Galvanic Exchange as a Novel Method for Carbon Nitride Supported CoAg Catalyst Synthesis for Oxygen Reduction and Carbon Dioxide Conversion

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Abstract: A bimetallic alloy of CoAg nanoparticles (NPs) on a carbon nitride (CN) surface was synthesized using a galvanic exchange process for the oxygen reduction reaction (ORR) and carbon dioxide electrocatalytic conversion. The reduction potential of cobalt is [(Co^{2+}(aq) + 2e^- → Co(s)], −0.28 eV) is smaller than that of Ag ([Ag^+(aq) + e^- → Ag(s)], 0.80 eV), which makes Co(0) to be easily replaceable by Ag^+ ions. Initially, Co NPs (nanoparticles) were synthesized on a CN surface via adsorbing the Co^{2+} precursor on the surface of CN and subsequently reducing them with NaBH_4 to obtain Co/CN NP. The Co NPs on the surface of CN were then subjected to galvanic exchange, where the sacrificial Co atoms were replaced by Ag atoms. As the process takes place on a solid surface, only the partial replacement of Co by Ag was possible generating CoAg/CN NPs. Synthesized CoAg/CN bimetallic alloy were characterized using different techniques such as powder x-ray diffraction (PXRD), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and electron diffraction spectroscopy (EDS) to confirm the product. Both the catalysts, Co/CN and CoAg/CN, were evaluated for oxygen reduction reaction in 1M KOH solution and carbon dioxide conversion in 0.5 M KHCO_3. In the case of ORR, the CoAg/CN was found to be an efficient electrocatalyst with the onset potential of 0.93 V, which is comparable to commercially available Pt/C having E_{onset} at 0.91 V. In the electrocatalytic conversion of CO_2, the CoAg/CN showed better performance than Co/CN. The cathodic current decreased dramatically below −0.9V versus Ag/AgCl indicating the high conversion of CO_2.

Keywords: carbon nitride; galvanic exchange; AgCo catalyst; oxygen reduction reaction; carbon dioxide conversion

1. Introduction

The use of fossil fuels for energy extraction has been convenient, though at a greater cost of CO_2 emissions. The increasing levels of carbon dioxide in the Earth’s atmosphere is of serious concern that needs to be addressed. The high amounts of CO_2 in the atmosphere drastically bring changes in the temperature of the Earth’s atmosphere. This problem not only increases the global temperature, but will also limit the use of fossil fuels. Alternatively, fuel cells and metal-air batteries have shown great promise for automotive industries. This is because of the fact that they work at low operating temperatures, possess high energy densities and are compatible to the environment on the basis of lower or zero harmful emissions [1–6]. Herein, this study attempts to design catalysts that are effective for clean energy production via fuel cell applications and suitable for catalytic conversion of carbon dioxide. It is a known fact that the efficiency of fuel cells and metal-air batteries are drastically affected.
by the slow kinetics of the oxygen reduction reaction (ORR) at the cathode. Thus far, only Pt and noble metal-based electrocatalysts have been designed and operated in commercially available devices. These catalysts are relatively effective and efficient, however due to the lack of noble metals in the Earth’s crust and high cost, a widespread commercialization of Pt based fuel cells and metal-air batteries does not seem to be feasible. Synthesizing efficient catalysts to replace Pt group metals (PGM) utilizing economical alternatives remains a critical challenge and a strategic issue for future applications. This can be achieved, to some extent, if attention is placed on the synthesis of new metal electrode support material that is able to enhance the catalytic efficiency and activity of metallic phase, without disturbing the chemical and mechanical stability. The nature of support is appreciated because it brings some interesting properties to the catalyst, such as proper dispersion of the active phase, preventing the loss of the catalyst during operation [7–11], morphological changes to increase the electrochemical active area [12–14].

Carbon nitride (CN) is a cheap, easily synthesized, photo active organic semiconductor that has displayed a remarkable performance in the field of catalysis [15]. The CN contains nitrogen atoms adjacent to carbon atoms. The interest in CN has recently increased because of the stimulated electropositivity in carbon atoms induced by the adjacent nitrogen atoms, which shows potential for the electronic interactions with various chemicals to affect their adsorption and reactivity. Due to this effect, a reduction in the activation energy barrier for oxygen adsorption and activation is expected that could possibly extend to the activation of challenging molecules, like CO2 [16]. Lyth et al., described that in acidic solution, the onset potential of CN is 0.69 V (versus normal hydrogen electrode (NHE)) for ORR [17]. However, the reported catalytic activity for ORR is not satisfactory yet, which could be due to the weak electrical conductivity of CN [18]. Some reports suggested that graphene CN can be used as solid supports to synthesize metal and metal oxide nanoparticles (NPs) which increase the conductivity and enhance their catalytic efficiency [19–21]. The importance of using CN as a support for electrocatalytic reactions is valuable for many reasons. The presence of N-atoms in the repetitive S-triazine unit can coordinate and stabilize NPs. The nitrogen functional groups also enhance strong coordination, and the interaction between NPs and the substrate providing large and accessible sites for electron transportation [22,23]. The porous structure assists in the diffusion of reactants to the active sites and the removal of formed products from there [24].

Nanoscale silver (Ag) and silver alloys have shown good potential for catalytic applications making them a promising candidate for ORR and CO2 reduction [25–31]. It is anticipated that ORR activity on Ag NPs takes place through a direct four-electron transfer mechanism as compared to the slow two-electron pathway by avoiding the formation of peroxide, which is a competent product in ORR [32]. However, Ag alone is not always appreciated for ORR and has proven to be less efficient than Pt on account of the strong bonding of Ag with the oxygen atom [33]. This interaction makes the O-O bond breakage less feasible on the Ag surface compared to Pt [34–36]. However, reports indicate that Ag in the presence of other metals, particularly Co to form bimetallic AgCo or alloyed AgCo, showed enhanced catalytic properties [26,27,33,37–39]. An interface containing the optimum interaction of Ag and Co binds effectively with oxygen to enhance the adsorption and subsequent reduction, possibly due to the synergistic effects induced in the presence of Co [40–43]. This effect is expected to facilitate other reactions as well, such as CO2 reduction that this study intends to investigate along with ORR.

Considering the nature of improved catalytic properties of CoAg alloy, this study proposes to synthesize bimetallic alloy type CoAg NPs on the CN surface via galvanic exchange to combine the effects of CoAg alloying and nitrogen induced polarity in CN. The choice of galvanic exchange is based on the natural reduction potentials of Co2+ and Ag+ that are expected to easily form an alloy on the CN surface. Initially, cobalt nanoparticles are synthesized on the surface of a semiconducting CN surface using a strong reducing agent, NaBH4, to form Co/CN. As the reduction of cobalt is difficult in the aqueous phase, therefore, the presence of CoO, Co3O4 and Co(OH)2 along with cobalt nanoparticles are anticipated. The lower reduction potential of Co2+ compared to Ag+ facilitates the galvanic exchange of cobalt nanoparticles, including its oxides and hydroxides, by Ag to give CoAg/CN nanocomposites.
Both Co/CN and CoAg/CN catalysts were investigated for ORR and CO\textsubscript{2} reduction. As evident in the results and discussion section, the CoAg/CN shows better performance for both the reactions.

2. Results and Discussion

The preparation of bimetallic alloy type (CoAg) NPs on the CN surface via galvanic exchange is discussed in detail in the experimental section. Initially, Co/CN monometallic NPs was synthesized using a simple reduction technique and then sacrificial Co atoms were galvanically exchanged with Ag\textsuperscript{+} to get CoAg NPs.

The structural conformity, purity and composition of the already synthesized compound were determined with the help of a powder X-ray diffraction analysis. In Figure 1, the diffraction peak at 2\(\theta\) = 27.49\(^o\) is associated with (002) plane of CN. The PXRD patterns of Co/CN in Figure 1 shows the peaks with 2\(\theta\) = 27.49\(^o\), 33.20\(^o\), 43.71\(^o\) and 59.21\(^o\). The peak with 2\(\theta\) = 33.20\(^o\) and 59.21\(^o\) corresponds to (100) and (110) planes of Co(OH)\textsubscript{2}. While the peak with 2\(\theta\) = 43.71\(^o\) is due to (111) crystal plane of Co nanoparticles. After galvanic exchange, CoAg, bimetallic NPs were produced. The PXRD patterns of CoAg/CN showed 2\(\theta\) = 27.49\(^o\), 32.20\(^o\), 38.10\(^o\), 44.17\(^o\), 64.40\(^o\), 77.41\(^o\), and 81.62\(^o\) peaks. As mentioned earlier, the peak at 27.49\(^o\) belongs to the (002) plane of CN. The peak at 2\(\theta\) = 32.20\(^o\) represents (100) plane of Co(OH)\textsubscript{2}. After galvanic exchange, there is marginal shift of 1\(^o\) in Co(OH)\textsubscript{2} peak that represents (100) plane. The peak is shifted to 2\(\theta\) = 32.20\(^o\) from 33.20\(^o\). The other peaks of CoAg/CN correspond to (111), (200), (220), (311) and (222) Crystal planes of Ag, which corroborates with the fcc lattice structure (JCPDS 04-0783). The peak with 2\(\theta\) = 43.71\(^o\) due to (111) crystal plane of Co nanoparticles is not visible, which could be due to the overlap by the (200) broad peak of Ag. Furthermore, the EDS data on atomic percentage of Co and Ag shows 1.61\% and 1.41\% respectively, confirming close to 1:1 stoichiometry of CoAg in the sample.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Powder X-ray diffraction patterns of Co/CN and CoAg/CN. During PXRD measurement, 2\(\theta\) varies from 20-90\(^o\) and the scanning rate was fixed at 2\(^o\) per min.
Cobalt NPs are highly unstable like Fe and Ni. They were readily oxidized in aqueous medium immediately after preparation [44–46]. During the synthesis, there is a high chance of dissolved oxygen in the reaction medium. Mostly, the dissolved oxygen oxidizes the surface of cobalt. To determine the surface composition and oxidation states of the elements in CoAg/CN NPs, XPS was performed. As shown in Figure 2a, the CoAg/CN shows two core level binding energies at 780.9 eV and 796.1 eV for Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peak, respectively. These binding energies correspond to Co$^{3+}$ of CoO and are well matched with the literature report [47]. Another doublet with binding energies 782.7 eV and 797.6 eV for Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peak that may be possibly due to the formation of Co(OH)$_2$ on the surface [48]. In addition, two satellite peaks are found at approximately 788.2 eV and 798.4 eV, respectively. From Figure 2b, the peaks at 368.3 eV and 374.6 eV are due to the presence of 3d$_{5/2}$ and 3d$_{3/2}$ of Ag(0) [23], along with two Ag3d spectrum peaks at 370.9 eV and 377 eV. These two signals correspond to a shift in 3d$_{5/2}$ and 3d$_{3/2}$ orbitals, which infers a possible bond between the silver and oxygen atoms [49].

![Figure 2](image_url)

**Figure 2.** High-resolution deconvoluted X-ray photoelectron spectroscopy (XPS) analysis of (a) Co (b) Ag, on CN surface.

The morphologies of nanoparticles were studied by SEM techniques as shown in Figure 3. The SEM images of Co/CN and CoAg/CN are shown in Figure 3a,b respectively. As it can be seen, both Co/CN and CoAg/CNNPs seem to have a porous fibrous structure with uniform consistency of CN where the NPs are deposited. To study the crystal structure and arrangement of crystal planes, the HRTEM analysis was performed. It was confirmed from the TEM image that Co/CN NPs exhibit spherical shapes with nanoparticle >40 nm sizes, as shown in Figure 4a. The TEM image shows a near homogeneous distribution of Co particles on the CN surface. The HRTEM image of Co/CN shown in Figure 4b depicts lattice fringes of Co NPs, with an interplanar spacing ‘d’ = 0.203 nm corresponding to (111) plane of Co. The TEM and HRTEM of CoAg/CN are shown in Figure 4c,d, respectively. The CoAg particles appear to be spherical in nature with the size being much greater than the Co particles in Co/CN. The HRTEM image of CN/CoAg shows interplanar spacing ‘d’ = 0.23 nm corresponding to (111) plane of Ag, along with ‘d’ = 0.203 nm that corresponds to Co as in case of Co/CN nanoparticles.
Techniques as shown in Fig. 1, along with 'd' values, indicate that potential density in oxygen saturated solution. From the LSV curves in this study, electrode (to measure the potentials that were converted to potentials with respect to ORR activity. The experimental data collection was performed using (CV) techniques. The oxygen reduction reaction was studied by linear sweep voltammogram (LSV) and cyclic voltammetry on a carbon electrode. The preliminary catalytic activity of CoAg particles appear to be spherical in nature with respect to (111) plane of Ag, similar to (111) plane of Co. Figure 2 shows the homogeneous distribution of Co particles on the surface, as shown in the SEM images of CoAg/CN and Co/CN. The HRTEM image exhibits the d-spacing calculation for Ag and Co particles. Figure 4 depicts lattice fringes of Co NPs, with an interplanar spacing 'd' = 0.203 nm corresponding to (111) plane of Co.

By comparing the ORR activity of Co/CN and CoAg/CN, the LSV polarization curves indicate that CoAg/CN performs better than Co/CN. Co(OH)2 on the surface has peaks at 368.3 eV and 374.6 eV due to XPS analysis of Co3d. In addition, two satellite peaks are found at 370.9 eV and 377 eV. These two peaks correspond to a shift in 3d orbitals, which infers a possible bond between silver and oxygen that is accompanied by successive anodic shifts in the onset potential of Ag(0) [23].

The mottled porous fibrous structure with uniform consistency of CN is evident in the FESEM images of Co/CN and CoAg/CN. Remarkable increase in the current density for Co/CN is observed, much greater than the Co particles in the presence of oxygen. The TEM image shows a neard homogeneous porous fibrous structure with uniform consistency of CN, as shown in Figure 3a, and a remarkable increase in the current density for Co/CN is evident. Co(CN)2 //Ag, on CN surface. The HRTEM image of CoAg/CN exhibits the d-spacing calculation for Co. Figure 4b depicts lattice fringes of Co NPs, with an interplanar spacing 'd' = 0.203 nm corresponding to (111) plane of Co. TEM and HRTEM of CoAg/CN exhibit remarkable increase in the current density. TEM and high-resolution transmission electron microscopy (HRTEM) image of Co exhibits the d-spacing calculation for Co and Ag particles. Figure 4a shows the LSV diagram for Co/CN and CoAg/CN, the LSV polarization curves indicate that CoAg/CN performs better than Co/CN. The preliminary catalytic activity of CoAg/CN seems to have a remarkable increase in the current density for Co/CN, much greater than the Co particles in the presence of oxygen.

Figure 3. FESEM images of (a) Co/CN, (b) CoAg/CN.

Figure 4. (a) TEM and high-resolution transmission electron microscopy (HRTEM) image of Co/CN. (b) HRTEM image shows the d-spacing calculation for Co. (c) TEM and (d) HRTEM image of CoAg/CN. HRTEM image exhibits the d-spacing calculation for Ag and Co particles.
2.1. Application in Oxygen Reduction Reactions

To check the ORR catalytic activity, Co/CN and CoAg/CN catalysts were loaded on the glassy carbon electrode. The preliminary catalytic activity of Co/CN and CoAg/CN catalysts towards the oxygen reduction reaction was studied by linear sweep voltamogram (LSV) and cyclic voltammetry (CV) techniques. The aqueous solution of 1M KOH and the scan rate of 5 mV/sec were used to study ORR activity. The experimental data collection was performed using the Ag/AgCl reference electrode to measure the potentials that were converted to potentials with respect to reversible hydrogen electrode (RHE). There was a negligible response from the bare GCE in the potential window used in this study. Figure 5 shows the LSV diagram for Co/CN and CoAg/CN catalysts in the nitrogen and oxygen saturated solution. From the LSV curves, it is clear (Figure 5a,b) that there is no peak in the nitrogen saturated solution. Both, Co/CN and CoAg/CN exhibit a remarkable increase in the current density in the presence of oxygen that is accompanied by successive anodic shifts in the onset potential. By comparing the ORR activity of Co/CN and CoAg/CN, the LSV polarization curves indicate that CoAg/CN performs better than Co/CN.

The onset potential (E_{onset}) of Co/CN and CoAg/CN are 0.89 V and 0.93 V, respectively. The activity of CoAg/CN is comparable to commercially available Pt/C with E_{onset} is 0.91 V. The LSV polarization curves in Figure 5d reveal that there is an increase in the current density with an increase in the scan rate. The cyclic voltammetry (CV) diagrams for the two electrodes (Figure 6a,b) show that the reduction peaks are absent under N_2 saturated conditions. While after purging with oxygen, the reduction peak in the case of Co/CN was at 0.47 V, while for the CoAg/CN, the reduction peak appeared at
approximately 0.7 V. By comparing Co/CN with CoAg/CN (Figure 6c), the reduction peak for CoAg/CN is more intense and shows an increase in the current density. This better activity of CoAg/CN with respect to Co/CN was also observed with the rotating ring disc cyclic voltammetry (RRDCV). The scan rate 5 mV/sec with a rotating speed 1500 rpm were the parameters taken to run RRDCV for Co/CN with CoAg/CN electrodes. The information from RRDCV (Figure 7) also infers better ORR activity of CoAg/CN than Co/CN. The better activity of CoAg/CN with respect to Co/CN may be due to the synergistic effect of Co and Ag alloy type nanoparticles. The literature reports also convey that the synergistic effect is not only responsible for better activity, but the galvanic exchange approach modifies the surface to enhance the electron transfers [23]. It is quite evident that during galvanic exchange, there are surface modifications, such as voids, which are formed and probably make the galvanic exchange material better electrocatalysts [23,50]. Compared with Pt, Hoon and co-workers have mentioned that the E_{onset} of commercially is 0.91V for ORR, which indicates CoAg/CN to have a comparable onset potential of 0.93V [51].

Figure 6. (a) Cyclo voltammogram diagram of Co/CN after N\textsubscript{2} and O\textsubscript{2} purge. (b) Cyclo voltammogram of CoAg/CN after N\textsubscript{2} and O\textsubscript{2} purge. (c) CV comparison of Co/CN and CoAg/CN at scan rate of 5mV/sec (d) CV of CoAg/CN at different scan rates.
2.2. Application in Carbon Dioxide Conversion

Both the Co/CN and CoAg/CN electrodes were also evaluated for electrocatalytic conversion of carbon dioxide. The CV scans of Co/CN and CoAg/CN electrodes with the RDE disc electrode were scanned between 0.8 and −1.2 V versus Ag/AgCl in 0.5 M KHCO₃ solution at 100 mV/sec scan rate. Figure 8a CV scans show the redox peaks at 0.08 and −0.3 V on the forward and reverse scans, respectively. It is quite clear that the cathodic current increases dramatically after −0.9 V in CO₂ saturated solution, as compared to N₂ saturation where not much activity is seen. The results reveal that there is an active utilization of electrons supplied to the cathode during CO₂ uptake. Figure 8b shows the redox peaks at −0.23, 0.35 on forward −0.13 and −0.9 V on reverse scans, respectively. The number of peaks increased after the CO₂ purge in the forward scan and there is clear sudden jump at approximately −0.9 V in the reverse scan. The reduction peak in the region −0.9 to −1 V indicates the carbon dioxide reduction. Figure 9 compares the activity of Co/CN and CoAg/CN electrodes under CO₂ saturated conditions and clearly depicts the superior performance of CoAg/CN as an active catalyst compared to Co/CN. The current density at −1.2 V jumps to 1.5 mV/cm² for CoAg/CN, almost three times the value for Co/CN, which is 0.55 mA/cm². The nature of the product formed on the surface of the disc electrode was estimated by using RRDE and matching with the oxidation potential of the expected products on the Pt (ring electrode) surface. This analysis was conducted only on the CoAg/CN electrode on the basis of higher activity and expectedly larger amounts of products that can be detected using the ring electrode. As the total amount of active phase on the disc electrode is extremely small, a reasonable amount of product should be present to be detected on the ring electrode. The CoAg/CN electrodes were scanned between 0 and −1.2 V versus RHE, and the ring electrode was held at 0.9 V versus RHE, which is the reported oxidation potential of formic acid on the Pt surface [52]. Figure 10 shows an initial CV scan for the N₂ purged electrolyte and Figure 10b shows the CV for the CO₂ purged electrolyte. The CV graph in Figure 10b reveals that there is an increase in the current density in both the ring and disc currents after purging the CO₂. There is also a peak (Figure 10b) at −0.9 V that corresponds to the formation of formic acid as indicated by a peak in the ring electrode current density. X. Zhu et al. did a series of experiments while scanning the ring electrode between 0 and 1.3 V keeping the disc electrode at −0.4, −0.5, −0.6, −0.7, −0.8 and −0.9 V [52]. They concluded that when the disc electrode is kept at a potential of −0.9 V, there is maximum intensity in the oxidation peak due to the conversion of carbon dioxide into formic acid at −0.9 V. The role of the ring electrode here is to oxidize the product formed due to CO₂ conversion. In order to maximize the product form, the disc electrode was kept at −0.9 V and the Pt-ring electrode was scanned between 0 and 1.3V to examine the oxidation potential of the product generated on the disc electrode. As shown in Figure 11, an oxidation
peak at 0.9 V is observed, which indicates the conversion of CO\textsubscript{2} to formic acid on the CoAg/CN surface [43]. Figure 12 shows a possible reaction pathway for CO\textsubscript{2} conversion on the CoAg/CN surface. The CO\textsubscript{2} molecules initially get adsorbed on the surface of the catalyst. The electron supplied by the cathode transforms CO\textsubscript{2} molecules to carbonate anion, which in the presence of a proton and an electron get converted to bicarbonate ion [8]. The bicarbonate ion in the presence of H\textsuperscript{+} is converted to formic acid and desorbs from the surface of the catalyst.

![Graph showing CV of Co/CN and CoAg/CN](image1)

**Figure 8.** (a) CV of Co/CN in 0.5 M KHCO\textsubscript{3} after N\textsubscript{2} and CO\textsubscript{2} purge (b) CV of CoAg/CN in 0.5 M KHCO\textsubscript{3} after N\textsubscript{2} and CO\textsubscript{2} purge.

![Graph showing CV comparison between Co/CN and CoAg/CN](image2)

**Figure 9.** CV Comparison of CoAg/CN and Co/CN in 0.5 M KHCO\textsubscript{3} at a scan rate of 100mV/sec after CO\textsubscript{2} purge.
Figure 8. (a) CV of Co/CN in 0.5 M KHCO₃ after N₂ and CO₂ purge (b) CV of CoAg/CN in 0.5 M KHCO₃ after N₂ and CO₂ purge.

Figure 9. CV Comparison of CoAg/CN and Co/CN in 0.5 M KHCO₃ at a scan rate of 100mV/sec after CO₂ purge.

Figure 10. Cyclic voltammetry scans of CoAg/CN with RRDE. Disc electrode was scanned between 0 and −1.2 V versus RHE, the ring electrode was held at 0.9 V versus RHE. (a) Initial CV scan for N₂ purged electrolyte. Ring electrode was held at 0.9 V versus RHE. (b) CV scan for the system after CO₂ saturation with the ring held at 0.9 V versus RHE. The experiments were all performed at room temperature. Scan rate: 100 mV s⁻¹. Constant rotation (1500 rpm) was used.

Figure 11. Cyclic voltammetry scan CoAg/CN of the ring electrode when the disc electrode was held at −0.9 V versus RHE. Ring electrode was scanned between 0 and 1.3 V versus RHE. A constant rotation of 1500 rpm was applied in each case. Scan rate: 100mV s⁻¹.
Figure 11. Cyclic voltammetry scan CoAg/CN of the ring electrode when the disc electrode was held at −0.9 V vs RHE. Ring electrode was scanned between 0 and 1.3 V vs RHE. A constant rotation of 1500 rpm was applied in each case. Scan rate: 100 mV s\(^{-1}\).

Figure 12. Possible mechanism of CO\(_2\) conversion to HCOOH on the CoAg/CN surface.

3. Experimental Section

All the chemicals were used as received from the supplier without any further purifications. Urea in its purest form was purchased from Bio-Red laboratories. AgNO\(_3\) (99.8%) was purchased from Samchun chemicals. Co(NO\(_3\))\(_2\)·6H\(_2\)O (98%), NaBH\(_4\) (98%), perfluorinated nafion, isopropyl alcohol were purchased from Sigma-Aldrich. Millipore water was used in all our experiments.

3.1. Synthesis of Carbon Nitride

The synthesis of CN was carried out by following the procedure mentioned in the literature [53,54]. CN in a powdered form was obtained by heating urea for 3 h at 550 \(^\circ\)C. Initially, the carbon and nitrogen rich urea (10 g) was dried in a water bath. The dried urea was transferred in a ceramic crucible covered with a lid and placed inside a muffle furnace that was set at 550 \(^\circ\)C. After 3 h of heating, a CN (a yellow colored powder) was obtained, which was cleaned with 0.1 M nitric acid and then dried at 80 \(^\circ\)C for 30 min.

3.2. Synthesis of Co/CN

Further, 40 mg of CN powder was sonicated in 40 mL water for 15 min. Cobalt nitrate hexahydrate (0.116 g) was added in the solution to make the final concentration of the solution 10\(^{-2}\) M. The mixture was stirred for 2 h, and thereafter 0.151 g of NaBH\(_4\) was slowly added to the reaction mixture. The stirring was continued for the next 3 h. Finally, the mixture was separated, cleaned 3 times with water and 1 time with ethanol in order to remove the impurities. After this procedure, the powder was dried at 80 \(^\circ\)C for 1 h to get Co/CN powder.

3.3. Synthesis of CoAg/CN Bimetallic NPs

The galvanic approach was applied to synthesize the bimetallic NPs from Co/CN monometallic NPs. A 20 mg of synthesized Co/CN powder was added in a beaker containing silver nitrate solution (10 mL of 10\(^{-2}\) M). The mixture was sonicated for 15 min. A change in color, from green to black, was observed during the addition of Co/CN NPs. After sonication, the mixture was stirred for 1 h. Then,
the product was subjected to cleaning, 3 times with water and 1 time with ethanol, in order to remove the impurities. After this procedure, the powder was dried at 80 °C for 1h to get CoAg/CN powder. The overall synthetic procedure is shown in Scheme 1a.

![Scheme 1. (a) Schematic representation for the synthesis of Co and CoAg bimetallic nanoparticles on a carbon nitride (CN) surface via galvanic exchange. (b) Schematic of the rotating ring disc electrode (RRDE) used for the carbon dioxide electrocatalytic reduction.](image)

### 3.4. Characterization Techniques

Powder X-ray diffraction measurements were performed with a Rigaku Mini Flex II Desktop X-ray powder diffractometer (Rigaku, Leatherhead, UK) with Cu-Kα radiation at 25 °C to determine the crystallinity of Co/CN and CoAg/CN nanocomposites. PXRD was recorded using 2θ = 10–80° with 2° per min scan rate. To check the surface morphology, a scanning electron microscope (Nova Nano 450, FEI Waltham, MA, USA), with magnification up to 200 kx was used. The TEM analysis was performed using a high-resolution transmission electron microscopy (HRTEM, TECNAI G²). The carbon coated copper grids with 400-mesh were used during sample preparation. A mixture of water/ethanol solution was used to prepare the dispersed solution of the samples by soninating them for 30 min. A 20 µL volume of the dispersed solution was drop casted on the surface of the TEM grid and dried before using in the electron microscope. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, Manchester, UK) was used to analyze the surface composition and oxidation states of the elements in the synthesized NPs.
3.5. Electrode Preparation

An ink containing 3mg of the catalyst 100 µL of isopropyl alcohol, 40µL nafion solution and 40 µL of DIW was prepared for electrocatalytic activity measurements of the NPs. The mixture was taken in a 20 mL of a glass vial and sonicated for 15 min. A 5 µL of ink was drop casted on GCE (PINE Research Instruments, RDE, d = 5.0 mm and geometric area, A = 0.196 cm²). The oxygen saturated 1M KOH was used as an electrolyte during electrochemical measurements for ORR, whereas a 0.5M KHCO₃ saturated with CO₂ was used for CO₂ conversion studies. The details of the scan rate and applied voltage are provided in the results and discussion section to avoid repetition. A rotating ring disc electrode (RRDE) assembly was used to conduct the electrocatalytic conversion reaction of carbon dioxide. A schematic of the RRDE assembly is shown in Scheme 1b, whereas a detailed description is provided in the results and discussion section.

4. Conclusions

A bimetallic alloy of CoAg was synthesized on the CN surface via a galvanic exchange process. First, the Co NPs were synthesized on the CN surface using NaBH₄, a strong reducing agent. The Co NPs were used as sacrificial atoms to be replaced by Ag NPs because of the low reduction potential of Co²⁺ as compared to Ag⁺. The electrocatalytic performance of both the catalysts, Co/CN and CoAg/CN, were evaluated for oxygen reduction reaction and carbon dioxide conversion. The CoAg/CN catalyst showed superior performance than Co/CN, for both ORR and CO₂ conversion reactions. The RRDE experiments indicate the reduction of CO₂ to formic acid on the CoAg/CN surface. The higher activity of CoAg/CN than Co/CN is credited to the synergistic effect of the alloy type CoAg NPs and the change in surface morphology of CoAg/CN during the galvanic exchange process.

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