



OPEN Decoration of Ag nanoparticles on CoMoO₄ rods for efficient electrochemical reduction of CO₂

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Hydrothermal and photoreduction/deposition methods were used to fabricate Ag nanoparticles (NPs) decorated CoMoO₄ rods. Improvement of charge transfer and transportation of ions by making heterostructure was proved by cyclic voltammetry and electrochemical impedance spectroscopy measurements. Linear sweep voltammetry results revealed a fivefold enhancement of current density by fabricating heterostructure. The lowest Tafel slope (112 mV/dec) for heterostructure compared with CoMoO₄ (273 mV/dec) suggested the improvement of electrocatalytic performance. The electrochemical CO₂ reduction reaction was performed on an H-type cell. The CoMoO₄ electrocatalyst possessed the Faraday efficiencies (FEs) of CO and CH₄ up to 56.80% and 19.80%, respectively at −1.3 V versus RHE. In addition, Ag NPs decorated CoMoO₄ electrocatalyst showed FEs for CO, CH₄, and C₂H₆ were 35.30%, 11.40%, and 44.20%, respectively, at the same potential. It is found that CO₂ reduction products shifted from CO/CH₄ to C₂H₆ when the Ag NPs deposited on the CoMoO₄ electrocatalyst. In addition, it demonstrated excellent electrocatalytic stability after a prolonged 25 h amperometric test at −1.3 V versus RHE. It can be attributed to a synergistic effect between the Ag NPs and CoMoO₄ rods. This study highlights the cooperation between Ag NPs on CoMoO₄ components and provides new insight into the design of heterostructure as an efficient, stable catalyst towards electrocatalytic reduction of CO₂ to CO, CH₄, and C₂H₆ products.

The dramatic increase in CO₂ concentration in the atmosphere leads to notable environmental issues¹. So, the conversion of CO₂ into valuable chemical products plays a vital role to minimize the greenhouse effect and maintain the global carbon balance that has recently attracted significant attention to researchers^{2–6}. Among different CO₂ conversion strategies, the electrochemical CO₂ reduction reaction (CO₂RR) reveals a perfect approach for usable chemicals and fuels productions^{7,8}. The combination of carbon-based electro-fuel production from CO₂RR with renewable energy exhibits the great hope of global carbon neutrality. However, slow reaction kinetics lowers the performance of the electrocatalyst for CO₂RR^{9,10}. Therefore, fabrication of a novel electrocatalyst is urgent to solve the problems related with sluggish kinetics and high overpotential.

Ag has been regarded as a promising CO₂RR catalyst due to its relatively low overpotential, high selectivity, tendency of lowering the CO₂ reduction reaction barrier, better solubility of CO₂, electron transfer, improvement of local catalytic environment, suppression of hydrogen evolution reaction (HER), and appropriate (neither too strong nor too weak) binding strength with products^{11–13}. It is considered as a benchmark electrocatalysts for selective conversion of CO₂ to CO with good Faradic efficiencies. Despite these advantages, pure Ag NPs suffer from maintaining the size/structure, high-cost, and stability due to their high level of surface energy¹⁴. So, the construction of heterostructure interface between pure metal and low-cost metal oxide materials is a perfect choice because it induces synergistic effects to promote the stability/selectivity/electrocatalytic efficiency, reduce the overpotential, and conversion of CO₂ to CO, C1 and multi-carbon products^{10,14}.

Nowadays, Ag NPs have been coupled with several metal oxides such as TiO₂, CuOx, Cr₂O₃, MnO₂, SnO₂, etc. for CO₂RR. However, these oxide materials suffer from low conductivity and insufficient catalytic performances^{15–19}. Also, these heterostructures cannot produce C₂ (C₂H₆) during electrocatalytic CO₂RR. To solve these issues, selecting cobalt molybdate (CoMoO₄) is the best metal oxide material because Co-based oxides provide excellent catalytic activities and Mo-based materials demonstrate outstanding electrical conductivity²⁰. Also, the synergistic integration of Co and Mo improves the electrocatalytic properties of CoMoO₄. In addition, it has several advantages such as stable crystal structure, redox performance, favorable physical/chemical properties, enhancement of electrolyte–electrode surface area, excellent mechanical stability, ionic conductivity, generation of active sites, small overpotential, environmentally friendly, inexpensive, and abundant resources^{21–25}. The

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multiple oxidation states of cobalt involved at the intermediate state for CO₂RR²⁶. Furthermore, rods like structure or nanorods can contribute a higher contact area along with great electron pathways than other morphologies²¹. Although lots of paper has been published for Ag NPs towards CO₂RR, Ag NPs decorated CoMoO₄ rod heterostructure has rarely been reported for CO₂ reduction to CO, C1 and multi-carbon compounds.

In this study, Ag/CoMoO₄ heterostructure was synthesized by hydrothermal and photoreduction/deposition methods. The hydrothermal method revealed several advantages as compared to others, such as low cost, mass efficiency, high product purity, mild preparation conditions, and simple equipment^{20,24,27–31}. In addition, photoreduction process is simple and inexpensive and can be operated at room temperature³². The formation of heterostructure is well characterized by X-ray diffractometry (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), elemental mapping, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and Inductively coupled plasma optical emission spectroscopy (ICP-OES). The electrochemical measurements (cyclic voltammetry, electrochemical impedance spectroscopy, linear sweep voltammetry, and chronoamperometry) of catalysts were performed in an H-type cell for electrochemical CO₂RR. Tafel plots were analyzed. The gaseous products were detected by gas chromatography (GC). The Faradic efficiencies (FEs) of CO₂RR was calculated, and possible mechanisms were proposed.

Experimental section

Materials

All chemicals consist of analytical grade. These were used without any further purification. Copper foil (CF) with 0.1 mm thickness was purchased from Merck, Germany. Molybdic acid (H₂MoO₄) and cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O], potassium bicarbonate (KHCO₃), and aqueous ammonia (aq. NH₃) were used for the synthesis of samples and obtained from the Sigma-Aldrich. Silver nitrate (AgNO₃) was purchased from Fisher chemical, Belgium.

Synthesis of CoMoO₄ and Ag/CoMoO₄

CoMoO₄ was synthesized from hydrothermal process. In this synthesis technique, 2×10^{-2} mol of H₂MoO₄ was placed in 40 mL of water. In addition, 2×10^{-2} mol of Co(NO₃)₂·6H₂O was dissolved in 40 mL of water. These were magnetically stirred until clear solution was obtained. Then, the prepared solutions were mixed dropwise by using pipette under magnetic stirring and precipitation was occurred. The pH of the solution was adjusted at pH 7 by using aqueous ammonia (NH₃). It was magnetically stirred for 4 h. After that, the suspension solution was transferred into a 100 mL Teflon-lined stainless autoclave and kept at 200 °C for 4 h. After completion of hydrothermal treatment, the solution was centrifuged and washed with water and ethanol multiple times. Subsequently, it was dried in a vacuum oven at 70 °C for 8 h. The powder was obtained and calcined at 400 °C for 5 h. At last, the powder sample (CoMoO₄) was grounded with the help of mortar and piston.

Ag/CoMoO₄ was fabricated by hydrothermal followed by photoreduction/deposition techniques. According to this technique, hydrothermal synthesized 1 g of CoMoO₄ powder was taken and placed in 100 mL beaker. 80 mL ethyl alcohol (C₂H₅OH) was put in a beaker and magnetically stirred for 2 h. 5 wt% of Ag (source: AgNO₃) was placed in a beaker and magnetically stirred for 4 h under UV light irradiation. After this step, it was centrifuged and washed with water/C₂H₅OH several times. The obtained sample was dried in a vacuum oven for 70 °C for 4 h. Finally, it was grounded. The schematic illustration of material synthesis was presented in Fig. S1.

Material characterization

The crystal phase was determined using a powder X-ray diffractometer (Rigaku, Miniflex 600) with Cu K α radiation (2θ : 20 to 80°, continuous rate: 1°/minute, and step: 0.02). The morphologies of samples were investigated by field emission scanning electron microscopy (FESEM, JEOL, JSM-IT800). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected area diffraction patterns (SAED), EDS elemental mapping images were obtained by JEOL 1230. The X-ray photoelectron spectroscopy (XPS) analysis of the samples was performed using Thermo Scientific ESCALAB™ XI (Al K α and 200 eV). The Raman spectra of samples were measured on Horiba Raman confocal microscope. Fourier-transform infrared spectroscopy (FTIR) of samples were measured on IRTracer-100 (Shimadzu). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to find the leaching of Ag NPs after performance of electrochemical CO₂ RR by samples. It is also used to find out the metal ions in the samples. The detail explanation was provided in supporting information (Figs. S2, S3, and S4). Zeta potential of powder samples was measured by Zetasizer Nano ZS (Malvern Instruments, Malvern, UK). The powder was dispersed in 70% ethanol (15 mL) and placed in an ultrasonic bath for 1 h. The zeta potential was measured after diluting the samples with distilled water.

Electrochemical characterizations

All the electrochemical measurements were carried out on a CH Instruments with a typical three-electrode system in 0.5 M KHCO₃ electrolyte solution at room temperature, a platinum electrode (counter electrode), Ag/AgCl electrode (reference electrode), and working electrodes (CoMoO₄ and Ag/CoMoO₄). For the synthesis of working electrodes, 0.5 mL of C₂H₅OH, 50 μ L nafion, and 4 mg of powder sample were dispersed via ultrasonic processing. As a substrate, CF (2 cm $\times$ 2 cm) was washed with water and ethanol for 60 min under ultrasonication and dried at 70 °C for 4 h in a vacuum oven. The well-dispersed ink was placed in CF via controllable drop casting. The available working area in the electrode was 1 cm². Then, it was dried in an oven at 70 °C for 4 h.

Cyclic voltammetry (CV) with scan rate 20 to 150 mV/s of samples was measured. In addition, the electrical conductivity of the samples was performed through the electrochemical impedance spectroscopy (EIS)

that consists of 0.1 Hz to 100,000 Hz. The linear sweep voltammetry (LSV) of the samples was observed from 0 to -0.6 V versus RHE at scan rate 10 mV/s. Tafel plots were obtained at potential -1 to 1 V. The reversible hydrogen electrode (RHE) was calculated using following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \text{ pH}$ ($0.5 \text{ M KHCO}_3 \sim 8.52$), where $E_{\text{Ag/AgCl}}$ represents potential against the reference electrode and 0.197 V indicates the standard potential of Ag/AgCl at 25°C ³³.

The electrochemical CO_2RR was performed on H-type cell. A 50 mL electrochemical cell was used that consists of 35 mL electrolyte. The anodic and cathodic compartments were separated by Nafion 117 membrane. This membrane was washed with acid/water before using in H-type cell. A stream of pure (99.999%) CO_2 gas was continuously passed in the cell for saturation of electrolyte for 60 min at 5 sccm using mass flow controller (MC-100SCCM-D, Alicat Scientific). The gas outlet of H-type cell (cathodic compartment) was connected to a gas chromatograph (SRI 8610C). The GC is equipped with flame ionization detector (FID) for determining hydrocarbon and CO products during electrochemical CO_2RR . The carrier gas for FID is helium GC was calibrated using standard gas mixtures (ARC3) under 1 atm and 298 K. Amperometry $i-t$ experiments were conducted at fixed potentials -1.3 V versus RHE. The first injection of gas in GC was performed 400 s after the start of CO_2 reduction. The different concentration of gases in ppm was noted and Faradic efficiencies were calculated on -1.3 V versus RHE. (Supplementary information). In addition, electrocatalytic stability was evaluated for 25 h under similar applied potential. For comparison of efficiency of electrocatalyst, electrocatalytic performance of the copper foil was carried out.

Results and discussion

Characterization of synthetic materials

As shown in Fig. 1, XRD patterns of samples were well matched with monoclinic structure of pure $\alpha\text{-CoMoO}_4$ with space group $C2/m$ (JCPDS No. 21-0868)²⁵. After deposition of Ag NPs on CoMoO_4 , new crystal plane (111) was appeared that suggests the existence of cubic Ag NPs with JCPDS No. 4-0783³⁴. In addition, the intensities of XRD peaks were slightly reduced in Ag/ CoMoO_4 sample. Besides, it should be noted that the peak position of CoMoO_4 was not shifted, which suggested no substitutional doping. No impurities diffraction peaks were found in samples. The existence of Ag and CoMoO_4 in Ag/ CoMoO_4 suggest the successful fabrication of heterostructures.

The morphologies of synthesized materials were investigated by FESEM and TEM. The samples presented rod-like morphology with dimensions of $1\text{--}3 \mu\text{m}$ in length and $0.3\text{--}1 \mu\text{m}$ in width (Fig. 2a and b). The existence of Ag NPs on the CoMoO_4 rods was also observed in Fig. 2b. In addition, the loading of Ag NPs on CoMoO_4 rods did not change the morphology of materials. Figure 2c and d presented the TEM image of Ag/ CoMoO_4 . This image revealed the decoration of Ag NPs on the surface of CoMoO_4 rods. It also indicates the uniform distribution of Ag NPs on rods. The interplanar spacing of 0.33 nm and 0.23 nm calculated from Fig. 2e were corresponds to the (002) and (111) crystal planes of CoMoO_4 and Ag, respectively which are also strongest peak in the XRD spectrum. All the interplanar spacing calculated from HRTEM image are well consistent with crystallographic plane of CoMoO_4 and Ag. SAED patterns suggested the poly-crystalline nature of Ag/ CoMoO_4 (Fig. 2f). As shown in Figs. 2g–k and S5, the TEM-EDS mapping/spectrum of Ag/ CoMoO_4 indicated the existence as well as homogenous distribution of Co, Mo, O, and Ag (Table S1). According to the results of XRD, FESEM, TEM, HRTEM, SAED, and TEM-EDS elemental mapping images, it was concluded that the heterostructure was successfully formed between CoMoO_4 and Ag NPs.

The existence of elements and oxidation states in CoMoO_4 and Ag/ CoMoO_4 were investigated using XPS technique (Fig. 3). The Co 2p spectra of samples could be deconvoluted into $2p_{3/2}$, (CoMoO_4 : 781.12 eV and

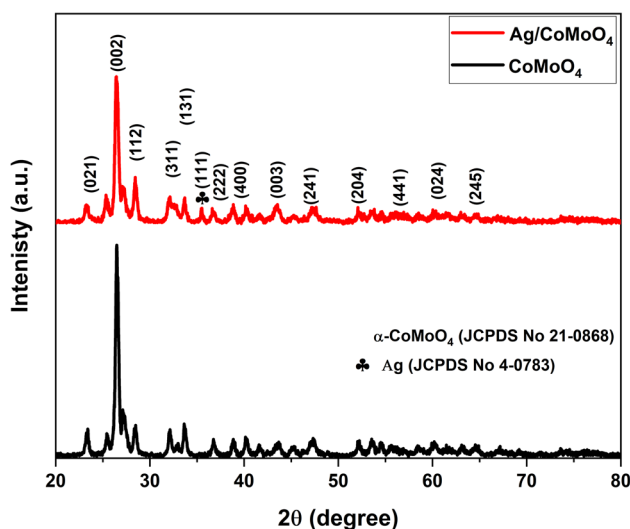


Figure 1. XRD analysis of CoMoO_4 and Ag/ CoMoO_4 samples.

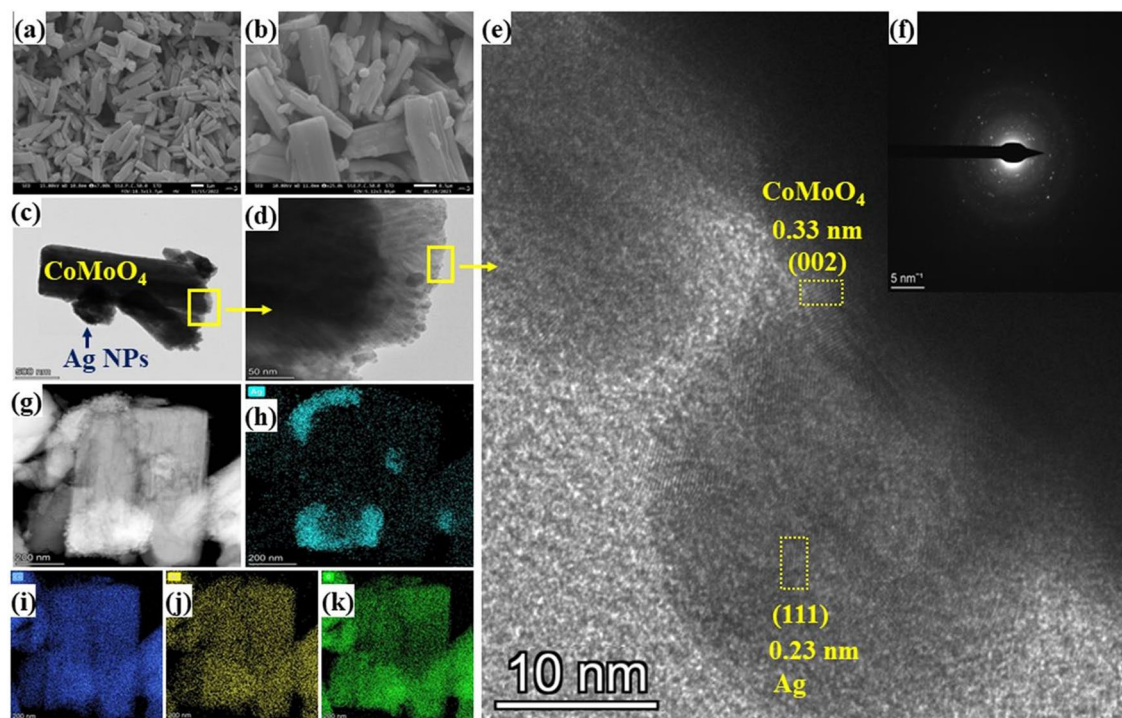


Figure 2. FESEM of (a) CoMoO_4 and (b) Ag/CoMoO_4 , (c and d) TEM, (e) HRTEM, (f) SAED pattern, (g–k) TEM elemental mapping (g: EDS layered image, h: Ag, i: Co, j: Mo, and k: O) images of Ag/CoMoO_4 . Scale bar (a: 1 μm , b: 0.5 μm , c: 500 nm, d: 50 nm, e: 10 nm, f: 5 nm⁻¹, and g–k: 200 nm).

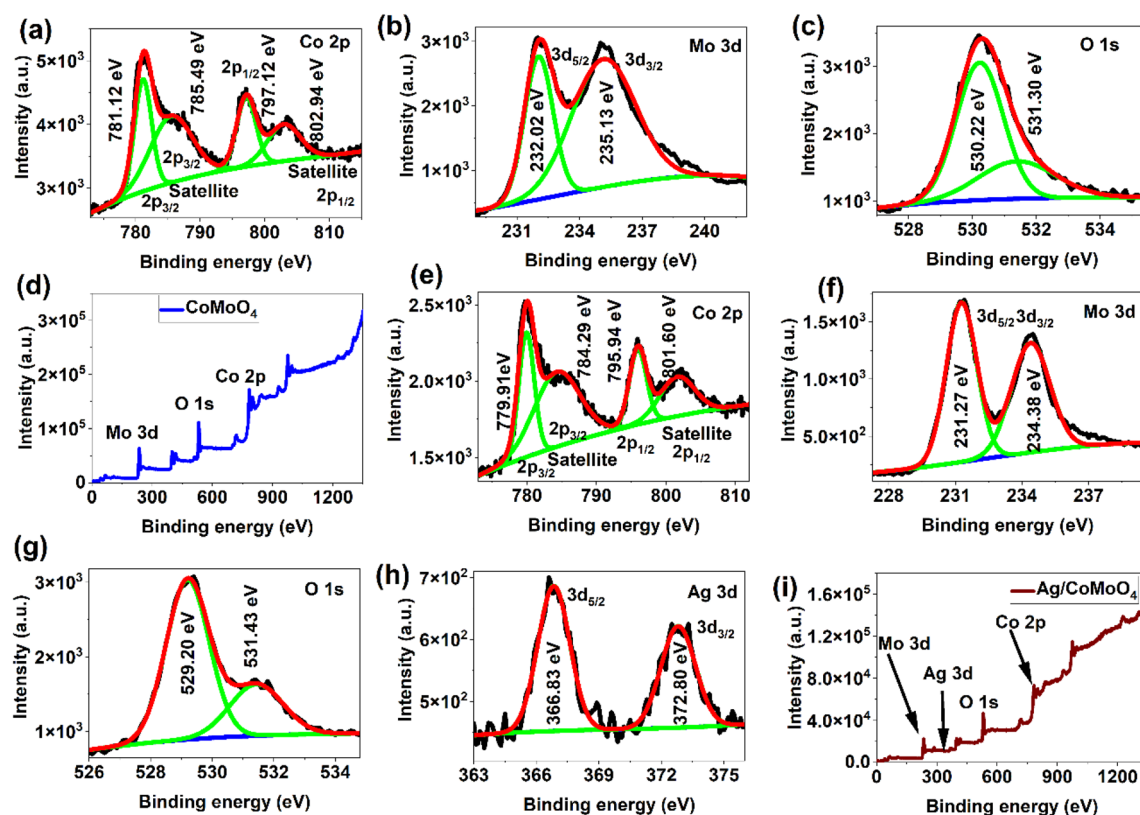


Figure 3. XPS spectra of CoMoO_4 (a–d) and Ag/CoMoO_4 (e–i).

Ag/CoMoO₄: 779.91 eV), satellite 2p_{3/2} (CoMoO₄: 785.49 eV and Ag/CoMoO₄: 784.29 eV), 2p_{1/2} (CoMoO₄: 797.12 eV and Ag/CoMoO₄: 795.94 eV) and satellite 2p_{1/2} (CoMoO₄: 802.94 eV and Ag/CoMoO₄: 801.60 eV) peaks that suggests the Co²⁺ oxidation state in samples (Fig. 3a and e)³⁵. The Mo 3d spectra were fitted into two peaks 3d_{5/2} (CoMoO₄: 232.02 eV and Ag/CoMoO₄: 231.27 eV) and 3d_{3/2} (CoMoO₄: 235.13 eV and Ag/CoMoO₄: 234.38 eV). It clearly shows the presence of Mo⁶⁺ in samples (Fig. 3b and f)³⁶. In addition, 0.75 eV and 1.2 eV shift of the binding energy were observed in Mo 3d and Co 2p peaks, respectively. It suggests the evidence for interaction between the CoMoO₄ and Ag³⁷. According to XPS results of O1s spectra, O²⁻ species in lattice (CoMoO₄: 530.22 eV and Ag/CoMoO₄: 529.20 eV) and oxygen vacancies (CoMoO₄: 531.30 eV and Ag/CoMoO₄: 531.30 eV) or defects were observed (Fig. 3c and g)³⁸. As shown in Fig. 3h, the presence of metallic Ag NPs in Ag/CoMoO₄ was proved by 3d_{5/2} and 3d_{3/2} peaks at 366.83 eV and 372.80 eV, respectively³⁹. Furthermore, the survey spectra suggested the confirmation of Co, Mo, O, and Ag in samples (Fig. 3c and g). Also, the results of ICP-OES indicated the presence of metallic ions (Co, Mo, and Ag) in samples (Supporting information). To find the surface charge in samples, the zeta potential of CoMoO₄ and Ag/CoMoO₄ was evaluated. The zeta potential of CoMoO₄ and Ag/CoMoO₄ was -12.30 mV and -15.33 mV, respectively. This results suggests that the surface of both samples are negatively charged.

Raman spectra of CoMoO₄ and Ag/CoMoO₄ was shown in Fig. S6. The vibrational modes were found at 926, 869, 808.70, and 355.61 cm⁻¹. The Raman mode located at 926.51 cm⁻¹ was associated with symmetric stretching mode of doubly coordinated bridging oxygen in Mo-O⁴⁰. The band at 869.20 cm⁻¹ was related to the symmetric stretching of Co-O-Mo bond. In addition, the band observed at 808.08 cm⁻¹ can be attributed to the asymmetric stretching mode of oxygen in O-Mo-O⁴¹. The symmetry bending modes of O-Mo-O was observed at 355.61 cm⁻¹⁴². The decoration of Ag NPs on CoMoO₄ did not alter the Raman bands that suggest the fabrication of heterojunction between Ag NPs and CoMoO₄. Furthermore, FTIR studies were performed of CoMoO₄ and Ag/CoMoO₄ over the range 500–4000 cm⁻¹ (Fig. S7). The band in lower frequency region (CoMoO₄: 692.90 cm⁻¹ and Ag/CoMoO₄: 632.96 cm⁻¹) was associated with Co-Mo-O stretching vibrations⁴³. The peaks appeared in CoMoO₄ (779.75, 832.78, and 926.54 cm⁻¹) and Ag/CoMoO₄ (779.76, 846.01, and 933.40 cm⁻¹) were assigned to Mo-O stretching bands⁴⁴. These bands provided the evidence of CoMoO₄ in samples.

Electrochemical CO₂ reduction

As shown in Fig. 4a and b, CV curves of CoMoO₄ and Ag/CoMoO₄ nanorods were recorded in a potential window of -0.6 to 0.6 V at different sweeping rates (20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s, 100 mV/s, and 150 mV/s). The observed redox peaks may be attributed to reversibly changing their oxidation states of Co²⁺ and Co³⁺⁴⁵. These redox peaks were obtained from redox mechanism that reveals the Faradic capacitive behavior of the CoMoO₄ and Ag/CoMoO₄ electrodes. In addition, the enhancement of conductivity by molybdenum (Mo) can improve the electrochemical performances of electrodes²⁸. Also, an increase in sweep rate provided the shifting of the oxidation and reduction peaks of electrodes towards right and left, respectively due to higher internal diffusion resistance. The CV curve area and current increased with increase in scan rate because of

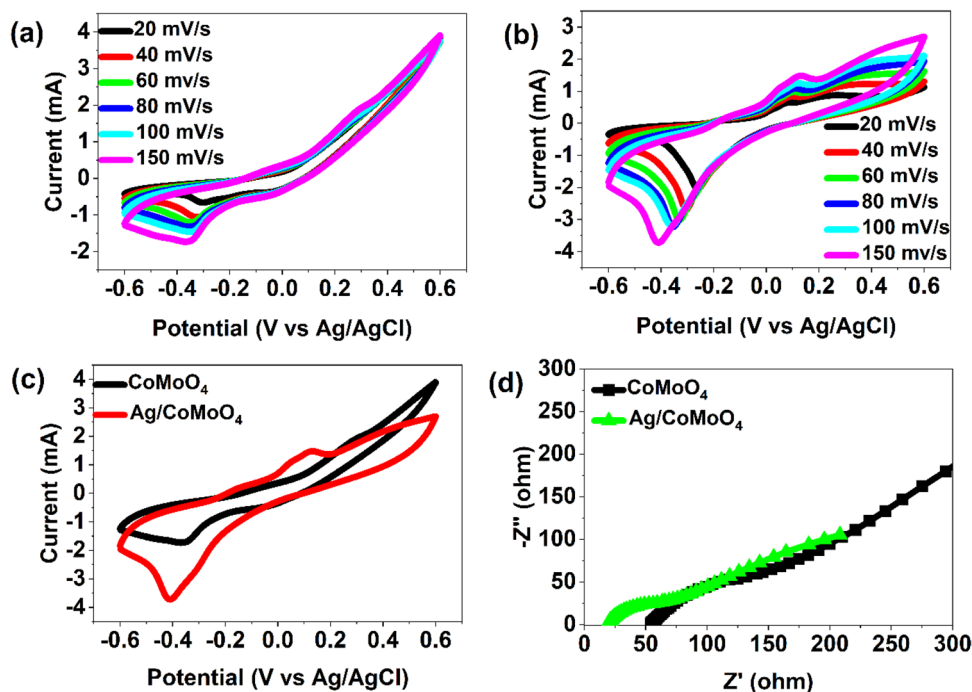


Figure 4. CV (a: CoMoO₄, (b) Ag/CoMoO₄, and (c) comparison of CoMoO₄ and Ag/CoMoO₄) and EIS (d) of samples.

fast reaction kinetics^{27,46}. The shape of CV peaks did not change at high scan rate that suggests the good rate performance of catalyst.

As depicted in Fig. 4c, compared with CoMoO₄ electrode, the increased loop of CV curves was observed for Ag/CoMoO₄ electrodes. In addition, presence of Ag NPs in CoMoO₄ enhanced the reduction ability. These factors indicate the improvement of charge transfer and transportation of ions by making heterostructure between Ag NPs and CoMoO₄. So, the fabrication of heterojunction between Ag NPs and CoMoO₄ rods enhanced the electrocatalytic performance which is beneficial for CO₂ reduction. To observe the effect of Cu-foil in fabricated electrodes, CV curve of Cu-foil was carried out (Fig. S8). It demonstrates the negligible current as compared to CoMoO₄ and Ag/CoMoO₄ CV curves. Also, insignificant contribution of Cu-foil was noted. Also, EIS was measured to observe the interfacial charge transfer on catalysts (Fig. 4d)⁴⁷. The obtained data was fitted, and equivalent circuit was made (Fig. S9). It was composed of solution resistance (R₁), charge transfer resistance (R₂), electric double layer capacitance (C₂), Warburg impedance, and constant phase element (Q). According to the Nyquist plots, Ag/CoMoO₄ (41.57 Ω) demonstrated lower charge transfer resistance in comparison to CoMoO₄ (309.50 Ω) suggesting its rapid electron transfer between the interface of electrolyte and electrocatalyst that may allow efficient electron, Ag NPs and CoMoO₄ interactions (Table S2). Therefore, decoration of Ag NPs on CoMoO₄ rods could promote the electron transportation between the electrocatalyst and CO₂ molecules that provides the electrochemical reduction capability of heterostructure.

The accelerated CO₂RR conversion kinetics upon the heterostructure was further confirmed by Tafel plots (Fig. 5a). The Tafel slope for CoMoO₄ and Ag/CoMoO₄ were estimated to be 273 mV/dec and 112 mV/dec, respectively. The lowest Tafel slope for Ag/CoMoO₄ suggests the enhancement of electrocatalytic activity by fabricating heterostructure between Ag NPs and CoMoO₄ because of rapid electron transfer from the electrode to electrocatalyst. This result also indicates that the transfer of first electron to adsorbed CO₂ molecules. It facilitates the production *CO₂ that can improve a second electron-transfer for *COOH generation⁴⁸. To compare the electrochemical performance of Ag NPs with other non-precious metal particles, Tafel slope was evaluated (Fig. S10). Ag NPs showed lower Tafel slope than Cu indicating great electrochemical performance of Ag NPs that is accordance to published report⁴⁹. Furthermore, the CO₂RR performance of the as-synthesized electrocatalysts was investigated by LSV graphs (Fig. 5c and d). Ag/CoMoO₄ revealed higher current density than CoMoO₄ at -0.6 V. Ag NPs decorated CoMoO₄ rods showed approximately fivefold enhancement of current density in comparison with CoMoO₄ rods (Fig. 5b). The current density of samples along with CO₂-saturated 0.1 M KHCO₃ electrolyte suggest demonstrated higher current density suggesting better reactivity in CO₂RR (Fig. 5c).

Steady-state current responses in a CO₂-saturated electrolyte for 400 s at -1.3 V versus RHE of samples were presented in Fig. S11. The obtained current densities for CoMoO₄ and Ag/CoMoO₄ were -3.35 mA and -4.62 mA, respectively. After that, the gas-phase products were detected by using a GC (Table S3). The FEs for various gas formation of CoMoO₄ and Ag/CoMoO₄ were calculated (Supporting Information)³³. According to Fig. 5d, CoMoO₄ presented FEs for CO and CH₄ were 56.80% and 19.80%, respectively. In this case, CO and CH₄ act as a major and minor gaseous products during CO₂RR, respectively. In addition, Ag/CoMoO₄ revealed FEs for CO and CH₄, and C₂H₆ were 35.30%, 11.40%, and 44.20%, respectively. It was noted that loading of Ag

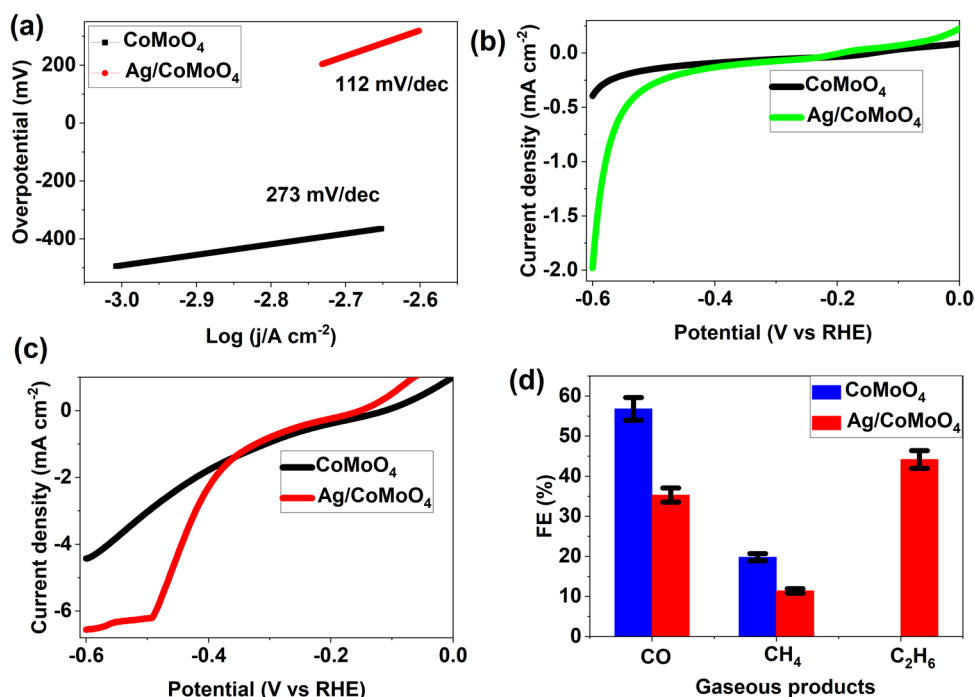


Figure 5. Tafel plots (a), LSV (b: before CO₂ saturated and c: after CO₂ saturated in 0.1 M KHCO₃), and FEs (d) of samples at -1.3 V versus RHE.

NPs on CoMoO₄ reduces the FEs for CO and CH₄, and C₂H₆. These results clearly indicate that C₂H₆ is a major product in Ag NPs decorated CoMoO₄ rods. In addition, electrocatalytic stability of cu-foil was evaluated after a 400 s amperometric test at − 1.3 V versus RHE (Fig. S12). Low current density along with unstable nature were observed. It suggests the Cu-foil did not contribute the significantly for steady-state current responses. Stability curves of Ag/CoMoO₄ at − 1.3 V versus RHE was shown in Fig. S13. Notably, the electrocatalyst exhibited outstanding stability even upto 25 h. Also, the current density was not changed during stability. ICP-OES analysis of electrolyte solution revealed no leaching of Ag ions after 25 h stability test. Table 1 revealed the comparison of FEs of various Ag-based electrocatalysts with Ag/CoMoO₄^{16–19,34,48,50,51}. This Table suggests the fabrication of various morphologies of Ag and Ag-based heterostructure by several techniques for electrochemical reduction of CO₂ to CO and C₂H₄ under different applied potential. Although several gaseous products were found on Ag-based electrocatalysts, electrocatalytic reduction of CO₂ into C₂H₆ by using Ag/CoMoO₄ heterostructure has not yet been reported in the literature.

Based on the above results, the possible reaction mechanisms/pathways were purposed. In CoMoO₄, Co consists of loosely bonded d-electrons that provides the multiple oxidation state. Moreover, transition of Co (II) to Co (I) is considered as an intermediate state for CO₂ reduction²⁶. At first, Co²⁺ is reduced to Co⁺ under the applied potential. When CO₂ is adsorbed on the (002) catalyst surface, oxidation of Co⁺ to Co²⁺ is occurred. Due to this reason, electron is transferred to the adsorbed CO₂ and stabilization of CO₂ radical is happened. Also, the presence of oxygen vacancy in catalyst can improve the stabilization of CO₂ radical¹⁵. After that, CO₂ radical has ability to capture the proton (H⁺) and electron (e[−]) that may dissociate from HCO₃[−] ion to produce COOH* intermediate because of small potential obstacles. Then, this intermediate reacted with H⁺/e[−] continuously to generate CO molecule. The possible reasons for formation of CO as a major product is related with existence of π-back donation between the center of Co metal and CO₂ ligand that can enhance the C–O cleavage⁵². Furthermore, *CO may transform into *CHO via hydrogenation⁵³. The stabilization of *CHO intermediate play significant role for mitigating the overpotential for CH₄ production. This *CHO intermediate may convert into *CH₂O and *CH₃O during transfer of H⁺/e[−] during CO₂RR. Finally, *CH₃O intermediate transforms into CH₄^{53,54}.

The decoration of Ag NPs (111) on the surface of CoMoO₄ rod may reduce the energy barrier for conversion of CO₂ to CO, CH₄ and C₂H₆ products that can change the reactions pathways. C–C coupling mechanism plays a vital role to achieve the high selectivity of C₂H₆ species. The possible reason for generation of C₂H₆ species may associate with existence of active sites in catalyst. According to this mechanism, *CO dimerization process is occurred at the catalyst surface^{53,55}. The double bond between the C and O is broken and proton can attack the O site to form -OH during reaction with H⁺/e[−]. In addition, -OH functional group is eliminated with the reaction with proton to produce H₂O. Due to this reaction, double bonds are created between C to C and C to O. After transfer of two H⁺/e[−], 2H⁺ react with carbon to form HC=CH along with attachment of O on the surface of catalyst. Then, H⁺ may react with double bond containing C to form single bond between carbon along with attachment of O with surface and -CH₂. At last, surface attached O reacts with H⁺ to form H₂O and C₂H₆ is produced. The possible reason for obtaining the higher FEs of C₂H₆ than CO and CH₄ for Ag/CoMoO₄ may associate with higher chance of protonation (*CO → *COH) than desorption of *CO on interface⁵⁶. Also, decrease in FEs for CO and CH₄ of Ag/CoMoO₄ than CoMoO₄ could be related with covering the Ag NPs on CoMoO₄ rods. The synergistic effect between Ag NPs and CoMoO₄ rods can be attributed to generate the CO, CH₄ and C₂H₆.

Conclusion

Ag/CoMoO₄ electrocatalyst was prepared through hydrothermal and photoreduction/deposition methods. The existence of heterostructure between Ag NPs and CoMoO₄ rods was shown by structural and physicochemical characterization techniques. The excellent electrochemical behaviors of catalysts were proved by CV, EIS, LSV, chronoamperometry, and Tafel plots. The electrochemical CO₂RR of CoMoO₄ favored for CO (FEs: 56.80) and CH₄ (FEs: 19.80) at − 1.3 V versus RHE in a H-type cell containing 0.5 M KHCO₃. However, the heterostructure revealed selectivity for reducing mainly CO₂ to C₂H₆ (FEs: 56.80) along with lower FEs for CO and CH₄ at same condition. The selectivity for reducing CO₂ to CO, CH₄, and C₂H₆ by electrocatalyst was attributed to adequate

Catalyst	Synthesis methods	Morphology	FEs	Potential (V vs. RHE/SCE)	References
Ag-Au	Self-assembly	Nanowires/nanosheet	99.0% (CO)	− 0.9	50
Ag	Chemical/photoreduction	Triangular/nanoplates	96.0% (CO)	− 0.856	51
Ag@ZnO@rGO	Hydrothermal/functionalization	Dodecahedral	70.0% (CO)	− 1.6	34
Ag/CuO	Hydrothermal and impregnation	Nanosphere	40.0% (C ₂ H ₄)	− 1.1	48
Ag/CuO	Solution-phase	Nanosheet	91.2% (CO)	− 0.7	16
Ag/Cr ₂ O ₃	Electrochemical	Hexagon	99.6% (CO)	− 0.8	17
Ag/SnO ₂	Oil bath	Sphere	99.2%(CO)	− 0.9	18
Ag/MOx (M = Cr, Sn, Bi, Cu, Pb, and Mn)	Reduction	Dendritic	98.0% (CO)	− 0.7	19
Ag/CoMoO ₄	Hydrothermal and photoreduction	Rods and nanoparticles	35.30% (CO), 11.40% (CH ₄), and 44.20% (C ₂ H ₆)	− 1.3	Our work

Table 1. The comparison of the electrochemical CO₂RR results of this work with other Ag-based electrocatalysts.

active sites, oxygen vacancies, and excellent conductivities. In addition, the synergistic effect of Ag-CoMoO₄ active sites provided the C–C coupling for reduction of CO₂ to C₂H₆ electrocatalytically. The electrocatalyst showed excellent stability upto 25 h without reduction of current density that can be applied for practical application towards electrocatalytic CO₂ reduction. The possible mechanisms/pathways were proposed for CO₂RR. Finally, the outcomes of this work present a new approach for improving electrochemical performances/reduction of CO₂ to CO and hydrocarbon by using the Ag/CoMoO₄ heterostructure catalyst.

Data availability

The data generated or analysed during this study are available within the article and its supplementary material. Raw data of cyclic voltammetry, Electrochemical Impedance, Faradaic Efficiency, IT curves, LSV plot, Tafel plot, Raman, XPS and XRD spectra are provided in supplementary material (Raw data). All other data is available from the corresponding author upon request.

Received: 2 September 2023; Accepted: 8 January 2024

Published online: 16 January 2024

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Acknowledgements

This research was supported by National Science Foundation Excellence in Research Award (2100710) USA. The samples were characterized in the Joint School of Nanoscience and Nanoengineering, a member of the Southeastern Nanotechnology Infrastructure Corridor and National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542174). The authors would like to express their gratitude to Dr. Kiran Subedi and the Analytical Services Laboratory (ASL) at CAES (College of Agriculture and Environmental Sciences) for their assistance with elemental analysis.

Author contributions

S.K.R. did experiment and wrote manuscript. R.D. and M.D.A. contribute in materials characterization and revision of the manuscript. B.P.B. supervised the project and revised the manuscript. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-024-51680-w>.

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