Development of Cu$_3$N electrocatalyst for hydrogen evolution reaction in alkaline medium

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A wide variety of electrocatalysts has been evolved for hydrogen evolution reaction (HER) and it is reasonable to carry out HER with low cost electrocatalyst and a good efficiency. In this study, Cu$_3$N was synthesized by nitridation of Cu$_2$O and further utilized as an electrocatalyst towards HER. The developed Cu$_3$N electrocatalyst was tested and results showed a low overpotential and moderate Tafel slope value (overpotential: 149.18 mV and Tafel slope 63.28 mV/dec at 10 mA/cm$^2$) in alkaline medium with a charge transfer resistance value as calculated from electrochemical impedance spectroscopy being 1.44 Ω. Further from the experimental results, it was observed that the reaction kinetics was governed by Volmer–Heyrovsky mechanism. Moreover, Cu$_3$N has shown an improved rate of electron transfer and enhanced accessible active sites, due to its structural properties and electrical conductivity. Thus the overall results show an excellent electrochemical performance, leading to a new pathway for the synthesis of low cost electrocatalyst for energy conversion and storage.

With the depletion of fossil fuels and an increasing threat of global warming and environmental pollution, there is a huge quantum of research in the development of new energy resources$^{1-3}$. Of the various important fuels, hydrogen is an excellent alternative as it is clean with CO$_2$ neutral, having high gravimetric energy density and eco-friendly green renewable energy source$^{4-6}$. The diverse techniques for the production of H$_2$ include electrochemical and photoelectrochemical water splitting, thermolysis, biomass pyrolysis, hydrocarbon steam reforming, and coal gasification$^{7-10}$. Among these techniques, electrochemical hydrogen evolution reaction (HER) is a simple and an efficient technique to meet the future energy demand. The cathodic HER involves 2e$^-$ transfer process with multi-step reaction consisting of absorption, reduction and desorption.

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(g).$$  

(1)

The initial step is Volmer reaction (Eq. (2)) in which coupling of protons with electron occurs at the surface of catalysts forming adsorbed hydrogen atom. Then, adsorbed hydrogen atom reacts with another proton from solution in conjunction with electron transfer to form hydrogen molecule via Heyrovsky reaction (Eq. (3)). In the final step, two adsorbed hydrogen atoms combine to form hydrogen molecule—Tafel reaction$^{11,12}$ (Eq. (4)), where
\[ H^+ + e^- \rightarrow H_{ads}, \]  
(2)

\[ 2H_{ads} + H^+ + e^- \rightarrow H_2, \]  
(3)

\[ 2H_{ads} \rightarrow H_2. \]  
(4)

In general, platinum is the ideal catalyst for HER with the desired characteristics such as low onset potential, Tafel slope and high durability but the high cost and scarcity hampered its large scale application in hydrogen production.\(^\text{13-21}\) Thus, it is crucial to develop abundant and highly efficient electrocatalysts for large scale hydrogen production. Over the past few decades, research is focused on developing first row transition metals as efficient electrocatalysts for HER.\(^\text{22-29}\) Copper is a promising catalyst and a similar analogue to Pt metal, but has a limited activity towards HER due to its deficiency in the capture of H atom.\(^\text{17-20}\) Numerous efforts have been taken to synthesize copper with transition metal sulphides, carbides, phosphides and dichalcogenides.\(^\text{21-25}\) Numerous efforts have been taken to synthesize copper with transition metal sulphides, carbides, phosphides and dichalcogenides to overcome this issue for improving HER performance.\(^\text{22-29}\) Copper Nitride (Cu₃N) is a metastable semiconductor that has been proposed as efficient cathodic materials for energy conversion and storage applications, because of their unique physiochemical properties, electrical and its thermal properties.\(^\text{30-32}\) Cu₃N has drawn attention in other fields like optical device storage, fuel cells, high-speed ICs, metallic microscopic links, CO₂ reduction, energy storage and energy production.\(^\text{30-32}\) Various routes have been explored for the reduction of particle size and different morphologies of Cu₃N. For instance, Pereira et al. prepared Cu₃N from CuF₂ at 300 °C in NH₃ atmosphere. XRD measurements revealed dark green power of Cu₃N without any trace of oxidation or residual CuF and TEM images exhibited nanodomains of Cu₃N materials.\(^\text{36}\) The obtained Cu₃N were used as negative electrode for lithium battery application.\(^\text{19}\) Deshmukh and co-workers reported the synthesis of ultra-small Cu₃N nanoparticles via a one step reaction between copper (II) methoxide and benzylamine. TEM images confirmed that Cu₃N has ultra-small particle morphology with ~ 2 nm thickness. These Cu₃N nanoparticles provided pathways for the development of efficient cathode materials to enhance lithium ion batteries application.\(^\text{35}\) Herein, Cu₃N nanoparticles have been explored as an efficient electrocatalyst for electrochemical hydrogen evolution reaction. The prepared Cu₃N material as electrocatalyst possesses intrinsic HER activity, which might be related to their electronic structure and oxidation state of Cu, resulting in Cu⁺ increasing the electrochemically active surface to enhance hydrogen evolution performance. In this work Cu₃N nanoparticles were synthesized from nitridation of Cu₂O and to further confirm the formation and morphology, various investigations were done like XRD, FTIR, SEM and BET measurements. Cu₃N as electrocatalyst exhibited a considerable catalytic performance of HER in alkaline electrolyte, a reasonable current density of 10 mACm⁻² at an overpotential of 149.18 mV. The good HER performance might owe to the large surface area and favourable electrical conductivity of Cu₃N particles.

**Experimental**

All the chemicals and reagents used were of analytical grade and used without any further purification. Copper (II) sulphate pentahydrate (CuSO₄·5H₂O), Sodium hydroxide (NaOH), L-Ascorbic acid (C₆H₈O₆) were purchased from Sigma-Aldrich Chemicals Pvt. Ltd and double distilled water was used in the synthesis by using Milli-Q water.

**Preparation of Cu₂O nanoparticles.** The synthesis procedure of cuprous oxide (Cu₂O) was adopted from the previous literature with slight modifications. Typically, 2 mmol of copper sulphate solution was dissolved in 50 ml of DI water and simultaneously 20 mmol of NaOH was added drop wise into the mixture. Then the mixture was continuously stirred at ambient temperature. Later, a capping agent of 4 mmol ascorbic acid was added into the above solution. Finally the reaction mixture was stirred continuously, stirred for 30 min at ambient temperature, which is labelled as Cu₂O-300/120 ml/min. The tubular furnace was heated at a temperature of 250 °C for 30 min. The resultant product was transferred into a petri dish, dried 21 h under ammonia atmosphere. The flow rate of ammonia gas was 60 ml/min for 1.5 h and the product was isolated by centrifugation (7500 rpm for 10 min). The resultant product was transferred into a petri dish, dried at 80 °C for 12 h. Further, Cu₂O nanoparticles were heated with NH₃ gas of different concentrations at different temperature, which is labelled as Cu₂O-300/120 ml/min, Cu₂O-300/160 ml/min and Cu₂O-250/60 ml/min.

**Preparation of Cu₃N nanoparticles.** The Cu₃N nanoparticles were prepared via nitridation process of Cu₂O. Briefly, Cu₂O nanoparticles were washed with DI water and ethanol for several times and dried at 60 °C for 12 h in vacuum oven.

**Mechanism of Cu₃N formation.** Copper sulphate (CuSO₄) reacts with NaOH solution in the reaction to form copper hydroxide Cu(OH)₂. Then ascorbic acid as surfactant was added into copper hydroxide solution leading to the formation of copper oxides (Cu₃N). In the last step, Cu₃N powder was heated in NH₃ atmosphere, which reacts with CuO to form Cu₃N. The reaction mechanism for the formation of Cu₃N is given below:

\[ 2CuSO_4 + 2NaOH \rightarrow 2Cu(OH)_2 + 2NaSO_4, \]  
(5)
After nitridation of Cu₂O to Cu₃N,

\[ 3 \text{Cu}_2\text{O} + 2\text{NH}_3 \rightarrow 2\text{Cu}_3\text{N} + 3\text{H}_2\text{O}. \]  

Material characterization. The crystalline structure and phase identification of the synthesized material was characterized by Rigaku Miniflex Powder X-ray diffraction technique equipped with Cu-Kα (λ = 1.546 Å) over 2θ range of 10°–50°. The size and morphology of the as synthesized material were analysed using FESEM (Hitachi S-4800). Thermo gravimetric analysis (TGA) was performed in an air atmosphere with an SDT Q600 (TA Instruments).

Preparation of electrodes. The glassy carbon electrode having a geometrical surface area of 0.07 cm² was first polished with alumina slurry of 0.05 micron, followed by rinsing it with DI water, ethanol and acetone. The working electrode was prepared from 5 mg of Cu₃N catalyst dissolved in 250 µl of ethanol. Later, 5 µl of the catalyst/5 µl of Nafion was pipetted with a micro syringe and coated on cleaned glassy carbon electrode (GCE) surface using drop casting method. The coated electrode was then dried at room temperature for 12 h. Electrochemical testing was carried out by CHI 660C electrochemical workstation. Cyclic voltammetry, linear sweep voltammetry, Tafel plot and electrochemical impedance spectroscopy techniques were done to evaluate HER performance.

Results and discussion

Structure and morphology. The nature of crystallinity and phase structure of the synthesized cuprous oxide (Cu₂O) nanoparticles were confirmed from XRD measurements as given Fig. 2a. In the pattern, peaks at 29.3°, 36.4°, 42.5°, 61.4°, 73.4° and 77.5° are indexed to the crystallographic planes of (110), (111), (200), (220), (311) and (222). Cu₂O has a cubic phase with lattice constant ‘a’ being 0.4266 nm, which has oxide ions (O₂⁻) coordinated with two cuprous ions (Cu²⁺) and exactly close to the JCPDS card number value of 5–66736,39. The size of Cu₂O particles as estimated from the diffraction peaks widths using Debye Scherrer equation was approximately 15 nm. Various trial experiments were done for the preparation of Cu₃N at various temperatures and concentration of ammonia gas. In the first trial, Cu₂O was preheated at 250 °C in NH₃ atm (flow rate 60 ml/min). In the XRD pattern, peaks at 23.6°, 33.5°, 35.91°, 38.87°, 41.1°, 43.62°, 47.8° and 54.0° correspond to the crystal planes of (001), (110), (111), (111), (111), (002) and (210) respectively. In trial-1, Cu₃N was not found with a trace mount of CuO and residual of Cu in the material. With an enhanced temperature and flow rate of NH₃ gas in trial-2, Cu₂O was preheated at 300 °C in NH₃ atm (flow rate 120 ml/min), wherein Cu₂O was not obtained as shown in Fig. 3a,b. Finally, Cu₂O was preheated at 300 °C in NH₃ atm (flow rate 160 ml/min) and given in Fig. 2b. The diffraction peaks observed at 23°, 33°, 41°, 48°, 54°, 59°, 69° and 74° corresponds to the crystal plane (100), (110), (111), (200), (210), (211), (220) and (300) respectively, which confirm the formation of Cu₃N nanocrystal as per the JCPDS card No. 47-1088 with a crystalline size of Cu₃N being 12 nm. The morphology and structural features of the Cu₃N (300 °C/160 ml/min) were analysed by scanning electron microscopy as given in Fig. 4a,b. Cu₃N materials are nanoclustered flower like morphology with nanoflowered structure. The
The average particle size was calculated to be 18.8 nm and particles distribution ranged from 30 to 40 nm respectively as given in the inset of Fig. 4b and the corresponding morphology of the Cu2O nanoparticles is given in Fig. 4c,d. Figure 5 shows the TEM image of Cu3N and from the result the lattice was found to be cubic crystal and further from the SAED pattern, it could be seen that apart from the Cu3N pattern, a trace amount of impurities could be seen that might be due to the presence of minor amount of unreacted Cu2O but the proportion was very less as observed from XPS. To further investigate the functionality and molecular structure, Fourier transform infrared spectroscopy (FTIR) analysis was carried out for Cu3N catalyst. As shown in Fig. 6a, FTIR spectrum of Cu3N nanoflower exhibited prominent peaks at 652 cm\(^{-1}\), which is ascribed to the intrinsic lattice mode vibration of Cu–N. The sharp peaks at 819 cm\(^{-1}\) is assigned to the surface of Cu–N\(_3\) bond. The peak at 2049 cm\(^{-1}\) corresponds to the stretching vibration of N\(_3\) azide confirming the formation of Cu3N. Further Raman spectrum was conducted to examine the Cu3N electrocatalyst and as given in Fig. 6b, two distinct peaks at 625 cm\(^{-1}\) and 1570 cm\(^{-1}\) correspond to the stretching and bending of Cu–N bond and the peak at 218 cm\(^{-1}\) is assigned to the vibrational mode of Cu. The porosity of electrocatalyst was investigated by nitrogen adsorption–desorption isotherm to understand the accessible surface properties, as shown in Fig. 7. The Brunauer–Emmett–Teller (BET) surface area was calculated to be 70.731 m\(^2\)/g for Cu3N obtained at 300 °C/160 ml/min. It shows type II adsorption isotherm and hysteresis loop has been observed, which shows mesoporous pore size structure. The cumulative pore volume was calculated to be 5.448 \(\times\) 10\(^{-2}\) cc/g with a diameter pore size of 1.92 nm. This high surface area and micropores can offer efficient active sites and also promote diffusion of ions in the electrolyte to accelerate the electrochemical process of HER. Further TGA analysis was done to understand the thermal stability of the synthesized samples. The thermogravimetric analysis of the material synthesized at various temperatures under N\(_2\) atmosphere was done and given in Fig. 8. As observed from the figure, the TGA curves could be identified into three different weight loss regions. During the first stage, a minor weight loss occurred at a temperature ranging...
from 0 to 150 °C, which is related to the loss of trapped water molecules. The second stage weight loss occurring at 250 °C is associated to the removal of organic solvents present on the surface of the particle. The third stage weight loss at 400 to 550 °C is due to the thermal decomposition of Cu and N₂. Moreover, thermogram of Cu₃N exhibited three weight losses, which is in agreement with the previous reported Cu₃N materials. DSC is a very effective characterization tool for analysing the thermal properties and heat capacity of the material and the synthesized Cu₃N material has an exothermic peak at 520 °C. To further analyse the material, XPS was taken for Cu₂O and Cu₃N samples (Fig. 9a,b) and from the figure, it could be observed that Cu-related peaks exhibit a symmetric shape with no satellite peak around 943 eV, ruling out the presence of Cu²⁺. In the deconvoluted XPS spectrum of Cu₃N, Cu 2p peak at binding energy of 932.4 eV was found with a shoulder around 934 eV. The first peak around 932 eV is attributed to Cu₃N; two other peaks around 933 eV and 934 eV are attributed to Cu 2p³/₂ and Cu²⁺ respectively. The former energy is close to the reported value of Cu₃N from the energy of Cu metal (932.1 eV; not shown), and this slight difference between Cu and Cu₃N agrees with close binding energies of Cu⁰ and Cu¹⁺ as shown in Fig. 10.

Electrochemical characterization. The electrochemical HER testing was carried out in three electrode cell by using electrochemical workstation (CHI660C instrument) at ambient temperature. Platinum wire, Ag/AgCl electrode was used as counter and reference electrodes respectively. The catalyst coated glassy carbon electrode was used as working electrode in 1 M NaOH alkaline solution as electrolyte for HER. All the potentials were measured with reference to Ag/AgCl (aq.) electrode and the same was calibrated to the potential versus reversible hydrogen electrode (RHE), in accordance with the equation.

\[ E_{\text{Vs.RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, \text{pH} + 0.199(V) \]

The electrocatalytic activities of Cu₂O and Cu₃N towards HER were investigated by cyclic voltammetry at various scan rates (10 mVs⁻¹ to 100 mVs⁻¹) in non-faradic current region to evaluate the manifest of electrochemical double layer capacitance (Cdl). HER polarization current was recorded at 2 mVs⁻¹ to determine the onset potential, overpotential, Tafel slope and current density. To improve the electrocatalytic performance of Cu₂O and Cu₃N materials in basic medium towards HER, the electron transport and electrochemical surface area are compared (Fig. 11a–d). Thus, ECSA of the catalyst could be directly reflected from the double layer capacitance (cdl) as estimated from the cyclic voltammetry (CV) curves vs. scan rate (10 mVs⁻¹ to 100 mVs⁻¹).
By following McCrory’s theory, the capacitance from EDLC was calculated and the double layer capacitance value calculated for Cu$_2$O and Cu$_3$N was calculated to be 0.472 mF cm$^{-2}$ and 0.803 mF cm$^{-2}$ in 1 M NaOH. This could be reflected in the higher electrocatalytic activity due to large $C_{dl}$ value. The results indicated that Cu$_3$N has higher electrocatalytic activity than Cu$_2$O, because Cu$_3$N materials have higher electron transfer and conductivity properties. To elucidate the possible kinetic reaction of hydrogen evolution reaction, the involvement of Cu$_3$N and Cu$_2$O in the reaction is explored using steady state polarization. The linear sweep voltammetry (LSV) curve was recorded at a potential window of −0.2 V to 0.2 V at a scan rate of 2 mV in 1 M NaOH alkaline medium. In Fig. 12a at the onset potential at 10 mA cm$^{-2}$ for Cu$_3$N and Cu$_2$O catalyst, it can be seen that Cu$_3$N nanostructure exhibits a remarkable electrocatalytic activity towards HER with onset potential of 0.085 V for
Figure 7. BET surface area analysis calculated from N₂ adsorption–desorption isotherms of Cu₃N nanoparticles (synthesized at 160 ml/min ammonia flow rate and 300 °C).

Figure 8. TGA/DSC analysis of the synthesized Cu₃N at 160 ml/min ammonia flow rate and 300 °C.

Figure 9. X-Ray photoelectron spectroscopy analysis of (a) Cu₂O, (b) Cu₃N (synthesized at 160 ml/min ammonia flow rate and 300 °C).
Cu$_3$N lower than that of Cu$_2$O (0.035 V). Thus, results indicated that high surface area and favourable electrical conductivity of Cu$_3$N nanoflower promotes accessible active sites and fast electron transfer than Cu$_2$O nanoparticles. Further the enhanced electrochemical HER activity can be illustrated by comparing the Tafel slope. The Tafel plots are directly measured from LSV curves (overpotential vs. Log j) graph as given in Fig. 12b and these plots are used for the quantitative analysis of kinetics reaction of HER. Tafel plots were fitted in the linear portion of the Tafel equation as η = a + b log J: where J is current density, η is overpotential, b Tafel slope. The Tafel slope was calculated to be 63.28 mV/decade at an overpotential of 149.18 mV for Cu$_3$N smaller than Cu$_2$O nanoparticles (77.25 mV/decade and 200.6 mV). Here in numerous Cu$^{2+}$ species was formed at Cu$_3$N material.
during electrochemical process, which might be regarded as active sites for enhancing the electrical conductivity of Cu₃N nanoflower beneficial for boosting the HER performance. The kinetics reaction of HER was analysed by Tafel plot. The pathway of kinetics for the conversion of (H⁺ to H₂) in basic medium in general follows three mechanism viz. Volmer, Heyvosky and Tafel reaction. Volmer is the proton discharge electroosorption (Eq. (8)), electrochemical desorption is the Heyvosky reaction (Eq. (9)) and last step Tafel indicates the recombination of two surface-absorbed H₂ atom (Eq. (10)).

$$M + H_3O^+ + e^- \rightarrow MH_{ads} + H_2O - (b \sim 120 \text{ mV}),$$

$$MH_{ads} + MH_{ads} \rightarrow M + H_2 - (b \sim 40 \text{ mV}),$$

$$MH_{ads} + H_3O^+ + e^- \rightarrow 2M + H_2 + H_2O - (b \sim 30 \text{ mV}),$$

where MH_{ads} represent the absorbed H₂ atom over the surface of the metal and M represents the catalytically active free sites for HER. The Tafel slope was calculated to be 63.28 mVdec⁻¹ and 77.25 mVdec⁻¹ for Cu₃N and Cu₂O associated to Volmer–Heyvosky mechanism for the hydrogen evolution. The extrapolation of Tafel plot gives the exchange current density, which was calculated to be 24.2 mA/cm² and 11.3 mA/cm² respectively. A comparison table of reported Cu₃N results are discussed in Table 1. Thus, Cu₃N materials promote electron penetration exposing active sites and mass transfer ability, which suggest the better electrocatalytic activity towards HER. The comparison of HER activity of Cu₂O and Cu₃N are given in Table 2.

Electrochemical impedance spectroscopy (EIS) measurements were further done to analyse the interfacial properties of the as obtained electrocatalyst. As given in Fig. 12c,d, the semicircle in the high frequency area of the Nyquist plot was ascribed to the charge transfer resistance (Rct) and higher value of Rct denotes slow reaction rate and lower value of Rct denotes faster reaction rate.
The cyclic stability test was conducted using linear sweep voltammetry from −0.2 to 0.2 V and from the result, it was observed that the stability of Cu3N was good compared to the Cu2O as given in Fig. 13a,b. Overall results show that the synthesized Cu3N is an effective catalyst for electrochemical HER (Fig. 14).

Table 1. A table of comparison of the reported catalysts with the present material reported in this work.

| S. no. | Electrocatalyst       | Tafel slope (mV/dec) | References |
|-------|-----------------------|----------------------|------------|
| 1     | Cu3N-Copper foam      | 168                  | [28]       |
| 2     | Cu3N-Nickel Foam      | 122.06               | [31]       |
| 3     | Cu3N-Cu3P-Nickel foam | 69                   | [41]       |
| 4     | Cu3N-PdO              | 122.83               | [42]       |
| 5     | Cu3N-NiP              | 122                  | [47]       |
| 6     | Cu3N-Cu2N             | 55.0                 | [49]       |
| 7     | Cu3P-CoP nanowire     | 96                   | [50]       |
| 8     | Cu2O                  | 77.35                | This work  |
| 9     | Cu3N                  | 63.28                | This work  |

Table 2. Tafel slope and exchange current density for HER with Cu3N electrode.

| Electro-catalyst     | Tafel slope (b mV/decade) | Log Jo (mA/cm²) | α value | Overpotential (mV) |
|----------------------|---------------------------|-----------------|---------|--------------------|
| Cu3N                 | 63.28                      | 24.2            | 0.92    | 149.18             |
| Cu2O                 | 77.45                      | 11.3            | 0.76    | 200.6              |

Figure 13. Cyclic stability tests of (a) Cu2O, (b) Cu3N (synthesized at 160 ml/min ammonia flow rate and 300 °C) tested using cyclic voltammetry at a scan rate of 2 mV/s vs. Ag/AgCl.

The cyclic stability test was conducted using linear sweep voltammetry from −0.2 to 0.2 V and from the result, it was observed that the stability of Cu3N was good compared to the Cu2O as given in Fig. 13a,b. Overall results show that the synthesized Cu3N is an effective catalyst for electrochemical HER (Fig. 14).

Conclusion
In summary, Cu3N was synthesized successfully from nitridation of Cu2O nanoparticles. The electrochemical hydrogen evolution reaction was carried out using Cu3N in alkaline medium in 1 M NaOH. By using Cu3N as electrocatalyst, a low Tafel slope of 63.28 mV/decade with a low overpotential of 149.18 mV was observed, which follows Volmer–Heyrovsky reaction mechanism. Thus overall results show that the catalyst has good electrocatalytic activity for HER thus making it a potential candidate for cost effective catalysts in electrochemical hydrogen production.
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Acknowledgements
Author Abdullah Alodhayb acknowledges Researchers Supporting Project number (RSP-2021/304), King Saud University, Riyadh, Saudi Arabia. This work was funded by the National Research Foundation of Korea (NRF) (2021R1A4A3027878). This research was also funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under Grant Number 104.05-2020.15.

Author contributions
A.S., A.M.P.—Experimental work. R.N., K.G., T.S.G.—Testing. G.J., M.M.—Characterization. S.P., A.A., S.Y.K., Q.V.L.—Material analysis. P.L.S., S.K.J. and A.N.G.—Ideas conceiving.

Competing interests
The authors declare no competing interests.

Additional information
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