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Advanced Co₃O₄-CuO nano-composite based electrocatalyst for efficient hydrogen evolution reaction in alkaline media

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Abstract

In this study, we incorporate a copper impurity into (Co₃O₄) nanowires precursor that turn them into an active catalyst for the hydrogen evolution reaction in 1M KOH. The XRD and XPS results are in good agreement and confirmed the formation of Co₃O₄-CuO nano- composite by wet chemical method. To date, the performance of hydrogen evolution reaction in alkaline for the composite catalyst is comparable or superior to cobalt oxide based HER electro-catalysts. The HER catalyst exhibits the lowest Tafel slope of 65 mVdec⁻¹ for the cobalt-based catalysts in alkaline media. A current density of 10 mA/cm² is achieved at a potential of 0.288 V vs reversible hydrogen electrode (RHE). The mixed transition metal oxide Co₃O₄-CuO based HER electro-catalyst is highly stable and durable. The EIS results demonstrates that HER is highly favorable on the Co₃O₄-CuO due to the relatively small charge transfer resistance (173.20 Ohm) and higher capacitance values (1.97mF).

Keywords. Composite metal oxide, electro-catalyst, hydrogen evolution reaction

1. Introduction

Hydrogen being a neat and the potential renewable energy resource has been considered as a promising alternative to replace the fossil fuels [1-4]. The electrochemical water splitting into hydrogen and oxygen in an electrolyzer is the most exciting technology to produce high purity molecular hydrogen [5-10]. Despite the advantageous features of water electrolysis for hydrogen production, still, it is limited by the poor performance of non-precious catalysts and high scarcity of the noble catalysts [2, 11]. To date, platinum (Pt) is only up to the mark catalyst for the hydrogen evolution reaction (HER), but its high cost and low abundance do not allow it for the widespread applications [13]. To replace Pt, transition metal-based compounds including metal sulfides [13-18], selenides [19,20], phosphides [21-23], nitrides [24,25], carbides [26,27], oxides [28], and metal alloys [29,30] have been employed due to their low cost and earth abundant nature. Also, different recent works on the hydrogen production are reported recently [31-36]. Moreover, the industrial catalysts such as nickel (Ni) and stainless steel are also frequently used as water reduction and oxidation in alkaline media [37]. It is proved that nickel is not a perfect HER catalyst because of its high overpotential approximately and large Tafel slope values [37, 38]. Importantly, nickel is carcinogenic substance reported elsewhere. Also, a wide range of active and stable non-noble metal based HER catalysts in alkaline media are reported [39-46]. In order to achieve performance like Pt from non-precious catalysts is still at an early stage since a single nonprecious catalyst is lacking either due to the absence of high activity or stability issues.

Since few decades, transition metal oxides are found promising oxygen evolution reaction OER catalysts in alkaline solution [51]. Recently, transition metal oxides are combined with noble metals to enhance the HER activity in alkaline media. Heterostructured electrocatalyst can be designed at the nano- or micro levels [52-57]. However, pristine transition metal oxides are known as poor catalysts for HER due to their high unsuitable hydrogen adsorption energy. Moreover, perovskite oxide shows a remarkable effectiveness for HER electrocatalyst that is active and stable in alkaline media. The most recent achievements of perovskite oxide for the electrocatalysis enhanced the functionality and provide a possible future research direction for double perovskites [53]. But the metal oxides based on earth abundant materials are of great interest to materialize for large scale and practical applications, thus more investigations are needed to improve their functional properties. In the present research hypothesis, a small incorporation of the copper

concentration into the Co_3O_4 nanowires precursor brought a significant enhancement in the catalytic activity due to the possible decreases in the hydrogen adsorption energy and an enhanced conductivity.

Herein, we report for the first time a new class of composite namely Co_3O_4 -CuO nanostructure exhibiting an excellent HER activity and good stability in alkaline media. The structural and composition characterization are carried out by various analytical techniques such as SEM, EDS, XRD, and XPS. The composite catalyst is mainly composed of Co_3O_4 and CuO and no other impurity is detected. This electro-catalyst achieved a current density of 10 mA/cm^2 at a potential of 0.288V vs RHE in alkaline media.

2. Materials and Methods

Cobalt chloride hexahydrate, copper chloride dihydrate, 20% Pt/C, 85% potassium hydroxide KOH, fluorine-doped tin oxide FTO and urea of 99.5% purity were purchased from Sigma Aldrich Stockholm, Sweden. In a typical synthesis, 2.37 grams of cobalt chloride hexahydrate, 1.20 grams of copper chloride dihydrate and 0.6 grams of urea were dissolved in 100 mL of the deionized water. The solution was stirred for 20 minutes until a homogeneous solution is obtained. Then FTO substrate was sonicated in acetone and washed several times with the deionized water. The cleaned FTO substrates were coated with a colloidal seed solution of cobalt chloride by a dip coating method. The dip coating was done gently and the FTO seed coated substrates were annealed at 130°C for 25 minutes in order to firm binding of seed particles. The seed layered FTO substrates were vertically dipped into the growth solution by exposing the seed-coated FTO facets towards the growth solution. Then samples in the growth solution were covered with the aluminum foil and kept in a preheated electric oven for 5 hours at 90°C . Afterward, the samples were taken out and washed several times with the deionized in order to remove unwanted particles from the surface of the nanostructured material grown on the FTO substrates. The samples were annealed at 500°C for 4 hours in order to convert the hydroxide phase into composite oxide nanostructures. The same method was used for the collection of powder of mixed transition metal oxide nanostructures. Pristine Co_3O_4 nanostructures were also prepared by the same method without the addition of copper salt. The synthesis of pristine CuO nanostructures was carried out by the mixing of copper chloride and urea in 100 mL of the deionized water. The FTO substrate was seeded with CuO nanoparticles and was hanged vertically in the precursor's the solution at 90°C for 5 hours.

Then a black layer on the FTO was found and it indicated the presence of CuO. Likewise, CuO nano-powder was collected by filtration. The morphological features of the nanostructured material were investigated by scanning electron microscopy (SEM) using a Hitachi model H-800 at an accelerating voltage of 3 kV, while Philips powder X-ray diffraction technique was used to determine the crystalline structure, phase, and purity, and energy dispersive spectroscopy (EDS) technique was used for composition analysis of the as-prepared samples. The electrochemical characterization was performed in 1M KOH at room temperature. A catalyst ink of various materials was prepared by dispersing 10 mg powder of each catalyst into 2.5 mL of the deionized water and 0.5 mL of 5% Nafion. Prior to the surface modification, the cleaning of glassy carbon electrode (GCE) was done through polishing with 0.05 μm alumina powder and then rubbed with silica and washed several times with the deionized water. The deposition of 10 μL of the catalyst ink on the clean GCE was done via drop casting method. The modified GCE as working electrode, a platinum wire as a counter electrode and silver-silver chloride (Ag/AgCl) saturated with 3M KCl as a reference electrode was configured into three electrode electrochemical cells. The reference electrode Ag/AgCl was calibrated using 15% hydrogen gas in Argon then bubbled into the 1M KOH electrolyte. The counter Pt electrode and reference electrodes were connected with the two probe multi-meter and potential was recorded. Linear sweep voltammetry and cyclic voltammetry were used to evaluate the catalytic response and durability of the catalyst. The chronopotentiometry was used to investigate the stability of electrocatalyst at a constant current density of 10 mA/cm^2 . Electrochemical impedance spectroscopy was conducted for the investigation of the HER kinetics in a frequency range of 100 kHz to 0.1 Hz at an amplitude of 10 mV and onset potential of -0.3V vs RHE (reversible hydrogen electrode) in 1M KOH electrolyte. All the potentials are reported into RHE without iR drop. All the experiments were performed at room temperature.

3. Results and Discussion

3.1. The structural and compositional characterization of various nanostructured materials

Scanning electron microscopy was employed to explore the morphological features of various nanostructured materials. Figure 1a, b shows the leaf-like features of the CuO nanostructures at different magnifications. The thickness of each leaf is a few hundred nm and they are uniform in distribution on the FTO glass substrate. Figure 1c, d shows the Co_3O_4 nanowires at different

magnifications, the length of each nanowire was few microns, and the average diameter of each nanowire is approximately 200 nm to 500 nm. But the nanowires are not well oriented and randomly distributed on the FTO substrate as clearly seen from Figure 1c, d. Figure 1e, f shows the structural features of composite $\text{Co}_3\text{O}_4\text{-CuO}$ and it exhibited a nanowire like structure. The top surface of the nanowire is very thin and sharp due to the incorporation of copper metal atoms into the cobalt oxide nanowire. The length of the nanowires is several microns and the average diameter is around 100 nm to 300 nm. The SEM results of the mixed transition metal oxide are clearly indicating that the self-assembly of nanoparticles turned into a nanowire morphology. The sharpness of nanowire for the composite material has more surface area which provide more contact area with the electrolyte and thus it accelerates the HER kinetics. The SEM study was carried out on the composite catalyst after stability and durability experiment as shown in S1. It can be seen that composite catalyst has tendency to retain the morphology and a slight top surface of the nanowires is etched due to alkaline nature of the electrolyte. The elemental composition of each sample was investigated by the energy dispersive spectroscopy. The elemental mapping of the pristine CuO and Co_3O_4 was also carried out as shown in the supplementary data in Figures S2 and S3. In the CuO sample, the Cu and O are the main components derived from the CuO and in a sample of the Co_3O_4 , Co and O are inherently visible. In both samples, Sn is involved from the FTO substrate. Figure 2a shows the elemental mapping of $\text{Co}_3\text{O}_4\text{-CuO}$ samples and it indicates the uniform distribution of Co, O, and Cu in the nanowire morphology. The contribution of Sn is also visible, and it is coming from the FTO substrate. The relative amount of Co, O, and Cu is presented in the EDS spectrum as shown in Figure 2b. Importantly, the amount of Co and Cu in the composite material has shown significant role in the HER process and it opens the gate way for the development of functional catalysts based on the Cu-Co systems.

The crystal structure of various nanostructured materials on the FTO substrate was confirmed by powder X-ray diffraction (XRD). Figure 3a-c describe the diffraction patterns of the CuO, Co_3O_4 , and composite $\text{Co}_3\text{O}_4\text{-CuO}$ at 2θ range of $10\text{--}80^\circ$. All the materials exhibit sharp peaks, which indicate their high crystalline quality. Four different diffraction patterns are also identified for the FTO substrate as shown in Figure 3a-c. The diffraction patterns of pure CuO are well matched to the standard JCPDS card no.96-900-8962 and the material exhibits monoclinic phase. The Co_3O_4 nanowire reflection peaks are in good agreement with the

standard JCPDS card no.96-900-5890 and it has a cubic phase. The mixed transition metal oxide sample has shown well-resolved diffraction patterns for both Co_3O_4 and CuO and they are fully supported by the standard JCPDS cards of pristine Co_3O_4 and CuO cases. The incorporation of CuO into the Co_3O_4 nanowires has shown the suppression of intensity for the reflection peaks of cobalt oxide which might induce the defects in the crystal structure of composite materials, and they could be responsible for the favorable HER process. No other impurity was found in all the samples.

The XPS characterization was carried out on the composite $\text{Co}_3\text{O}_4\text{-CuO}$ sample. The wide scan survey spectra confirm the presence of Co, Cu, and O in the sample as shown in Figure 4a. The $\text{Co}2\text{p}$ XPS spectrum is shown in Figure 4b that indicates the satellite peaks at the binding energies of 795.06 eV and 779.68 eV related to $\text{Co}2\text{p}_{3/2}$, and $\text{Co}2\text{p}_{1/2}$, respectively. The spin-orbit energy difference between them is 15 eV which is indexed to the Co^{2+} valence state [58]. Figure 4c shows two peaks at binding energies of 529.66 eV which is the characteristic peak for the metal-oxygen bonds and another peak at 531.01 eV that is attributed to the presence of surface oxygen vacancies [59,60]. Figure 4d shows the oxidation states of the Cu investigated by the high-resolution $\text{Cu}2\text{p}$ spectrum that contains shake-up satellite peaks which confirms the typical features of CuO [61-64]. Further, the existence of CuO in the composite sample is verified by the binding energies of the $\text{Cu}2\text{p}_{3/2}$ and the $\text{Cu}2\text{p}_{1/2}$ measured at 933.66 eV and 953.65 eV, respectively [62,63,64, 65-66]. The XPS results revealed that the composite is successfully obtained and that it is completely in good agreement with the XRD results. Furthermore, XPS technique was used to investigate the composition of the pristine cobalt oxide and CuO as shown in S4 and it confirms the presence of Co, Cu and O as main elements and no other element was detected. No, any other impurity was found in the sample during the XPS characterization. Based on the XPS results, it is confirmed that incorporation of Cu into the Co_3O_4 nanowires has tune its electronic properties, thus HER activity is strongly increased.

3.2. HER activity of the newly developed composite $\text{Co}_3\text{O}_4\text{-CuO}$ electro-catalyst

HER activity of the $\text{Co}_3\text{O}_4\text{-CuO}$ mixed transition metal oxide was evaluated in an alkaline solution. Various catalysts were deposited on the GCE and it was configured into the electrochemical cell as a working electrode. The performance of the mixed transition metal oxide was compared with that of the pristine Co_3O_4 and CuO and noble catalyst 20%

Pt/C. Linear sweep voltammetry was used to record the HER polarization curves at a scan rate of 5 mV/s. CuO is not active for HER due to its high over-potential, but the Co₃O₄ has shown poor HER activity. However, composite Co₃O₄-CuO has shown significant enhancement in the HER activity at the low potential that is close to the noble Pt/C catalyst as shown in Figure 5a. A current density of 10 mA/cm² is achieved at the potential of 0.288V vs RHE which is very comparable to the recently reported CoO based catalysts [67].

The HER mechanism on the surface of the metal oxide proceeds through either Volmer–Heyrovsky or Volmer–Tafel mechanism in alkaline media [68].

The Tafel slope values of 120, 40 and 30 mV dec⁻¹ are associated to Volmer reaction, Heyrovsky reaction, and Tafel reaction, respectively.

It is proved that the transition metal oxides are not suitable catalysts for transforming the H* to H₂ due to strong H* adsorption on the O, but relatively weak H* adsorption on metal ion [57, 53, 54]. However, they have demonstrated very well for the cleavage of OH-H bond in the Volmer step [59, 62, 55, and 69]. Recently, a published work on CoO nanorods [67] has Tafel slope of 82 mVdec⁻¹. But the proposed catalyst based on composite Co₃O₄-CuO has smaller Tafel slope value of 65 mVdec⁻¹ as shown in Figure 5b. It follows that the Volmer–Heyrovsky mechanism further confirms that the desorption step (Heyrovsky reaction) is the rate-determining step during the HER process. Similarly, the Co₃O₄ has shown Heyrovsky-Volmer mechanism and exhibited a Tafel slope of 94 mVdec⁻¹ which is comparable to that of reported work [67]. The Pt/C has Tafel slope of 49 mVdec⁻¹ and it follows the Volmer–Heyrovsky reaction mechanism. The Tafel slope of GCE and CuO are 328 mVdec⁻¹ and 243 mVdec⁻¹, respectively. These are very large in magnitude due to self-resistance offered by the material and the electrode [70, 71]. Looking into the consideration of the SEM and the XRD results, it is obvious that the Co₃O₄-CuO has less intense reflections for cobalt oxide when compared to the pristine Co₃O₄. This suggests that crystal defects might enhance the HER activity and SEM study has also shown that nanowires of mixed metal oxide are thinner than the pristine cobalt

oxide with large catalytic sites and surface area which are in great contact with the electrolyte and favors the active HER process. Additionally, the EDS study confirms that Co is replaced by copper in mixed transition metal oxide sample as shown in Figure 2b and the presence of Co and Cu in the mixed transition metal oxide synergistically enhance the HER activity. It is true that the content of Co and Cu is low in the mixed sample as shown in Figure 2b when compared to the amount of Co and Cu in the pristine samples as shown in S2-S3. In the composite sample, some of the cobalt atoms are replaced by copper, thus the presence of two transition metals i. e. cobalt and copper possibly generated synergetic effect in the oxide phase, thus superior HER performance is demonstrated. This further emphasizes that the relative amount of Co and Cu in the sample can alter the HER activity which needs to optimize for the development of future generation of HER catalysts. Moreover, the copper concentration in the composite has tendency to lower the adsorption energies of atomic hydrogen [72] and consequently faster HER is demonstrated.

The stability of the composite based HER catalyst was evaluated for three hours via chronopotentiometry as shown in Figure 6a. The response of catalyst is highly stable, and it showed a negligible potential drop with time. Thus, we assume that this catalyst can be used for widespread applications. In addition, the durability of the $\text{Co}_3\text{O}_4\text{-CuO}$ catalyst was investigated through cyclic voltammetry at a scan rate of 10 mV/s and after 2000 cycles of CV, the LSV response in terms of potential shift was found to be negligible as shown in Figure 6b. The considerable stability and durability of composite catalyst gives alternative possibility to replace the precious Pt-based catalysts for hydrogen production.

To make a deeper insight on the HER kinetics, the electrochemical impedance spectroscopy (EIS) was performed in a frequency range of 100kHz to 0.1 Hz in 1 M KOH solution at the onset potential of -0.3 V RHE and an amplitude of 10 mV. The Nyquist plots and the equivalent circuit (as an inset) are shown in Figure 7a. Also, the bode plots are developed using same EIS data as

shown in Figure 7b and 7c. The fitted resistance values are summarized in Table 1. This equivalent electric circuit contains the solution resistance (R_s), Faradaic charge-transfer resistance of HER (R_{ct}), and the double-layer capacitance (C_{dl}). As shown in Figure 7, the R_{ct} (173.2Ω) for $\text{CuO-Co}_3\text{O}_4$ is apparently smaller and the higher C_{dl} (1.97 mF) compared to the pristine CuO and Co_3O_4 suggesting a decrease in the HER resistance and consequently favorable HER catalytic activity in

alkaline solution is demonstrated [73-75]. The performance of the developed electrocatalyst is superior the recently reported HER catalysts in terms of Tafel slope and at low potential of -0.288 V for the current density of 10 mA/cm² as given in Table S1.

4. Conclusions

This study indicates that the incorporation of copper into the precursors of Co₃O₄ nanowires can activate the cobalt oxide material into a highly efficient electro-catalyst toward HER. The composite Co₃O₄-CuO has performance comparable to the best HER catalysts reported in alkaline media. The addition of copper did not change the morphology of Co₃O₄, but it tuned the electronic, catalytic sites and consequently excellent HER performance is achieved. The performance of the proposed catalyst in terms of Tafel slope, approximately 65 mVdec⁻¹, and to produce 10 mA/cm² current density at a low potential of 0.288 V vs RHE are showing an advancement in the catalyst design based on Co₃O₄ materials for HER. The Co₃O₄-CuO material has shown a good stability and durability in an alkaline solution. The EIS results have shown that the HER is highly favorable on the Co₃O₄-CuO surface due to the smaller charge transfer resistance and higher capacitance values. These results provide new horizons for the development of a future generation of high-performance cobalt based electro-catalysts. Also this functional material can be capitalized into diverse energy storage systems.

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Figure Captions

Figure 1: Scanning electron microscopy images at different magnifications a-b. pure CuO, c-d. pure Co₃O₄, e-f. Co₃O₄-CuO composite.

Figure 2: EDS elemental mapping a Co₃O₄-CuO composite oxide, b EDS spectrum. Co₃O₄-CuO composite.

Figure 3: XRD spectra for various nanostructured materials a. pure CuO, b. pure Co₃O₄, c. Co₃O₄-CuO composite.

Figure 4: XPS spectrum (a) Wide scan survey spectrum of Co₃O₄-CuO, (b) Co 2p of Co₃O₄-CuO, (c) O 1s of Co₃O₄-CuO (d) Cu 2p of Co₃O₄-CuO

Figure 5: 5a. LSV polarization curves for different catalysts GCE, pure CuO, pure Co₃O₄, and Co₃O₄-CuO composite, 20% Pt/C at scan rate of 5 mV/s in 1M KOH solution at room temperature, 5b. the corresponding Tafel slopes from HER polarization curves for different electrocatalysts

Figure 6: 6a. The chronopotentiometry response at 10 mA/cm² of Co₃O₄-CuO composite for 3 hours, **6b.** durability response after 2000 cycles of cyclic voltammetry in 1M KOH at a scan rate of 100 mV/s in the potential window of 0.864 to 1.164 V vs RHE.

Figure 7: a, Nyquist plots for the HER under an applied potential of -0.3 V vs RHE, a frequency range of 100 kHz to 0.1Hz and amplitude of 10 mV in 1M KOH and Bode (b,c) plots The inset in Figure 7a is the equivalent circuit used to fit the data. R_s is the ohmic resistance of the solution, R_{ct} is the charge transfer resistance and C_{dl} the double layer capacitance.

Figure 1:

Figure 2:

Figure 3:

Figure 4.

Figure 5 (a, b):

Figure 6 (a, b):

Figure 7

Table 1. The fitted values for the elements of equivalent circuit

Sample	R_s (Ohm)	R_{ct} (Ohm)	CPE (mF)
Co_3O_4 -CuO	2.82	173.20	1.97
Co_3O_4	2.04	384.50	0.85
CuO	2.25	656.90	0.35

Advanced Co₃O₄-CuO nano-composite based electrocatalyst for efficient hydrogen evolution reaction in alkaline media

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Supplementary data

S1: SEM of composite catalyst after stability and durability experiment

S2: EDS mapping for the elemental distribution in pristine CuO

S3: EDS mapping for the elemental distribution in pristine Co_3O_4

S4. a. Co 2p XPS spectra of pristine Co_3O_4 , Fitted O 1s for pristine Co_3O_4 **b.** XPS spectra of CuO

b

Table S1 Comparison of HER activities of the composite Co₃O₄/CuO with efficient previously reported electrocatalysts in 1M KOH

Catalyst	Tafel slope mVdec ⁻¹	Overpotential mV@ 10 mA/cm ²	References
CoP/CC, 500	129	500	1
N, P-G	145	700	2
MoS _x		540	3
Co-S/FTO		480	4
Co-NRCNTs		450	5
Co-N-C		270	6
CoO _x @CN		235	7
Ni ₃ FeN-NPs		238	8
Ni ₂ P on Ni foam		221	9
CoP@PNC		120	10
Co/CoP@NC		180	11
Co@CNF		196	12
CoP ₃ NSs/CC		121	13
CoNPs@C		153	14
Co _{0.9} S _{0.58} P _{0.42}		141	15
Co ₃ O ₄ -CuO	65	0.288V vs RHE @ 10 mA/cm ²	This work

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