Synthesis of hydroxide nanoparticles of Co/Cu on carbon nitride surface via galvanic exchange method for electrocatalytic CO2 reduction into formate

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ABSTRACT

Herein we report Co and Cu based metal hydroxides (Co(OH)2/Cu(OH)2) on carbon nitride (C3N4) surface via replacement of Co nanoparticles (NPs) through galvanic exchange method for electrocatalytic carbon dioxide reduction. The lower value of reduction potential in case of cobalt ([Co2+ (aq) + 2 e− → Co(s)], −0.28 eV) compared to copper ([Cu2+ (aq) + 2 e− → Cu(s)], +0.34 eV) makes Co(0) easily susceptible to galvanic exchange process. On the basis of this significant difference in the reduction potential of Cu(0) and Co(0), 0.62 V, Cu2+ can replace Co(0) via galvanic exchange without using any external bias. The synthesis of (Co(OH)2/Cu(OH)2) involves two steps, where in the first step on surface of C3N4, Co NPs were synthesized via reducing of Co2+ ions with a strong reducing agent NaBH4. In presence of aqueous medium, formation of cobalt hydroxide also takes place. In the second step these cobalt nanoparticles on C3N4 were subjected to the process of galvanic exchange in which the sacrificial Co NPs were exchanged by Cu atoms and forming Cu(OH)2 in presence of an aqueous medium. Overall, the whole synthesis process results in deposition of hydroxides of cobalt and copper (C3N4/(Co(OH)2/Cu(OH)2) on C3N4 surface. The synthesized materials were characterized using PXRD, EDS, XPS, TEM and SEM. The two electrocatalysts C3N4/(Co/Co(OH)2 C3N4/(Co(OH)2/Cu(OH)2) were evaluated for their performance towards carbon dioxide reduction. C3N4/(Co(OH)2/Cu(OH)2 showed superior performance with electrocatalytic activity more than three times of C3N4/(Co/Co(OH)2. The product of CO2 electro-reduction was identified, using a rotating ring disc electrode (RRDE) system, to be primarily formate.

1. Introduction

Increase in anthropogenic levels of carbon dioxide (CO2) in the earth’s atmosphere is a global concern [1–3]. Massive burning of fossil fuels not only have increased the carbon dioxide concentration in earth’s atmosphere, but also have triggered extensive concerns about the energy shortage. Rise in levels of CO2 in earth’s atmosphere can bring drastic change in the earth’s temperature. This may limit also the utilization of fossil fuels. The problems with our environmental, such as ocean acidification and global warming are the main issues that need to be addressed if we and the future generations have to sustain on earth. This negative impact of undesirable level of carbon dioxide in earth’s atmosphere can drive the research and discovery of new technologies to mitigate the emission of carbon dioxide by capturing, sequestering and conversion of this greenhouse gas into other hydrocarbons [4–6]. Out of these approaches that have been explored, photocatalytic (PC) and electrocatalytic reduction (EC) of carbon dioxide are most promising solutions to sustain environmental challenges. It is a known fact that linear molecule like CO2 is thermodynamically stable with the C=O bond energy equal to 750 kJ mol−1. So breaking of CO= bond and production of fuels and valuable chemicals (CHOOH, CH4, CH3OH etc) via reducing CO2 is a tricky process. In the electrochemical systems, the product of carbon dioxide reduction depends upon the applied potentials and in this regard, a judicious potentials bias may drive reactions that can lead to the desirable products. It has been proved via electrocatalysis that at a potential of −0.9 V vs RHE carbon dioxide is converted in formate [17]. The reports have also revealed that copper and copper oxides are the state of art catalysts for electrocatalytic conversion of CO2 into methane, ethane, formaldehyde and ethanol [12,18,19]. Unfortunately there are still challenges that hinders the activity of Cu based catalysts, including low selectivity, poor Faradaic efficiency (FE) and production of hydrogen as a strong competitive side reaction. There have been attempts to explore synergistic effect concept in different Cu alloys like In-Cu, Sn-Cu, Pd-Cu, Au-Cu, Ag-Cu and Ni-Cu type alloys to improve poor selectivity and activity towards CO2 conversion [18]. Cobalt based electrocatalysts
have also been reported to be promising materials for CO2 reduction [20,21]. Alloy of CoCu is shown to perform better as an electrocatalyst than the individual Cu NPs alone, and a drastic influence in CO2 reduction activity is observed when Co is mixed with Cu [20,21].

Recent studies reveal a growing trend in the use of nitrogen and carbon containing 2D materials as a non-metal oxide support in catalysis. Both theoretical and experimental conclusions demonstrate the catalytic CO2 conversion by C3N4 based materials actually arises because of electronic modulation between conjugated sp2 C atoms surrounded by N atoms [22,24,29]. The incorporation of N atoms in framework of carbon atoms breaks the electro-neutrality of π-orbital electrons thus creating CO2 activation active sites [32]. For this reason carbon nitrides, N doped graphene, carbon nanotubes etc. have been keenly studied for carbon dioxide reduction. Considering the fact carbon nitrides have shown great promise as a catalyst, particularly for carbon dioxide reduction, so it would be interesting to explore the properties of bimetallic NPs, CuCo alloy type or CuCo based oxides or hydroxides by synthesizing them on the surface of carbon nitride. As discussed earlier, both Cu, Co and C3N4 have shown great promise for CO2 conversion, and integrating them together could result in further enhancement.

2. Experimental section

All Chemicals were obtained from the suppliers and used as such, without any further treatment. Copper nitrate (Cu(NO3)2⋅3H2O) and urea were obtained from Bio-Red laboratories. Cobalt nitrate (Co(NO3)2⋅6H2O), isopropyl alcohol, sodium borohydride (NaBH4) and perfluorinated nafion were supplied by Sigma Aldrich, whereas KHCO3 was obtained from Intra laboratories UK. All the solutions were prepared deionized Millipore water (DW).

2.1. Synthesis of carbon nitride

Previously reported work was followed to synthesize the carbon nitride, C3N4 used in this study [30,31]. A carbon and nitrogen rich area (10 g) was placed in a muffle furnace with covered crucible. The furnace temperature was maintained at 550 °C for 3 h. After this stimulated time, the area in crucible was converted into a yellowish powder of C3N4. The C3N4 was then cleansed with 0.1 M nitric acid in order to remove all the unwanted impurities and dried for 30 min at 80 °C.

2.2. Synthesis of C3N4/Co/Co(OH)2

40 mL of DI water was taken in a 100 mL beaker, where 40 mg of C3N4 powder was added and sonicated for 50 min. Then cobalt nitrate hexahydrate (0.116 g) metal precursor was added in this solution which makes 10−2 M the final concentration of metal precursor in the solution. The mixture was sonicated for 2 h and a 0.151 g of NaBH4 was added to initiate the reduction of cobalt salt. The solution was continuously stirred for the next 3 h. Finally, the process of mixture separation was carried out using centrifugation technique. Then the mixture was cleansed with ethanol and water to get rid of all the unnecessary impurities. After completing this whole process the powder was placed in oven at 60 °C for 3 h to get C3N4/Co/Co(OH)2.

2.3. Synthesis of C3N4/Co(OH)2/Cu(OH)2 NPs

Galvanic exchange synthetic method was used to deposit the hydroxide of Cu by replacing the Co NPs. A weight equal to 20 mg of already synthesized C3N4/Co/Co(OH)2 powder was added in a 50 mL beaker containing 10−2 M of Cu(NO3)2⋅3H2O solution. The mixture was then sonicated for 15 min to replace the sacrificial Co2+ by Cu2+ ions and in presence of aqueous medium Cu was deposited as Cu(OH)2 on the surface of C3N4 that gives C3N4/Co(OH)2/Cu(OH)2 as final product. During this process a color change, from green to brownish white, was also noticed. Then the mixture was cleansed with ethanol and water to get rid of all the unnecessary impurities. After completing this whole process the powder was placed in oven at 60 °C for 3 h to get C3N4/(Co (OH)2)/Cu(OH)2.

Reports reveal that unlike Ag, Au, Pd and Pt NPs; cobalt NPs are highly unstable, and in aqueous medium are prone to easy oxidation immediately after preparation [33,34]. During the process of synthesizing Co NPs on C3N4 surface, Co(OH)2 species are also expected to form. After galvanic replacement Cu2+ ions replaced the sacrificial Co2+ ions. As galvanic replacement took place in an aqueous medium the XRD and XPS results, as shown later, reveal the formation of Cu (OH)2 on the C3N4 surface.

2.4. Characterization techniques

PXRD measurements of C3N4/Co/Co(OH)2 and C3N4/Co(OH)2/Cu (OH)2 powders was taken with Rigaku Mini Flex II Desktop X-ray powder diffractometer (Rigaku, Leatherhead, UK). The radiation source was Cu-Kα radiation at 25 °C. PXRD range was with 20 range 10−80° with the scan rate of 2° per min. Nova Nano 450, FEI Waltham, MA, USA, Scanning Electron Microscope was used to check surface morphology C3N4/Co/Co(OH)2 and C3N4/Co/Co(OH)2/Cu(OH)2 catalysts. TEM analysis was carried out using HRTEM, Tecnai G2 transmission electron microscope. A 400-mesh copper grids were used during the process of sample preparation. A dispersed solution of C3N4/Co/Co(OH)2 and C3N4/Co/Co(OH)2/Cu(OH)2 samples in water/ethanol solution was prepared. The uniform dispersion of solutions was formed by sonicating them for half an hour. This completely dispersed solution with volume equal to 20 mL was casted on TEM grid drop wise and dried before doing TEM. XPS, Kratos AXIS Ultra DLD, Manchester, UK was used in carrying out X-ray photoelectron spectroscopy to determine the possible oxidation states and surface composition of C3N4/Co/Co(OH)2 and C3N4/Co/Co(OH)2/Cu(OH)2 samples.

2.5. Electrode preparation

For electrocatalytic activity measurements an ink containing 4 mg of the catalyst, 40 μL nafion solution, 100 μL of isopropyl alcohol, and 40 μL of DIW was prepared. This mixture was prepared in vial with volume equal to 10 mL vial and was sonicated for 20 min. On GCE (geometric area, A = 0.196 cm2 and RDE, d = 5.0 mm) ink with volume equal to 5 μL was drop casted. A CO2 saturated solution of Potassium bicarbonate (0.5 M) was used as an electrolyte for CO2 reduction experiments. To avoid repetition, scan rate and applied voltage used during experimental process are discussed in the results and discussion section.

3. Results and discussion

The purity, conformity and composition of C3N4/Co/Co(OH)2 and C3N4/Co(OH)2/Cu(OH)2 was confirmed through powder X-ray diffraction analysis. Fig. 1 displays the PXRD pattern of C3N4/Co/Co(OH)2 with the 2θ = 27.49°, 33.20°, 43.71° and 59.64°. The XRD peak having 2θ = 33.20°, 59.64° is due to (100) and (110) plane of Co(OH)2. While the peak having 2θ = 43.71° is attributed to the crystal plane (111) of Co NPs. The peak with 2θ = 27.49° ensures the (002) plane of C3N4. After galvanic exchange, Co NPs were replaced by copper hydroxide NPs. The PXRD patterns of C3N4/Co(OH)2/Cu(OH)2 showed 2θ = 11.63°, 23.35°, 27.49°, 38.63°, 59.91°. As already discussed, the peak at 2θ = 27.49° belongs to the (002) plane of C3N4 whereas the peak with 2θ = 11.63°, 23.35°, 33.62° and 38.63° corresponds to (001), (021), (002) and (022) planes of Cu(OH)2. The xrd peak having 2θ = 33.64° and 59.91° is due to (100) and (110) plane of Co(OH)2. The absence of peak at 2θ = 43.7° that represents (111) crystal plane of Co NPs indicates that copper hydroxide NPs are formed at the cost of cobalt NPs.
via galvanic exchange. There is also a marginal shift in the peak of Co(OH)\(_2\). The peak at \(2\theta = 33.20^\circ\) is shifted to 33.64° while the peak with \(2\theta = 59.64^\circ\) is shift to 59.91°. There may be possible overlap of peaks at 33.64° corresponding to (100) plane of Co(OH)\(_2\) and (002) plane of Cu(OH)\(_2\). The oxidation states of Cu in C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\) was confirmed by performing XPS experiments (Fig. 2) on the synthesized samples. The xps spectra was obtained by deconvolution of measured signal and peaks were assigned accordingly. Fig. 2a represents xps spectra of carbon. The peak at 285.2 eV is for N\(_{6}(C)_{3}\) signal, and is the expected position for sp3-hybridised carbon. Likewise, the signal for C\(_{\text{NC}}\) appears at 288.03 eV. Fig. 2b shows decovolution spectra of nitrogen. C\(_{\text{NC}}\) peak appears at 398 and N\(_{6}(C)_{3}\) peak appears at 400 eV. The Oxygen deconvolated peaks appear at 532.9 eV, 531 eV and 529 eV respectively (Fig. 2c). Signal at 532.9 eV and 529 eV is attributed to oxygen species in Cu(OH)\(_2\) and Co(OH)\(_2\) respectively. While signal at 529 eV represents oxides of metals. Fig. 2d describes the binding energy (B.E) levels at 935.03 and 955.18 eV s corresponding to Cu 2p\(_{1/2}\) peak and Cu 2p\(_{3/2}\) peak respectively. These peaks represents copper in Cu(II) phase and are assigned to Cu(OH)\(_2\) [35]. In addition, two satellite peaks are found around 943.12 and 962.93 eV respectively. Fig. 2e describes two peaks with the binding energies at 782.11 and 797.53 eV. These two core level binding energies are attributed to Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\) peak respectively. The literature report authenticates that these binding energies are attributed to Co\(^{2+}\) of Co(OH)\(_2\) [36]. Furthermore, two satellite peaks are found around 786.67 and 804.23 eV respectively. Fig. 2f represents survey spectrum of C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\).

Morphological nature of C\(_3\)N\(_4\)/Co/Co(OH)\(_2\) and C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\) was studied by using SEM technique as illustrated in Fig. 3. From SEM images (Fig. 3a and b) of C\(_3\)N\(_4\)/Co(OH)\(_2\) and C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\) porous fibrous structure of the electrocatalysts is revealed. Uniform distribution of Co/Co(OH)\(_2\) and Co(OH)\(_2\)/Cu(OH)\(_2\) can be seen from the SEM images. Elemental mapping of C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\) substantiates the presence of Co, Cu, C, O and N as shown in Fig. S1. TEM studies of Co/Co(OH)\(_2\) and Co(OH)\(_2\)/Cu(OH)\(_2\) were also carried out to detect the fine size and structure of electrocatalysts (Fig. 4). TEM studies reveal sheet like structure of C\(_3\)N\(_4\) with distribution of Co and Cu(OH)\(_2\) NPs (Fig. 4a, 5–70 nm). HRTEM analysis confirm the presence of Co and Cu(OH)\(_2\) crystal planes as depicted in Fig. 4b, in which the lattice fringes of Co NPs, with an inter planar spacing of \(d’ = 0.203\) nm is attributed to (111) plane that depicts the presence of Co. The lattice fringes of Cu(OH)\(_2\) NPs, with an inter planar spacing \(d’ = 0.27\) nm correspond to (100) plane of Cu(OH)\(_2\) NPs. TEM and HRTEM images of C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\) is shown in Fig. 4c and d respectively. The TEM images of C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\) display the distribution of Co(OH)\(_2\) and Cu(OH)\(_2\) NPs with average size equal to 7–70 nm. The HRTEM image

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**Fig. 1.** PXRD patterns of C\(_3\)N\(_4\)/Co/Co(OH)\(_2\) and C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\). A scan rate of 2° per min with 2\(\theta\) range from 20–90° was taken.

**Fig. 2.** High-resolution de-convoluted XPS analysis of (a) Carbon (b) nitrogen (c) Oxygen (d) Co(OH)\(_2\) (e) Cu(OH)\(_2\) of C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\). (f) survey spectrum of C\(_3\)N\(_4\)/Co(OH)\(_2\)/Cu(OH)\(_2\).
infers that Co(OH)₂ and Cu(OH)₂ has inter planer spacing \(d' = 0.27\) and 0.24 nm, which is attributed to (100) plane of Co(OH)₂ and (002) plane of Cu(OH)₂ respectively, confirming the formation of Co(OH)₂ and Cu(OH)₂.

3.1. Application in CO₂ conversion

Both C₃N₄/Co/Co(OH)₂ and C₃N₄/Co(OH)₂/Cu(OH)₂ were applied for the electrocatalytic carbon dioxide reduction using a rotating ring disc electrode (RRDE). The potential range between 0.8 and −1.2 V vs Ag/AgCl was used for CV scanning of C₃N₄/Co/Co(OH)₂ and C₃N₄/Co(OH)₂/Cu(OH)₂ disc electrodes (Fig. 5). The CV scans were carried out in 0.5 M KHCO₃ solution with the scan rate of 25 mV/sec. The visuals from Fig. 5a, b depicts that, after −0.9 V the cathodic current increases dramatically for saturated solution of CO₂ as compare to saturated solution of N₂. Two redox peaks one at 0.08 V in the forward bias and at −0.3 V in the reverse bias can be seen from Fig. 5a. From the results, it is evident that during CO₂ uptake on the surface of cathode, there is utilization of electrons actively. Fig. 5b also shows a sudden jump in current density around −0.9 V with redox peak at 0.05 V in forward scan and at −0.25 V in the reverse scan. This increase in current density in the potential region of −0.9 V to −1 V indicates active utilization of electrons and CO₂ consumption. Fig. 6a shows the comparison of C₃N₄, C3N4/Co/Co(OH)₂ and C₃N₄/Co(OH)₂/Cu(OH)₂ at 25 mV/sec towards CO₂ reduction activity. A significant jump in current density at −1.2 V is clear as
C$_3$N$_4$/Co/Co(OH)$_2$ shows a value of only $-0.50$ mA/cm$^2$, that means 3.4 times lower than the former and C$_3$N$_4$ shows the value of $-0.19$ mA/cm$^2$ which predicts 2.63 times lower activity than C$_3$N$_4$/Co/Co(OH)$_2$ and 8.94 times lower activity than C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$. A similar trend is observed when the scan rate is increased to 100 mV/sec (Fig. S2). The activity of C$_3$N$_4$/Co/Co(OH)$_2$ was further measured at various scan rates as shown in Fig. 6b, which signify increasing in the scan rate increases the current density.

3.2. Detection of products

A rotating rind disc electrode (RRDE) system with a Pt ring electrode was used to detect the products formed during the reduction of CO$_2$. Pt acts as second working electrode to identify the products formed on the primary working electrode, which is glassy carbon electrode (GCE) with deposited catalysts. The amount of catalyst deposited on the surface of the disc is extremely low (only 0.11 mg), and the expected amount of product formed is too little to be detected after being dissolved in the bulk of the electrolyte solution. However, the concentration of the product formed is relatively higher near the working electrode, which can produce measurable current density under the oxidation/reduction by a Pt ring electrode placed near the working disc electrode. As Pt electrodes have been widely used, the oxidation potentials for the most of the expected products from CO$_2$ conversion reaction (such as HCHO, HCOOH, CO, CH$_3$OH etc.) are known, and they can act as standard values for identifying the products. This approach seems more realistic and resembles in-situ monitoring of products as they are formed. A convenient way to detect the formation of a specific product is to scan the disc potential while keeping the ring potential constant, at a value equal to the oxidation potential of the targeted product. Similarly, the potential of working electrode can be fixed at the CO$_2$ reduction potential giving high current density, while the ring electrode can be scanned to identify the product formed at the applied disc potential.

The potential range between 0 and $-1.2$ V vs RHE was used for CV scanning of C$_3$N$_4$/Co/Co(OH)$_2$ and C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ disc electrodes, while the ring electrode was kept at a fixed potential of 0.9 V vs RHE that is reported to be the oxidation potential of formate on Pt surface [17,19]. Fig. 7a and b shows RRCV experiment results in N$_2$ and CO$_2$ saturated electrolyte for C$_3$N$_4$/Co/Co(OH)$_2$ electrode. From the graph (Fig. 7b) it is evident that there is a significant increase in the current density of the disc electrodes as well as the ring electrode in the CO$_2$ saturated solution as compared to N$_2$ purged solution (Fig. 7a). From Fig. 7b, a prominent peak around $-0.9$ V on ring electrode confirms the formation of formate. Fig. 7c and d display RRCV experiment results in N$_2$ purged electrolyte and CO$_2$ saturated electrolyte with C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ electrode. Similar to C$_3$N$_4$/Co/Co(OH)$_2$ electrode there is a noticeable increase in the current density of the disc electrodes as well as ring electrode. However, the ring current density

**Fig. 5.** (a) CV diagram of C$_3$N$_4$/Co/Co(OH)$_2$, after N$_2$ and CO$_2$ purge. (b) CV of C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ after N$_2$ and CO$_2$ purge.

**Fig. 6.** (a) CV comparison of C$_3$N$_4$, C$_3$N$_4$/Co/Co(OH)$_2$ and C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ at scan rate of 25 mV/sec (b) CV of C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ at different scan rates.
in C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ is much more pronounced as compared to C$_3$N$_4$/Co/Co(OH)$_2$ (Fig. 7b and d), confirming a higher conversion of CO$_2$ and improved production of formate on C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ electrode. Another set of experiments were conducted where the disc electrode was fixed, while the Pt ring was scanned. From the Fig. 8a the prominent peak at the potential of $-0.9$ V authenticates the formation of formate. From the figure it is quite clear that the formate peak is more intense in C$_3$N$_4$/Co(OH)$_2$/Cu(OH)$_2$ than C$_3$N$_4$/Co/Co(OH)$_2$. Hence it can be inferred that mixed Co(OH)$_2$/Cu(OH)$_2$ shows better activity than Co/Co(OH)$_2$. Copper-based catalysts have shown low selectivity, poor Faradaic efficiency (FE) and production of hydrogen as a strong competitive side reaction for CO$_2$ conversion. Despite all these limitations, Cu based catalysts are still explored for CO$_2$ conversion due to the possibility of producing a wide range of products including hydrocarbons and oxygenated hydrocarbons [12,37]. Cobalt based electrocatalysts have also been reported.
to be active for CO2 conversion, and recently they have gained significant research interest [20,21]. However, when copper and cobalt are present together, their performance for electrocatalytic conversion of CO2 is greatly improved compared to the individual constituents [20,38]. The superior performance of C3N4/Co(OH)2/Cu(OH)2 over C3N4/Co/Co(OH)2 may be due to the synergistic effect between the elements and possible enhancement in surface morphology due to galvanic exchange where more roughness and porosity is expected on account of atomic exchanges. Zhu et al. carried out a series of experiments keeping the disc electrode at a fixed potential value between −0.4, to −0.9 V and scanning the ring electrode between 0 and 1.3 V [17]. They observed a high current density on the ring oxidation step when the disc was kept at −0.9 V. Herein, we also kept the disc electrode potential for C3N4/Co(OH)2/Cu(OH)2 at −0.9 V and scanned the ring between 0 and 1.3 V to monitor the oxidation potential of the products formed. As seen in Fig. 8b, a current density peak around 0.9 V confirms the formation of formate, along with the possibility of other products indicated by the presence other peaks.

4. Conclusion
A cobalt copper based metal hydroxides C3N4/Co(OH)2/Cu(OH)2 electrocatalyst was prepared on surface of C3N4 through galvanic exchange process. Firstly, the Co NPs on C3N4 surface were synthesized using one of the strongest reducing agent NaBH4, where we observed the formation of cobalt hydroxide as well, possibly due to synthesis taking place in an aqueous solution. In the second step, the Co NPs were converted to Cu atoms via galvanic exchange, but in presence aqueous medium actually more stable Cu(OH)2 NPs were deposited on carbon nitride surface. The performance of both the electrocatalysts, C3N4/Co/Co(OH)2 and C3N4/Co(OH)2/Cu(OH)2 were evaluated for carbon dioxide conversion, where the C3N4/Co(OH)2/Cu(OH)2 catalyst showed superior performance. Application of RRDE experiments reveal the reduction of CO2 to formate on both the catalysts, C3N4/Co/Co(OH)2 and C3N4/Co(OH)2/Cu(OH)2, with the latter showing better activity and selectivity. The higher activity of C3N4/Co(OH)2/Cu(OH)2 than C3N4/Co/Co(OH)2 may be credited to the synergistic effect of both cobalt and copper hydroxides and possible enhancement is surface area generated during the process of galvanic exchange. As the galvanic exchange process brings changes in surface morphology that may potentially result in the more availability of active sites and suitable adsorbate-substrate interactions.

Author contribution
RN designed the work and write down the manuscript. AK and M.A.S.S commented on the manuscript. AA did few experiments.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.colsurfa.2020.124835.

References
[28] T. Bhownik, M.K. Kundu, S. Barman, Palladium nanoparticle–graphitic carbon nitride porous synergistic catalyst for hydrogen evolution/oxidation reactions over...
a broad range of pH and correlation of its catalytic activity with measured hydrogen binding energy, ACS Catal. 6 (2016) 1929–1941.


