


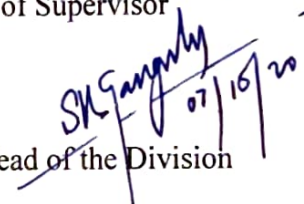
CO₂ mitigation and its simultaneous conversion to chemicals via Photoelectrochemical reduction

Submitted as a part of the requirement for the partial fulfillment of the course work of CSIR
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of Degree of PhD



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Declaration – I, Neha, hereby certify that the work presented in this report entitled “CO₂ mitigation and its simultaneous conversion to chemicals via Photoelectrochemical reduction” in partial fulfillment of the course requirement for the award of the Degree of PhD, being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of Project Research work carried out by me at CSIR-Indian Institute of Petroleum during the period Jan 2019-Aug 2020 and under the supervision of Dr. Suman Lata Jain.

Date 05 Oct. 2020



Signature of the student

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1. Introduction

The concentration of CO₂ in the atmosphere is growing enormously due to the combustion of fossil fuels and tropical deforestation. The excess of CO₂ and other greenhouse gases cause a major problem of global warming. Pointing towards controlling the CO₂ amounts and expanding the new energy storage techniques, CO₂, as a feedstock to produce useful chemicals, turns to be an excellent course to address the issue.¹ Although worldwide carbon balance is led on afforestation, sunlight driven CO₂ conversion dependent on semiconductors utilizing daylight is accepted as one of the generally sensible and alluring alternating ways to reduce CO₂ sums because of solar energy's infinite reservoir and environmental benign measure. Established researchers propose a few methodologies, including controlled discharges of unsafe gases, carbon catch, stockpiling, and use strategies to control the extent of CO₂ in the environment and a few improvements of greener and feasible vitality creation pathways. Even though CO₂ is an ozone harming substance, it is likewise a plentiful carbon source present in the earth. Various potential courses are known to change over CO₂ into commercially important chemicals. For example, thermocatalytic, electrochemical, natural transformation utilizing enzymes, photocatalytic measures, and photoelectrocatalytic processes.² These days, specialists concentrate more upon photocatalysis and electrocatalysis because of being less complicated and energy-efficient. Alongside photoelectrocatalysis, these three procedures are advantageous for the mitigation of CO₂. As in these procedures, the ample sunlight energy is used alongside the electrical energy to drive the reaction. In these reactions, CO₂ either be utilized as a C1 source for the amalgamation of another C1 or higher C synthetic compounds or as an added substance for bigger atoms to include one more carbon-containing gathering to the current one.³

The photocatalytic reduction process is related to the disadvantages, for example, lower product yield, higher recombination pace of electron and hole pair; subsequently, the use level of charge transporters diminishes in the necessary process, which appears to be a significant issue for effective CO₂

transformation. So, it requires an extensive overpotential to change over CO₂ into some useful products via the electrocatalytic redox process. It increases the energy demand for the whole process. A valuable and novel approach to bring down the active obstruction for CO₂ electro-reduction is by selectively modifying the binding energy of the reaction intermediates or by facilitating the charge carrier's excitation using photon energy. These ideas begin the photo-electrocatalytic reduction technique that consolidates the photocatalytic properties with electrochemical action, a productive framework to conquer the energy and activity issues in CO₂ transformation by catalytic materials.⁴ It opens up the route for mandate CO₂ to decrease and makes the cycle more beneficial and successful. PEC measure has a few points of interest as the recombination rate of charge transporters diminished to a minimum level due to applied potential effect, which guarantees the partition of electrons and holes. System overpotential wiped out somewhat, as fractional energy gave by inexhaustible photons that adjust the overall energy utilization. The rate of the reaction and selectivity builds, which relies on applied potential and cathode nature. Due to easy handling and effective results, this technique gains enormous interest. Several studies have been carried out to improve the catalytic material performance and quality, to control the reaction pathway and thermodynamics along with kinetic properties.^{1, 5} The use of semiconductors, particularly TiO₂ as a photocatalyst, is quite known since 1950⁴, but Fujishima and Honda reported great success in photo-electrocatalytic water-splitting reaction.⁶ PEC reduction of CO₂ was first reported by Halmann in 1978, on a p-GaP type semiconductor.⁷ After that, a critical study was described by Inou et al. on powdered semiconductors for CO₂ reduction in the aqueous medium.⁸ These novel studies open up the way of the new energy-saving chemical transformation method. Subsequently, several research groups work on photo-electrocatalysis for its further development and to make it more feasible and useful for the CO₂ conversion. The presented report gives a brief overview of the PEC field along with the catalysts used so far for the production of chemicals from CO₂ reduction. The work also includes catalysts development by the author and its application in the PEC

field. This piece of work points the importance of the PEC field, including the advantages and drawbacks.

2. Basics of PEC process

A simple PEC system for CO₂ reduction is shown in Figure 1. The light-harvesting process and the basic setup of PEC CO₂ reduction is similar to that of the water-splitting design.⁹ The system consists of a semiconducting photoelectrode, a counter electrode, and a reference electrode immersed in the specific electrolytic solution. In most cases, both the electrode chambers are separated by a conducting separation membrane.¹⁰ Both the electrodes are connected via an external circuit.

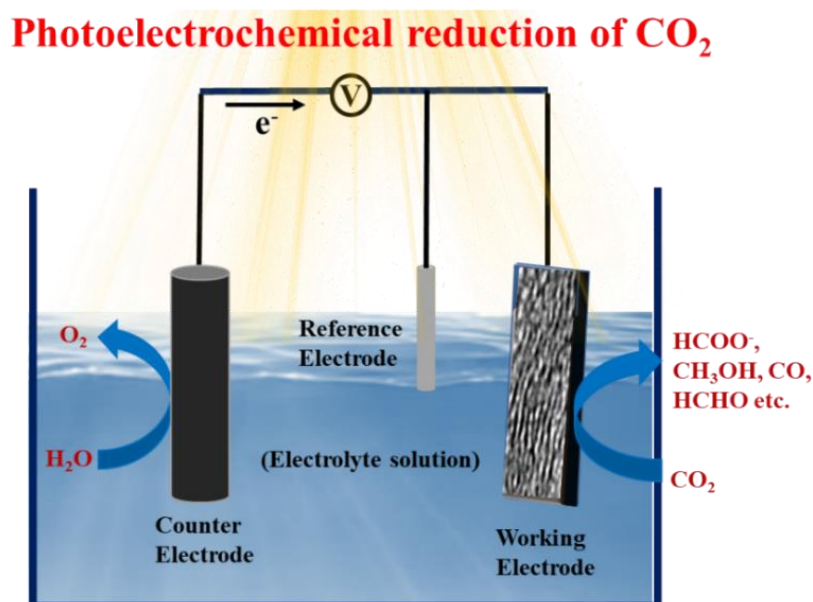


Figure 1: General representation of photoelectrochemical (PEC) CO₂ reduction process

In the presence of light having energy equal to or greater than the bandgap energy (E_g) of photoelectrode material, the valance band (VB) electrons absorb band gap equivalent energy and excite the respective conduction band (CB), creating the holes in VB. With the assistance of externally applied voltage, the electrons and holes migrate to the cathode and anode, respectively. This excess of electrons in CB will help in the efficient reduction of CO₂, and the holes created in VB will enhance the electron gaining tendency of our electrode material. Finally, these electrons reduce the CO₂

molecule, while the holes help in H₂O oxidation to O₂. Some semiconductor material with their band gap value is represented in Figure 2¹¹. Generally, PEC analysis was done in a single compartment cell or H-type cell with two different compartments. Two-compartment cell (H-type) was preferred because it separates the water oxidation chamber from the CO₂ reduction one, with a proton exchange membrane (Nafion). Recently, instead of using a Nafion membrane, a bipolar membrane (BPM) is used to maintain stable pH value in both the compartments. BPM is an anion and cation exchange membrane, which helps the transfer of proton to the cathode and hydroxide ions to the anode^{5b}.

Characteristics of a good photoelectrode

In practice, various characteristics of the photoelectrodes are essential, that must be fulfilled. For example

- the bandgap of photo-electrode must be low enough to collect efficient photons from the solar spectrum and sufficiently high such that the energy of excited electrons can reduce CO₂.
- Photoelectrode must be stable and active in the electrolytic system.
- Must show good surface charge transfer properties.

3. CO₂ reduction catalysts

The semiconductor materials were used as a catalyst for a low-lying valance band (VB) and a higher energy conduction band (CB) with a specific bandgap between them. A semiconductor must have a bandgap which lies in the visible region to be a promising photocatalyst, as sunlight contains only 4% of UV rays ($\lambda < 400$ nm), 53% of visible light ($\lambda = 400-800$ nm), and 43% of IR rays ($\lambda > 800$ nm). As in TiO₂, the bandgap is ~ 3.2 eV, which corresponds to the UV region, and in Cu₂O, it is ~ 2.2 eV, which corresponds to the visible region. There are many available metal oxides and sulfides like WO₃, ZnO, SnO₂, SrTiO₃, CdS, and Fe₂O₃, which are well established and can be used as photocatalytic semiconductors.¹² Some semiconductor material with their band gap value is represented in figure 2. In 1978, Halmann first reported the PEC reduction of CO₂ using p-GaP based semiconductor as a photocathode, carbon rod as an anode, and a saturated calomel electrode as a reference electrode in a

buffer solution of pH 6.8. Upon irradiation and with an external bias of -1.0 V, formic acid was produced in a significant amount.⁷ However, the selectivity of CO₂ reduction is low, and the system facilitates more water reduction. Thus, the need for co-catalyst arises, and the same gives the idea about the use of metal complexes as co-catalysts. Semiconductor acts as the light harvester, and the combined metal complex reduces CO₂ effectively.

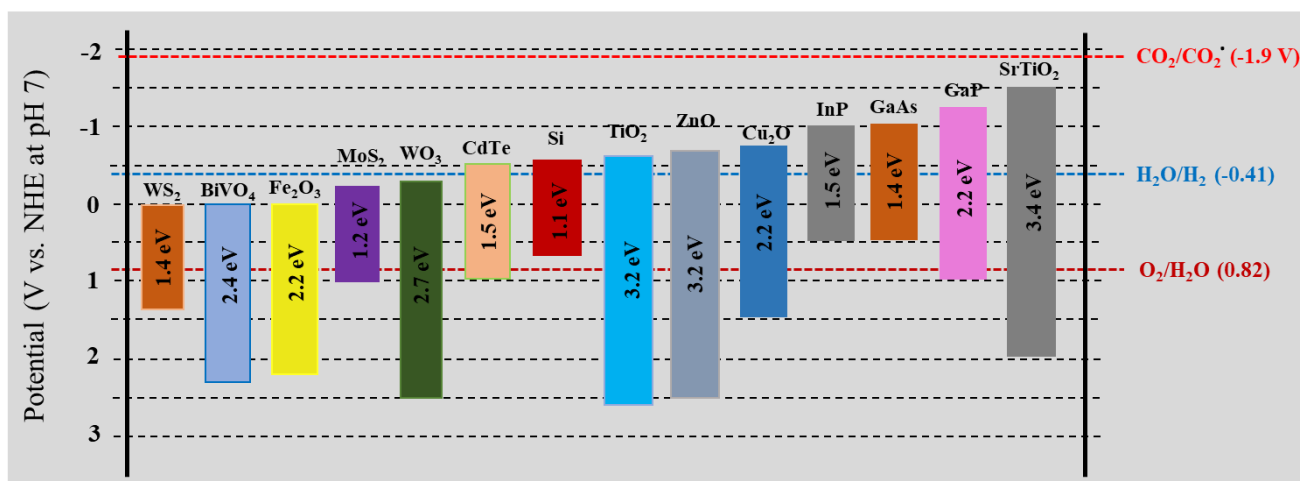


Figure 2: Band gap potentials of various semiconductors vs. Normal Hydrogen Electrode at pH=7

Nowadays, metal complexes are actively used along with the semiconductor material to increase sensitivity and selectivity of the system, where metal complexes immobilized on some semiconductor base are used as a photocathode.¹³ The metal complex is used as an activator for the CO₂ molecule. Often, the metal center offered the multiple oxidation states, which provide the multielectron reduction of CO₂. For an active system, the LUMO of the metal complex must be more positive than the semiconductor used as a light harvester, and more negative than the reduction potential of CO₂. Also, the interfacial interactions between the metal complex and the semiconductor surface play an essential role in electron transfer and hence the efficiency of the process. Some other properties, like physical state and crystallinity, play a major role in defining the activity of a photocatalyst. A highly crystalline semiconductor material exhibits higher activity because of the increase in numbers of photogenerated charge carriers.¹⁴ The molecular complexes are active in both homogenous and

heterogeneous phases. Consequently, a series of homogenous metal complex systems, along with heterogeneous hybrid semiconductor/co-catalysts systems, were developed for PEC reduction of CO₂. Some metal complex catalysts which produce liquid products from PEC CO₂ reduction are displayed in table 1.

Table 1: Some of the reported metal complexes for CO₂ reduction to liquid products by PEC process

Catalyst	Product	Conditions	Ref.
p-type InP/Ru complex	HCOO ⁻ (0.14 mM), TON=12	Purified water as electrolyte, Xe lamp, applied voltage -0.6 V vs. Ag/AgCl for 3 h, glassy carbon counter electrode	15
InP/[MCE2+MCE4]-TiO ₂ /Pt	HCOO ⁻ , TON >17, EFF=70%	10 mM NaHCO ₃ as electrolyte, Xe lamp, 24 h, Ag/AgCl reference	16
CZTS/RuCE	HCOO ⁻ (0.22 mM), EFF=80%	Water as electrolyte, applied voltage -0.4 V vs. Ag/AgCl for 3 h, visible light (400 < λ < 800 nm)	17
InP/RuCP- SrTiO ₃	HCOO ⁻ (1.45 μmol), EFF=71.6%	0.1 M NaHCO ₃ (aq.) + phosphoric acid, no external bias, irradiation for 3 h, Ag/AgCl as reference electrode	18
Co ₃ O ₄ / Ru(bpy) ₂ dppz	HCOO ⁻ (110 μmol), FE=86%	0.1 M aq. NaHCO ₃ as electrolyte, applied voltage -0.6 V vs. NHE, Xenon lamp (λ > 420 nm)	13b
Ru-Pyridine/FTO	CH ₃ OH (24.1 μmol), TON=38.4	0.1 M aq. KCl solution as an electrolyte, external bias -1.0 V vs. NHE for 8 h,	19
Ru-Pyridine/TNTAs	CH ₃ OH (84.8 μmol), TON=62.6	0.1 M aq. KCl solution as an electrolyte, external bias -0.9 V vs. NHE for 8 h, Xenon lamp	13d
[Cu ₂ (asp) ₄]/TiO ₂	CH ₃ OH (0.8 mmol)	0.1 M Na ₂ SO ₄ as an electrolyte, UV-Vis irradiation, external bias -0.35 V vs. SCE	20
CuBTC-rGO/Pt-Cu	CH ₃ OH + C ₂ H ₅ OH, FE=34.1%		21

CuBTC (C-Pd/Cu)	CH ₃ OH + C ₂ H ₅ OH (93.2%)	0.5 M H ₂ SO ₄ as anolyte + DMF as catholyte, external bias -2.0 V, simulated sunlight	22
CoPc-Rs/Fe ₂ O ₃ NTs	MeOH (138 μmol)	0.5 M H ₂ SO ₄ as anolyte + 0.5 M NaHCO ₃ as catholyte, Xenon lamp irradiation 0.1 M NaHCO ₃ as an electrolyte, external bias -1.3 V for 390 min.	23

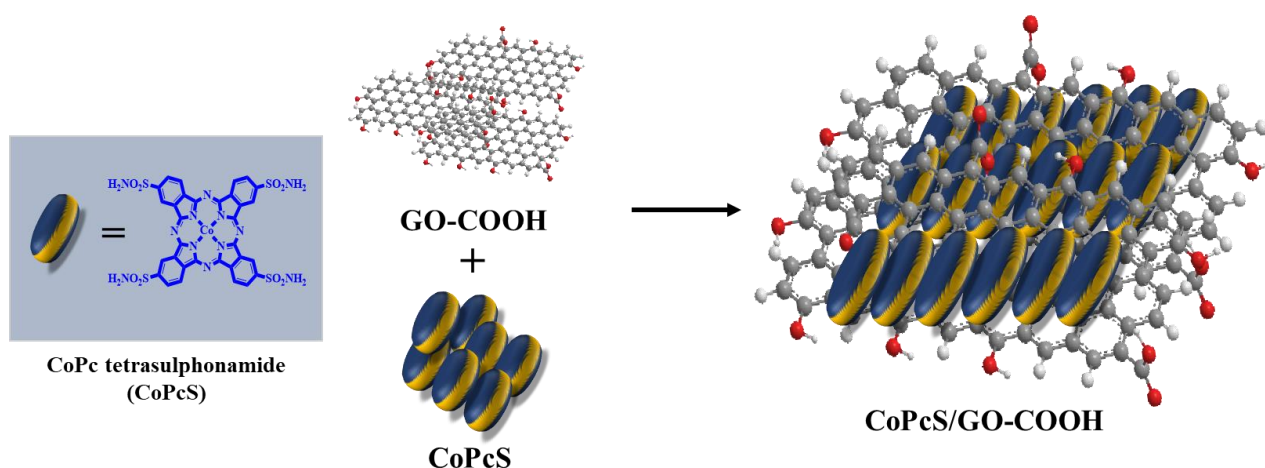
The most popular metal for the reduction of CO₂ is Ruthenium, Rhenium, Copper, and Cobalt.^{13b, 13c, 19-20, 23-24} Some of the active metal complex-based catalysts are displayed in Figure 3.

S. No	Catalyst name
1.	Ru ^{II} -pyridopyrazinophenanthroline ([Ru(phen) ₂ (ptpb)] ²⁺)
2.	Ru ^{II} -2,2'-bipyridine(dipyridophenazine) (Ru(bpy) ₂ dppz)
3.	Ru ^{II} -Pyridine complex
4.	Bipyridyl Rhenium complex (Re(bipy-Bu ^t)(CO) ₃ Cl)
5.	Rhenium-2-(2-pyridyl)benzo[b]-1,5-naphthyridine (Re(pbnHH))
6.	Rhenium-4-vinyl,4'-methyl-2,2'-bipyridine (Re(v-bpy)(CO) ₃ Cl)
7.	Cobalt phthalocyanine (CoPc)
8.	Cobalt-terpyridyl (CotpyP)
9.	Cu(II) aspirinate (Cu ₂ (asp) ₄)

Figure 3: Structure of some CO₂ reduction metal complex catalysts^{13b, 13c, 19-20, 23-24}

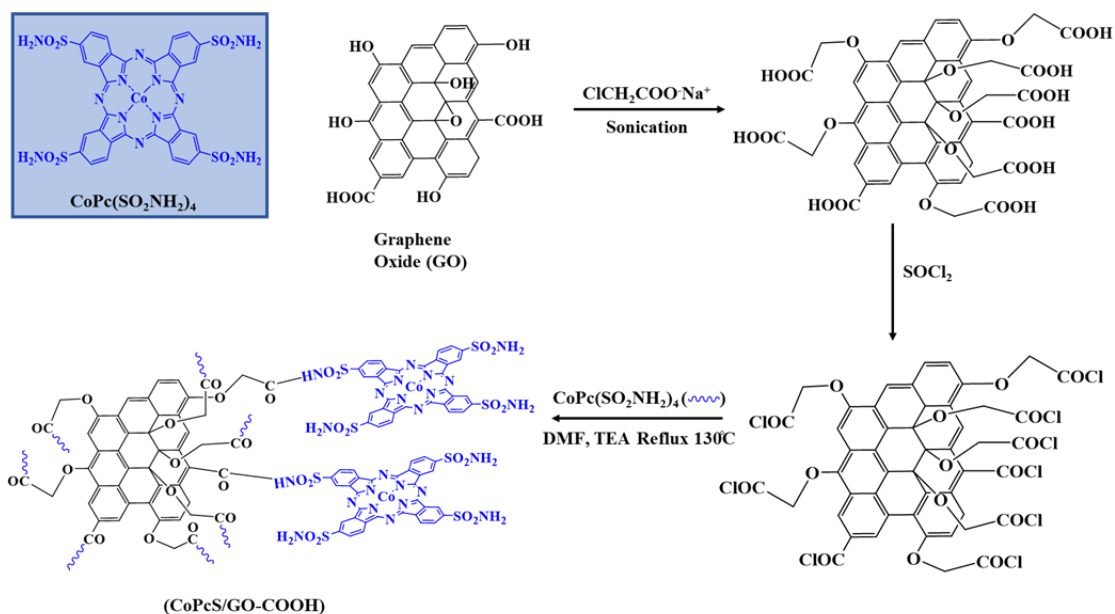
4. PEC reduction of CO₂ using CoPcS/GO-COOH

The presented study aims to develop an efficient molecular hybrid by combining Cobalt phthalocyanine tetrasulphonamide (CoPcS) with carboxylated graphene oxide (GO-COOH), which constructs the potential interface (Scheme-1) for the significant photoelectrochemical reduction of CO₂ into formate under visible light illumination. Based on the molecular and structural characterizations of the synthesized hybrid, we speculated the formation mechanism of CoPcS/GO-COOH to create a proficient interface for PEC CO₂RR under aqueous electrolyte. Notably, the conversion of CO₂ to formate with higher selectivity and current density (-1.7 mA cm⁻²) obtained with the developed hybrid was comparable or superior to the existing noble metal-based catalysts.



Scheme 1: Molecular interactions between CoPcS and GO-COOH constructs the potential interface for CO₂RR.

4.1 Material synthesis



Scheme 2 Scheme for immobilization of CoPcS on carboxylated GO (GO-COOH) to generate molecular hybrid (CoPcS/GO-COOH)

CoPcS was synthesized by a modified protocol²⁵. The carboxylated graphene oxide (GO-COOH) was used as a support matrix for the immobilization of CoPcS units to prepare CoPcS/GO-COOH hybrid. In a typical procedure (Scheme 2), 500 mg of GO-COOH was treated with 10 ml of thionyl chloride (SOCl₂) containing 1 ml dimethylformamide (DMF) and refluxed for 24 h at 70°C. The resulting mixture was concentrated by rotary evaporator at 90°C under vacuum to remove the unreacted SOCl₂. The obtained GO-COCl was washed with THF and dried under the vacuum. Subsequently, 50 mg CoPcS dissolved in 10 ml DMF and added with GO-COCl, followed by stirring the resulting mixture for 24 hrs at 130°C under the nitrogen atmosphere. The finally obtained hybrid was collected via centrifugation at 10,000 rpm for 30 minutes, washed successively with HPLC grade water, and dried at 60°C under vacuum for 12h. The yield of the final material was found to be 0.51 g.

4.2 Photoelectrochemical CO₂ reduction investigations

The photoelectrochemical (PEC) performance of the synthesized CoPcS, GO-COOH, and CoPcS/GO-COOH was tested for the reduction of carbon dioxide. The initial screening and

photocurrent determination were measured under dark and illumination conditions with minimum external bias required using 0.1M KHCO_3 as an electrolyte. It includes the current-voltage curves named as linear sweep voltammetry (LSV) that discloses the photoactive nature of the working electrodes. During all the measurements, the active surface area of the working electrode was 1 cm^2 . **Figure 4** shows the significant dark-light difference in their current density with the increased applied voltage. Comparatively, LSV plot of CoPcS/GO-COOH shows the highest photocurrent density of 1.7 mA cm^{-2} at -1.0 V vs Ag/AgCl [Figure 4 (e) & (f)]. Indeed, the current density of as such CoPcS has a synergetic impact over GO-COOH and generates a reasonable difference in their photocurrent density.

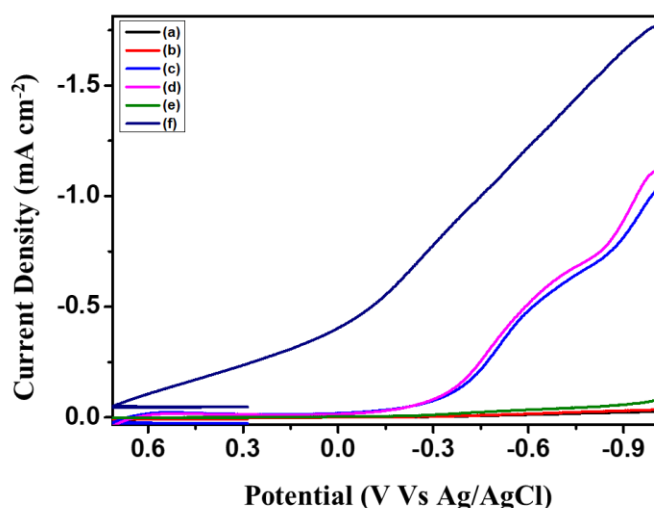


Figure 4. Linear sweep voltammetry (LSV) Plot (a) Dark-Pure Co-Pc; (b) Light-Pure Co-Pc; (c) Dark-CoPcS; (d) Light-CoPcS; (e) Dark- CoPcS/GO-COOH; (f) Light- CoPcS/GO-COOH

Moreover, CoPcS owing to its affinity towards carbonated water, shows its high reactivity in the dark condition Figure 4 (c) and dissociates in the electrolyte solution. However, the immobilized CoPcS/GO-COOH photoelectrodes exhibited stability and did not dissociate in the reaction solution. Thus, the hybrid CoPcS/GO-COOH material remained intact with the electrode plate and demonstrated a functional interface for the reduction of CO_2 . The electrode could be recovered quickly after the reaction for recycling experiments. **Figure 5** illustrates the

Electromagnetic Impedance Spectroscopy (EIS) plot to measure the change in their resistivity in the form of impedance. The EIS Nyquist plot presents the low arc radius upon illumination in the immobilized CoPcS/GO-COOH compared to the pristine CoPcS. Therefore, with a reduced arc radius, the charge transfer activity increases and separates the photogenerated electrons for CO₂RR. Thus, under light illumination, CoPcS/GO-COOH is distinguished as the most efficient molecular catalyst for PEC CO₂RR, a high charge transfer activity.

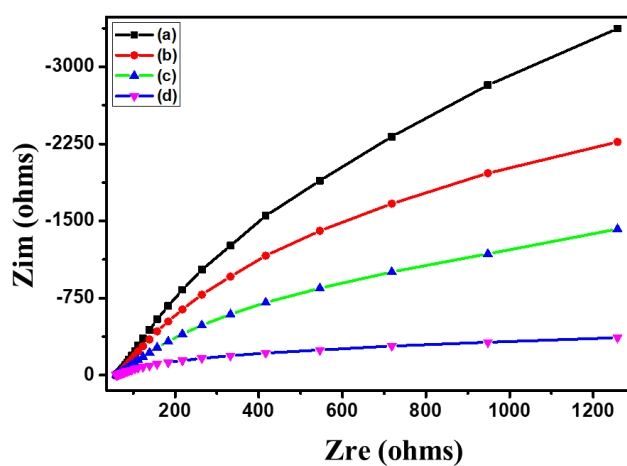


Figure 5. EIS Nyquist Plot (a) Dark-CoPcS; (b) Light-CoPcS; (c) Dark- CoPcS/GO-COOH; (d) Light- CoPcS/GO-COOH

4.2 Results

The report illustrates the combined use of CoPcS and GO-COOH molecular polymorph for solar-driven electrochemical CO₂RR. The CoPcS/GO-COOH hybrid material showed adequate intermolecular interactions for the selective production of formate in CO₂ saturated KHCO₃ solution. The excellent performance of hybrid CoPcS/Go-COOH molecular catalysts was attributed due to a proficient interface, which increases charge carrier density towards CO₂ reduction. Overall, the obtained results of PEC CO₂ reduction are comparable to the previously reported molecular complexes. Nevertheless, these polymeric hybrids are highly stable, examined by its reusability study,

and it can be applied to generate C1 and other reaction products. This study is a contribution to the development of active interfaces for PEC CO₂ reduction reactions to produce useful chemicals.

5. Conclusion

PEC process is an advanced method that provides a more improvised and efficient process for CO₂ utilization by combining the lead of photocatalysis and electrocatalysis. The working of the PEC system evolves from a homogenous to a heterogenous system and from a single photoactive electrode configuration to photocathode-photoanode-driven cells. By using separate chambers for oxidation and reduction processes increase the overall efficiency of the system. Great efforts are made in the last few years to develop energy-efficient and effective PEC systems using semiconductor materials. For a more advanced system, metal complex electrocatalysts are used along with semiconductors to get a highly active PEC system for CO₂ reduction. Several transition metals are explored for their activity towards the PEC system in variable solvent phases. In the case of p-type semiconductors, photo corrosion is the main drawback that makes these systems less effective. By using metal complexes (MC), selectivity towards products increased, but the homogenous nature of MC made the material non-recyclable. By combining both the materials (SC/MC), an advanced system was formed, which is more selective and has long-term stability. Using MC electrocatalyst also eliminates the problem of overpotential to some extent, and nowadays, even non-biased systems are developed for PEC CO₂RR. Further, the complicated reaction mechanisms and pathways for the process require more attention to thoroughly understand the utilization mechanism of photons and the formation of products. More attention is needed in this field to demonstrate and make a more reasonable and practical system that is applicable to a large-scale CO₂ reduction process.

6. Advancements and Future challenges

PEC is a prevalent strategy for chemical conversion in today's world. It is an energy-efficient and fast technique as compared to photocatalysis and electrocatalysis. Various versions of PEC reactors are

developed to utilize the reactant molecules for their conversions effectively. If we study the development of the CO₂ reduction process via PEC, it initially includes the homogenous electrocatalysts and metal oxides. The metal oxides are used as photocathode or photoanode to utilize the light energy, and only one compartment used to be irradiation active. But, by further studies, homogenous systems are converted to heterogeneous ones by the immobilization of catalysts over semiconductor surfaces, which can be used as electrodes. And, anode, as well as a cathode material, are designed such that both can utilize light energy to make the process more feasible. The material maturing gets more focus along with the reactor configuration. The shift towards metal complexes and further to molecular organic frameworks as catalysts give the process more highs in the product selectivity area. Broadly, the merits of the PEC process include 1) the separation of oxidation and reduction chambers enhance the process efficiency; 2) as compared to the electrochemical process, the electricity consumption of PEC is low because of extra energy provided by solar irradiation; 3) the applied external voltage minimizes the charge recombination and drives the migration of electron-hole pairs to respective electrodes. These advantages make the process more valuable for CO₂ reduction. Although many achievements have been obtained in the PEC field, many challenges are still remaining unsolved for the future. One of them is the enhancement in the light-harvesting efficiency of materials along with the charge separation. Electron-hole pair recombination is a big problem that decreases the overall effectiveness and productivity of the process. Also, the reaction mechanism is multistep and complicated, indicating the difficulty in directive products. And due to this reason, efficiency and selectivity are also limited. Another big problem is hydrogen evolution, a competitive reaction to CO₂ reduction, which decreases overall selectivity of CO₂ reduction. So, despite a lot of growth in the PEC field, there are still many stones left unturned to get a more efficient and effective method for CO₂ mitigation.

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