes in the catalyst after long-term durability experiment. The SEM images shown in Figs. S6a–b indicate the agglomeration of NPs after long-term HER performance, while the XRD spectrum of post-electrocatalysis is superimposed on the pre-catalysis XRD endorsing that the catalyst maintains the phase structure during the cathodic reaction (Fig. S6d). The XPS spectral analysis after HER performance showed minor positive shift in Ni and Cu binding energies compared to fresh samples demonstrating the surface oxidation of electrocatalyst (Fig. S7) [34]. The existence of new peak of Cu$^{2+}$ and strong satellite peaks in Cu XPS spectrum after long-term HER activity is due to the valence and outgoing electrons interaction that is the characteristics feature of Cu oxides and hydroxides [35]. The intensity of M – O peak in O XPS spectrum rises because of surface oxidation and adsorption of water molecules and hydroxyl species. These findings show the chemical stability of catalyst in these reaction conditions.

Inspired by the remarkable performance of synthesized catalyst as cathode for HER, the electrochemical performance was also evaluated for MOR in concentrated methanol solution (1 M KOH + 2 M methanol). The cyclic polarization curve revealed that the onset potential shifted towards the negative value after methanol addition to basic electrolyte. The NiCu.b2@Cu electrocatalyst demonstrated the best MOR activity and achieved higher current density compared to that of NiCu.a@Cu, Ni@Cu, and Cu@Cu. As shown in Fig. 6a, the porous 3D NiCu.b2@Cu and NiCu.a@Cu catalysts need a small input voltage of 1.31 V to oxidize the methanol, whereas the Ni@Cu and Cu@Cu needed 1.34 V and 1.38 V voltages, respectively, signifying superior MOR catalytic activity of bimetallic NiCu relative to the Ni@Cu and Cu@Cu catalysts. NiCu.b2@Cu needed only 1.32 V of potential to attain 10 mA cm$^{-2}$ current density, while NiCu.a@Cu, Ni@Cu, and
Cu@Cu needed 1.33, 1.37 and 1.43 V respectively (Fig. 6b). At higher current density, NiCu.b2@Cu showed lower oxidation potential for MOR as compared to NiCu.a@Cu. In 1 M KOH electrolyte, oxidation peak at 1.30 V onset vs. RHE is attributed to the oxidation of Ni$^{2+}$ to Ni$^{3+}$ (Fig. 6c and S8a). The oxidation peak of NiCu.b2@Cu is not detected in methanol electrolyte, as shown in Fig. 6a, and current shows a sharp and clear increment after the onset potential for methanol oxidation, suggesting that electrochemically generated intermediates i.e., M-OOH, by M$^{3+}$ cations can act as active sites for oxidation of methanol [36]. Such assumptions are in agreement with the latest reports in which electrocatalysts based on transition metal catalyze the oxidation of smaller molecules like urea and methanol [37,38].

The Tafel slope values were estimated from cyclic polarization curve close to onset potential to probe the reaction kinetics at NiCu surface in 1 M KOH + 2 M methanol. The Tafel slope value of NiCu.b2@Cu is 114 mV dec$^{-1}$, which is lower than that of NiCu.a@Cu (116 mV dec$^{-1}$), Ni@Cu (135 mV dec$^{-1}$), and Cu@Cu (145 mV dec$^{-1}$) (Fig. 6d). The Tafel slope value decreases after methanol addition to the basic electrolyte, suggesting the MOR kinetic is favorable over OER (Fig. S8b). The Nyquist plots for MOR were fitted and the equivalent circuit diagrams are given in Fig. S10. As shown, $R_{ct}$ charge transfer resistance of Ni@Cu (11.28 Ω), Cu@Cu (16.5 Ω) and NiCu.a@Cu (5.8 Ω) are greater than that of NiCu.b2@Cu foam (3.6 Ω), indicating faster interfacial electronic transfer of NiCu.b2@Cu during the methanol oxidation process. The chronopotentiometry results revealed the long-term durability of NiCu.b2@Cu in concentrated methanol solution (Fig. 6e). The XRD and XPS analyses were performed to investigate the compositional changes in NiCu.b2@Cu after long term MOR stability experiment. The XRD spectrum shows the presence of two additional peaks corresponding to copper oxide (CuO) (Fig. S11) [41]. In NiCu-based catalyst alloys, electronic transfer in Ni and Cu tunes the electronic structure of surface atoms, promoting catalytic activity. The XPS results revealed some changes in catalyst nature during methanol oxidation in an alkaline medium (Fig. S12). The Ni 2p$_{3/2}$ exhibits one new peak at the BE of 857.3 eV, while the Cu 2p$_{3/2}$ exhibits additional peak at the BE of 875 eV, suggesting the chemical transformation of Ni$^{2+}$ to Ni$^{3+}$ during the methanol oxidation reaction [42]. The small positive shift in binding energies for both Ni and Cu, existence of Ni$^{3+}$ and Cu$^{2+}$ as well as the strong satellite peaks in the Cu XPS spectrum, are due to the interactive relation of valence and outgoing electrons, which is a feature of significant surface oxidation of NiCu.b2@Cu into oxides and hydroxides [27].

Methanol conversion to the value-added products i.e., formaldehyde and formate is of great commercial interest.
Recent investigations have revealed that the anode selectivity depends on surface and electronic infrastructure of catalyst, and reaction conditions (applied potential, pH of electrolyte etc.). Two intermediates i.e., formaldehyde and formate, can be produced during MOR in basic electrolyte [43]. The CV tests were performed in KOH (1 M) with 1 M formaldehyde solution and 1 M electrolyte KOH with an electrolytic solution of 1 M potassium formate, to maximize oxidation procedure and methanol product on NiCu.b2@Cu electrode (Fig. 6f). Electro-oxidation of formaldehyde is highly active on NiCu.b2@Cu foam, though potassium formate electrooxidation is not, that indicates that intermediate of formaldehyde may further undergo electrocatalytic oxidation at NiCu.b2@Cu foam to form potassium formate, a value-added product, as the only MOR product at NiCu.b2@Cu foam electrode. Thus, we assume that the NiCu.b2@Cu is not able to oxidize methanol completely into CO₂ or CO but its selectivity assists in oxidizing methanol to yield another valuable chemical i.e., formate (equation 1-3).

\[
\text{CH}_3\text{OH} + 5\text{OH}^- \rightarrow \text{HCOO}^- + 4e^- + 4\text{H}_2\text{O} \quad (1)
\]

\[
4\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- + 2\text{H}_2 \quad (2)
\]

\[
\text{CH}_3\text{OH} + \text{OH}^- \rightarrow 2\text{H}_2 + \text{HCOO}^- \quad (3)
\]

Given exceptional performance of NiCu.b2@Cu both for methanol selective oxidation and hydrogen production, it is expected that NiCu.b2@Cu is a bifunctional electrode for instantaneous H₂ production and formate in two electrodes configuration using alkaline environment. As shown in Fig. 7a and b, NiCu.b2@Cu catalyst needs 1.62 V cell voltage at 10 mA cm⁻² for overall water electrolysis, which is comparable performance to the noble metal-free catalysts as reported elsewhere. Importantly, on adding 2 M solution of methanol in basic electrolyte, cell voltages at 10 mA cm⁻² are noticeably lowered to 1.45 V (Fig. 7b), substantially smaller than the previous organic/water electrolysis reports (Table S4). The durability of electrode was also verified in two electrodes co-electrolytic scheme (Fig. 7c). It exhibited good stability in methanol electrolyte at 10 mA cm⁻², with cell voltage remaining nearly constant during co-electrolysis reaction lasting for 18 h. The methanol oxidation reaction of anode doesn’t generate bubbles at all in Fig. 7a, while hydrogen evolution at cathode is substantial, and bubbles are produced. It is also evident that electrodes can simultaneously support the co-electrolytic process of hydrogen generation and selective methanol oxidation into formate.

The detailed electrochemical testing and physical characterization proved the capability of NiCu.b2@Cu as an efficient anode and cathode for HER and methanol oxidation. The outstanding catalytic intrinsic performance, anti-poison capability, and sustainability of NiCu.b2@Cu may be ascribed to these factors. (1) The bubble templating electrodeposition technique in the presence of Cl⁻ additives creates a robust interfacial interaction between electrode and electocatalyst.

Fig. 7 – Optical images of (a) Oxidation of methanol by two electrodes system. Bifunctional activities along with activity parameters in 1 M KOH with and without 2 M methanol (b) LSV and (c) Stability comparison of NiCu.b2@Cu.
ponsible for the high mechanical and structural durability. (2) The electronic engineering of catalyst by intermetallic bonding optimized chemisorption energy and enhanced intrinsic catalytic activity per active site with anti-poison capability. (3) The open channels presented a small channel for the diffusion of ions migration to overcome the mass limitation problem and decrease the activation barrier for MOR.

**Summary**

In summary, we present a scalable and facile bubble templating electrodeposition method for the development of hierarchical porous NiCu nanostructures embedded in Cu foil. By tuning the electrolytic engineering and optimizing the electrodeposition parameters, this work presents the structural and electronic modification of a bimetallic NiCu nanostructure, resulting in high current density methanol oxidation with high selectivity and durability in alkaline media. The experimental investigation revealed that the electronic and surface modulation of catalyst by making an intermetallic bonding and creating the open channels exponentially enhanced the catalytic activity for HER and MOR and sustained the high geometric activity. More significantly, the potential required at 10 mA cm\(^{-2}\) was negatively shifted by about 170 mV when anodic methanol oxidation replaced the traditional oxygen evolution reaction, requiring less energy to achieve the same hydrogen gas. The electrolyzer employing the bifunctional activity of NiCu.b2@Cu for cathodic HER and anodic MOR required a small input voltage of 1.45 V at 10 mA cm\(^{-2}\) with anti-poison ability, which is better than commercial RuO\(_2\)/Pt/C for water electrolysis. The superior electrochemical activity of bimetallic NiCu.b2@Cu electrode is mainly due to a combination of bimetallic synergistic effects, interconnected metallic connection, and high active surface area and enhanced electron transport flow rate at interfacial contact of catalyst-current collector.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2022.08.187.


