Article

A Nickel Coated Copper Substrate as a Hydrogen Evolution Catalyst

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Abstract: Replacing precious metals with low-cost metals is the best solution for large scale production. Copper is known for its excellent conductivity and thermal management applications. When it comes to hydrogen evolution reaction, it is highly unstable, especially in KOH solution. In this paper, we approached a simple method to reduce corrosion and improve the performance by depositing nickel-molybdenum oxide and nickel on copper substrates and the achieved tafel slopes of 115 mV/dec and 117 mV/dec at 10 mA/cm². While at first, molybdenum oxide coated samples showed better performance after 100 cycles of stability tests, the onset potential rapidly changed. Cu-Ni, which was deposited using the electron gun evaporation (e-gun), has shown better performance with 0.28 V at 10 mA/cm² and led to stability after 100 cycles. Our results show that when copper is alloyed with nickel, it acts as a promising hydrogen evolution reaction (HER) catalyst.

Keywords: copper; hydrogen evolution; nickel; coating

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1. Introduction

Water electrolysis is one of the best alternative methods to solve future energy storage problems in green industries [1]. Over the past decade, many alternative materials for hydrogen evolution reaction (HER) have been proposed to replace platinum and gold metals, due to scarcity and high-cost for large scale production. Among the earth-abundant and inexpensive oxides [2,3], sulphides [4,5], selenides [6,7], phosphide [8], carbide-based [9,10] semiconductors have been identified for stable HER. To verify the electrocatalytic performance, a good metal is preferred. Among these, transition metals have raised great interest, due to their vast availability in nature [11]. Moreover, durability-wise, these metals showed better performance in the case of HER.

Copper (Cu) substrate is known to be highly conductive and the best thermal management metal in transition metals [12], but in the case of electrolysis, it is unstable in solution, due to the formation of oxide on the surface [13]. However, researchers try to resolve this problem by alloying with other transition metals for oxygen evolution reactions (OER) and HER electrocatalytic activity [14–16]. Especially when copper has alloyed with nickel, in most cases it has been shown to be more stable and higher electrocatalytic activity, when compared to nickel electrodes [14,17]. This may be due to the synergistic effect of

the change in nickel composition on copper, which can enhance catalytic activity [18,19]. Similar reports have been reported when nickel is alloyed with molybdenum (Mo) metal, which enhances the performance of HER [20–28]. In general, nickel is known to have the best HER, due to hydrogen adsorption energy on its surface, but it suffers from lower resistance during electrolysis. This can be reduced by alloying with other transition metals [29]. In this case, alloying with molybdenum or molybdenum oxide is one of the best choices, due to its higher resistance and more surface area [30,31]. When these ternary Cu-Ni-MoO₃ composite materials are used for HER, it leads to better performance, due to mostly unpaired d-electrons in metals, which can donate electrons and adsorb hydrogen atoms, which is more advantageous for electrocatalytic activity [28].

The preceding reports inspired us to investigate the influence of Ni and Ni-MoO₃ on copper foil, and we present a simple method to reduce fabrication costs by using electron gun evaporation (e-gun), and the prepared samples have shown higher catalytic activity for HER application than OER. In both cases, initially, the Ni-MoO₃ has shown tremendous performance, while in the long run (100 cycles), Cu-Ni has shown better performance with 0.28 V and leads to stability. Our results show that when copper is alloyed with nickel, it acts as a promising HER catalyst and can be applied for electrolysis in large scale production.

2. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the Cu/Ni bi-layer substrate and Cu/Ni/MoO₃ stack. The XRD patterns revealed the polycrystalline nature for all sulfurized films. From the XRD pattern, it is perceived that all the profile peaks were positioned at 43.33, 50.46, and 74.15 degrees and were indexed with Miller indices (1 1 1), (2 0 0), and (2 2 0). All these XRD peaks were well matched with JCPDS: 003-1005 cubic crystal structure of Cu. The lattice parameters $a = b = c = 3.6077$ (Å), $\alpha = \beta = \gamma = 90^\circ$. The average crystallite size was calculated by using Debye-Scherrer's formula, and it was found to be 51.5 and 65 nm for Cu/Ni substrate and Cu/Ni (100 nm)/MoO₃ (50 nm) stack, respectively. From XRD patterns, the Cu/Ni/MoO₃ stack showed a wide peak at 89.20 degrees, which corresponded to the (361) plane of the orthorhombic structure of MoO₃ and closely matched with the JCPDS card num: 005-0507.

Figure 1. XRD peaks of Cu/Ni and Cu/Ni/MoO₃ stack.

The vibrational Raman spectrum of Cu/Ni/MoO₃ stack is shown in Figure 2. This can be clearly observed from the Cu/Ni Raman spectrum, as it consists of the only single strong absorption peak, at 933 cm⁻¹ and it belongs to the B1g symmetry of ν O = Mo stretching vibrational modes [32]. No more absorption peaks were observed in the sample, due to Cu and Ni. The Raman spectrum contracts the XRD spectra, in XRD studies Cu was only presented but remaining coated elements were not identified, but in Raman studies Cu and Ni were not detected. This is due to the Cu and Ni being lower layers and MoO₃ is the upper layer of the thin film.

Figure 2. Raman analysis of MoO₃ thin film.

The chemical composition and valance state of Ni-MoO₃ films on Cu substrates were analyzed using X-ray photoelectron spectroscopy (XPS), through this analysis analyzed the oxidation state of the transition metal ion. The shift of the binding energy, due to relative surface charging, was corrected using the C 1 s level at 284.8 eV as an internal standard (Figure 3a). The XPS spectra of Cu, Ni, Mo, and O elements in the films are shown in Figure 3b–e. Figure 3b shows the Cu 2p_{3/2} and Cu 2p_{1/2} binding energy peaks at 932.7 eV and 953.45 eV [33]. There is no shoulder peak observed in the spectrum, which indicates, Cu is not bonding with oxygen. In the Ni 2p spectrum, (Figure 3c) the peaks at 855.5 eV and 872.1 eV are assigned to Ni 2p_{3/2}, and Ni 2p_{1/2} binding energy levels indicate Ni²⁺. The distinct peaks at 232.68 and 235.88 eV are assigned to 3d_{5/2} and 3d_{3/2} of Mo⁶⁺ (Figure 3d), the spectra of O 1 s region (Figure 3e) shows a peak at 531.2 eV, corresponding to the lattice oxide ions on the surface. In order to check whether the formation oxide takes place on Ni thin film, we check with EDS in Figure 5a and find no evidence of oxidation on nickel film.

Microstructural analysis of Cu, Cu-Ni bi-layer, and Cu/Ni/MoO₃ stacks of prepared layers were analyzed using SEM analysis. Figure 4a,c,e shows a slightly smooth surface view of Cu, Cu-Ni, and Cu/Ni/MoO₃. When this is used for HER, irregularly shaped grains are observed on the substrate surface, due to corrosion, especially in the case of Cu, where it is higher, as shown in Figure 4b. In Figure 4d, the Cu/Ni stack has a lower impact than Cu. While the MoO₃ on the surface of the Cu-Ni substrate has been etched away, due to this layer in Figure 4f, the nickel suffers less damage than other substrates. SEM images clearly show the presence of MoO₃ leads to less damage for the HER application.

Figure 3. (a) Typical wide scan and core level (b) Cu 2p, (c) Ni 2p, (d) Mo 3d, and (e) O 1 s XPS spectra of Cu/Ni/MoO₃ stack.

Figure 5a shows the EDS spectrum of the Cu-Ni bi-layer, which clearly describes the presence of Cu, Ni elements in the layer; no other peaks were observed, due to surface etching of the layer. Figure 5b clearly represents the presence of Cu, Ni, Mo, and Oxygen elements in the Cu/Ni/MoO₃ stack.

In order to check OER, a standard three-electrode system with a Pt counter electrode and Ag/AgCl reference electrodes was used with the Cu, Cu/Ni, and Cu/Ni/MoO₃ as working electrodes. All the linear sweep voltammetry (LSV) was carried out in the potential region of 0–1.75 V vs RHE at a scan rate of 5 mV/sec, as shown in Figure 6. 0.1 M KOH

was used as an electrolyte solution for OER. Ni and MoO₃ were deposited at a deposition rate of 0.2 Å/s by an e-beam evaporation system.

Figure 4. SEM micrographs of Cu, Cu-Ni, and Cu-Ni-MoO₃(a,c,e), before the experiment and (b,d,f) after the experiment.

Figure 5. EDS spectra of (a) Cu-Ni bi-layer substrate and (b) Cu/Ni/MoO₃ stack.

The Cu-Ni-MoO₃ showed the best performance with a potential of 1.37 followed by Cu-Ni with 1.46 V, as shown in Figure 6a. We comparatively check the OER Over potential of all samples at 5 mA/cm². Cu-Ni-MoO₃, Cu-Ni has shown less Tafel slope 73 mV and 126 mV, as shown in Figure 6b but, after a while, Cu-Ni-MoO₃ was affected due to the corrosion and leads to slight stable at 1.44 V. While Cu-Ni is quite opposite to Cu-Ni-MoO₃ sample at beginning it starts with 1.46 V after 100 cycles of stability its onset potential is improved slightly to 1.44 V, as shown in Figure 6c. We expect that nickel, when reacting with electrolytes, may lead to form oxide known to be nickel oxide, which is effectively stable in KOH solution.

Figure 6. OER catalytic performances of three different electrodes in 0.1 M KOH electrolyte (a); Over potential of different electrodes (b); results of OER before and after 100 cycles (c).

As shown in Figure 7a Electrochemical results inform that Cu-Ni-MoO₃ and Cu-Ni are more favourable to HER. The potential at 10 mA/cm² is 0.36 V for Cu-Ni-MoO₃ and 0.41 for Cu-Ni. The acquired Tafel slope values, as shown in Figure 7b, are almost near for both Cu-Ni-MoO₃ and Cu-Ni is 117 mV and 115 mV. We notice after 100 cycles, as shown in Figure 7c. The catalytic activity has been gradually increased in both potential values Cu-Ni-MoO₃, Cu-Ni cases with 0.31 V and 0.28 V. Normally in MoO₃ oxygen vacancies (Vo) create Mo dangling bonds (DB), these generate defects near to conduction band [34,35]. The existence of DB in oxygen inefficient molybdenum oxides makes them highly responsive for HER [36]. Many theoretical reports suggest that surface defects like Vo can lead to emerging of gap states that act as shallow donors in metal oxides which may increase free charge carrier concentration [37,38]. As we deposited the MoO₃, using the e-gun, the probability of formation the of Vo and surface defects was higher; this may be one of the reasons for initial higher performance. As e-gun deposited samples especially in the case of metal oxides are highly corrosive due to the amorphous nature and also lack of strong bonding between Ni-MoO₃ interface. In order to check this, we perform electrical characterization and notice there is no response from Cu-Ni-MoO₃ and conclude the film grown is amorphous. The electrical characterization of the Cu and Cu/Ni was also performed. I-V scans taken from two different samples show the obvious Ohmic behaviour of both Cu and Cu/Ni up to 100 mV. The resistance of Cu and Cu/Ni was measured to be 48.5 Ω and 10.0 Ω, respectively, indicating that the heterostructure of Cu and Ni is more conductive than pristine Cu, as shown in Figure 8. In Table 1, we compared the results with other researchers' results.

Figure 7. HER catalytic performances of three different electrodes in 0.1 M KOH electrolyte (a); Tafel plot of different electrodes (b); results of OER before and after 100 cycles (c).

Figure 8. Electrical characterization of Cu-Ni.

Table 1. Comparison of the HER performance of Cu-Ni with other reports.

Catalyst	Tafel Slope (mV dec ⁻¹)	Reference
NiSe ₂ Nano sheets	184	[39]
Carbon paper/carbon tubes/Co-S	131	[40]
N, P, Co-doped graphene	145	[41]
Cu/Ni/MoO ₃	115	This work

3. Materials and Methods

3.1. Raw Materials and Preparation of Catalysts

Experimental Method: The pure copper substrate is cleaned with acetic acid at 70 °C to remove the residuals on the surface. Nickel is first deposited on copper at 0.2 A⁰/s for about 100 nm, followed by an e-gun deposit of 40–50 nm of molybdenum oxide at room temperature.

Technique: In order to deposit the nickel and molybdenum oxide, we use the ferrotec temescal FC-2800 model e-beam evaporation deposition system (e-gun), which was installed at National Tsing Hua University. We procured nickel pellets and a lump of molybdenum oxide was ordered from Gredmann Company (Taipei, Taiwan). The deposition starts at a high vacuum of 5×10^{-6} mbar at 0.2 A⁰/S. The thickness monitor is based on a quartz crystal oscillator connected to a deposition controller module. The quartz crystal sensor is mounted in such a manner that it is kept close to the substrate with the proper tooling factor. The deposition controller provides the final thickness of the film and also the deposition rate.

3.2. Characterization of Composition and Structure of Catalysts

In order to check the crystalline of prepared samples, X-ray diffraction (XRD) patterns were recorded using the AERIS diffractometer PANalytical, Model AERIS (40 KV, 7.5 mA, Almelo, the Netherlands). The average crystallite size was calculated by using Debye-Scherrer's formula. The chemical states of different elements present in the films were investigated by an X-ray photoelectron spectrometer (XPS, Thermo Scientific, Model: K-ALPHA surface analysis, Waltham, MA, USA). The XPS spectra were recorded in the binding energy range, 0–1300 eV using the Al K α source and calibrated using the C1s line. SEM images and energy-dispersive X-ray spectroscopy (EDS) were found using the field emission scanning electron microscope Joel JSM-6700F (Tokyo, Japan). Micro-Raman spectroscopy (Model: Lab RAM: HR800, Manufacturer: HORIBA Scientific SAS, Palaiseau, France), equipped with a 514 nm laser was used to examine Cu-Ni-MoO₃.

3.3. Electrochemical Measurement

Electrochemical measurements were performed in a three-electrode system using a Bio-Logic VSP potentiostat in a cylindrical cell made of Teflon with an O-ring in the bottom with a working electrode area of 0.264 cm^2 . The Cu, Cu/Ni and Cu/Ni/MoO₃ samples were contacted with double-sided Cu tape (3M) as working electrodes with a platinum wire counter electrode and Ag/AgCl (3M NaCl) reference electrode; 0.1 KOH were used as the electrolyte solution for HER and OER, respectively, during the measurements. All the experiments were conducted without magnetically stirring the solution, as shown in Figure 9. All the potentials were converted to RHE, using the equation given by $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.194$ [42], resulting in a shift of -0.2117 V versus RHE. Note all potentials in linear sweep voltammetry (LSV) were collected after applying 3–5 potential sweeps in order to avoid the redeposition of Pt on the working electrode after several cycles. LSV data was recorded at a scan rate of 5 mV/s for the first few cycles and long-term stability was assessed at an accelerated scan rate of 100 mV/s for 100 times. Cyclic voltammograms of Cu/Ni and Cu/Ni/MoO₃ were acquired at different scan rates of $20\text{--}200\text{ mV/s}$ in the voltage between $-0.2\text{--}0\text{ V}$ (vs RHE), as shown in Supplementary Data Figure S1.

Figure 9. Schematic image of the experiment.

4. Conclusions

In summary, XRD has proved that the average crystallite size of the catalyst produced was found to be 51.5 nm and 65 nm for the Cu/Ni substrate and Cu/Ni (100 nm)/MoO₃ (50 nm) stacks, respectively; the chemical state and composition of elements was recorded using XPS and EDS. Copper substrates are highly corrosive in nature for HER and OER application. Fabrication cost has been reduced by depositing the Ni and Ni-MoO₃ thin film on Cu, using the e-gun method, which is a cost-effective method. The prepared samples have shown higher catalytic activity for HER application than OER. The Ni-MoO₃ has shown tremendous performance, while in the long run (100 cycles) and Cu-Ni have shown better performance with 0.28 V and leads to stability. The copper is alloyed with nickel, acts as a promising HER catalyst, and can be applied for photo-electrolysis in large scale production and reduce the cost.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal12010058/s1>, Figure S1. Cyclic voltammograms at different scan rates in the potential range of $20\text{--}200\text{ mV/s}$ in 0.1 M KOH solution with (a) Cu/Ni and (b) Cu/Ni/MoO₃ (c) measured Capacitive currents.

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