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Selective synthesis of methanol by photoelectrocatalytic reduction of CO_2 over PANI-CuFe$_2$O$_4$ hybrid catalyst

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Abstract. In this work, a hybrid photocatalyst, PANI-CuFe$_2$O$_4$ was synthesized, characterized and used as a photocathode for the photoelectrocatalytic (PEC) reduction of CO_2 to methanol selectively under 470 nm wavelength light irradiation at applied potential -0.4 V vs NHE. The PEC results showed that the combination of PANI with CuFe$_2$O$_4$ could increase the rate of PEC CO_2 reduction to methanol owing to the increase of CO_2 chemisorption at the photocathode surface and at the same time by facilitating the separation of photogenerated electron-hole (e^-/h^+) pairs during CO_2 reduction. The rate of methanol formation was found maximum as 49.2 µmole g^{-1}.h^{-1} with 73% Faradaic efficiency. The incident photon current efficiency (IPCE) and quantum efficiency (QE) for PEC CO_2 reduction was achieved as 7.11% and 23.9% respectively. The PEC results demonstrated that the bias potential played a significant role in the separation of e^-/h^+ pairs and enhanced the PEC CO_2 reduction activity of the hybrid photocatalyst.

1. Introduction
Fossil fuels are in limited and they are producing huge amount of CO_2 gas during burning process which causes the atmospheric pollution and global warming simultaneously. Conversion of CO_2 in to value added chemicals has attracted the attention recently from various points of view especially in the context global warming, shortage of carbon resources and shortage of energy [1]. Electrocatalytic (EC) reduction of CO_2 to fuels and chemicals was very attractive and could effectively reduce the CO_2 concentration. However, it requires higher electrical energy (1.90 V vs NHE for single electron reduction) because of high stability of CO_2 molecule [2]. Alternatively, once the development of the photocatalyst for the conversion of CO_2 into valuable fuels by Inoue et al. [3], the photocatalytic (PC) CO_2 reduction has got the momentum as it requires solar light or it can use the solar light as the energy source [4]. However, the limitation of PC CO_2 reduction is the lower availability of electrons at the interface due to the only photogenerated electrons at the interface in PC system. Moreover, a significant portion of the photogenerated electrons in PC system are reduces because of the recombination of e^-/h^+ during the reduction period [5, 6]. PEC (combination of PC and EC) reduction of CO_2 to useful chemical is a subject of considerable interest in recent years because in PEC system

both the photogenerated electrons and electrons supplied from the external source can concurrently contribute to enhance the CO_2 reduction activity. Moreover, the electrons from the external source can inhibit photogenerated e^-/h^+ recombination rate [7]. PEC CO_2 reduction employing various metal oxides and their composites such as CuO foam cathode[8], $Cu_3Nb_2O_8$ [9], FeS_2/TiO_2[10] have been reported as good photocatalyst. Photocatalysts with higher electron conductivity, good photo-response properties along with the low e^-/h^+ recombination rate are preferential for PEC CO_2 reduction [11].

$CuFe_2O_4$ is a low band gap *p*-type ferrite material and proved to be a photocatalyst for CO_2 reduction [12, 13] and water splitting [14]. But due to the low band gap, the e^-/h^+ recombination rate in $CuFe_2O_4$ is high causes the low products yield. $CuFe_2O_4$ could be coupled with some other materials to create the hetero-junction that eventually increase the lifespan of electrons and holes leading the high efficiency of CO_2 reduction. Polyaniline (PANI) is reported to be a visible light responsive properties polymer possessing CO_2 adsorption sites [15]. The incorporation of PANI with $CuFe_2O_4$ may enhance the charge separation by transferring the photogenerated electrons to the N-containing functional groups of PANI which could acts as the CO_2 reduction site. The superior activity of PEC CO_2 reduction over PANI-$CuFe_2O_4$ photocathode surface could be attributed due to the synergistic effect of both constituents.

2. Experimental

$CuFe_2O_4$ was produced by Sol-gel method with slight modification followed by our earlier work [12, 16, 17] whereas PANI was produced by a conventional method [18]. In brief, during $CuFe_2O_4$ synthesis the major precursors $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ were taken in stoichiometric ratio 1:2 in a 500 mL beaker and then 300 mL distilled (DI) water was added to the precursor with continuous stirring for 3h followed by adding 6g of agar and 60 mL of HNO_3. After that, the mixture was heated at 80 °C in ultrasonic bath until a green gel was formed. The gel was dried overnight in oven at 120 °C and then grinded to powder. Finally, the grinded powder was calcined at 800 °C in a muffle furnace with the heating rate at 10 °C/min for 7h. The brown calcined powder was grinded to fine powder and stored as $CuFe_2O_4$. For the synthesis of PANI, 10 mL of monomer, aniline, was dissolved in 250 mL of 1 M HCl solution in a 500 mL beaker (kept in ice bath) with constant stirring. Then, 1.50 g of $(NH_4)_4S_2O_8$ (ammonium persulfate) was added to the mixture drop wise to avoid the secondary reaction during polymerization reaction. After that, the whole mixture was kept with constant stirring to complete the polymerization reaction for 24 h. At this stage, a green precipitate was formed which was separated by centrifugation. The green precipitated was dried in oven at 120 °C for 24 h and grinded as powder and stored as PANI. For the preparation of 5% PANI-$CuFe_2O_4$, 15mg of PANI was dissolved in 200 mL ethanol (95%) followed by the addition of 285 mg of $CuFe_2O_4$. The resulted suspension was ultrasonicated at 80 °C for 6h and thereafter it was calcined at 220 °C for 2h. The as-prepared catalysts were characterized by XRD (Rigaku MiniFlex2), TEM (transmission electron microscope) (Phillips Technai $G^2$20) and with UV-visible spectroscopy (UV 2600, Shimadzu spectrophotometer).

The photochemical activity was carried out with the help of linear sweep voltammetry (LSV) and chronoamprometry in a double chamber PEC cell reactor (separated by nafion-117 membrane) in 0.1M $NaHCO_3$ solution under 470 nm wavelength light irradiation. The photoelectrochemical reduction of CO_2 was carried out followed by our earlier work [12] in where the as-prepared electrodes (acted as photocathode) and Ag/AgCl electrode were used as working electrode and reference electrode respectively. The working electrode and reference electrode were placed in the cathode chamber of the PEC Cell reactor in where the reference electrode was placed very close to the working electrode with the help of luggin capillary. The 10% Pt/C electrode was used as counter electrode and was placed in anode chamber of the PEC cell reactor. Potentiostat (Autolab Compact PGSTAT 204, Netherland) was connected with the PEC cell and used for potential supply. Before CO_2 reduction analysis, both chamber of the PEC cell reactor was poured with 0.1M $NaHCO_3$ (~120 mL for each chamber) solution and then the electrolyte in cathode chamber was saturated with CO_2 (99.99%) for 45 minute. After that, photoelectrochemical reduction of CO_2 was carried under 470 nm

wavelength light irradiation at -0.4 V vs NHE applied potential for 4 h. The liquid product during PEC CO_2 reduction was collected at different time interval and was analyzed by GC-FID.

2.1. Characterization of the synthesized catalysts

To find out the lattice plane and the crystal size of $CuFe_2O_4$ in PANI-$CuFe_2O_4$, XRD was carried out in the range of 2Θ = 10-70 degree and the result is shown in figure 1a. The characteristics diffraction peaks were observed at 2Θ = 18.36, 30.02, 35.42, 36.99, 42.95, 55.25, 56.71, 62.48 and 66.34 degree for the plane of (111), (220), (311), (222), (400), (422), (333), (440) and (531) for the spinel $CuFe_2O_4$ [19] in PANI-$CuFe_2O_4$ (DB card number-9006199). Moreover, the crystal plane of (111), (202) and (113) were also observed at 2Θ = 38.84, 48.89 and 68.26 degree in PANI-$CuFe_2O_4$ for the presence of CuO (DB card number-9016105) which may be formed simultaneously with $CuFe_2O_4$ during calcination process. Among all the peaks, the crystal plane of (311) at 2Θ = 35.42 degree was the most prominent peaks and the crystal size of $CuFe_2O_4$ of that plane was determined using Scherer equation [20] which was found as 51.2 nm. The figure 1a inset shows the XRD pattern of PANI in where the plane (031), (200) and (132) were found at 2Θ = 15.17, 20.78 and 25.30 degree respectively for the emeraldine salt phase of PANI [21]. HR-TEM images of PANI-$CuFe_2O_4$ (Fig. 1b) indicate that $CuFe_2O_4$ nanoparticles were distributed in the PANI surfaces due to the electrostatic attraction between $CuFe_2O_4$ and PANI leading to the formation of PANI-$CuFe_2O_4$ hybrid catalyst [22]. The distance between the two adjoining (d_{hkl}) $CuFe_2O_4$ nanoparticles in hybrid catalyst was determined and was found as 0.25 nm, representing the existence of lattice plane of (311) for the spinel $CuFe_2O_4$.
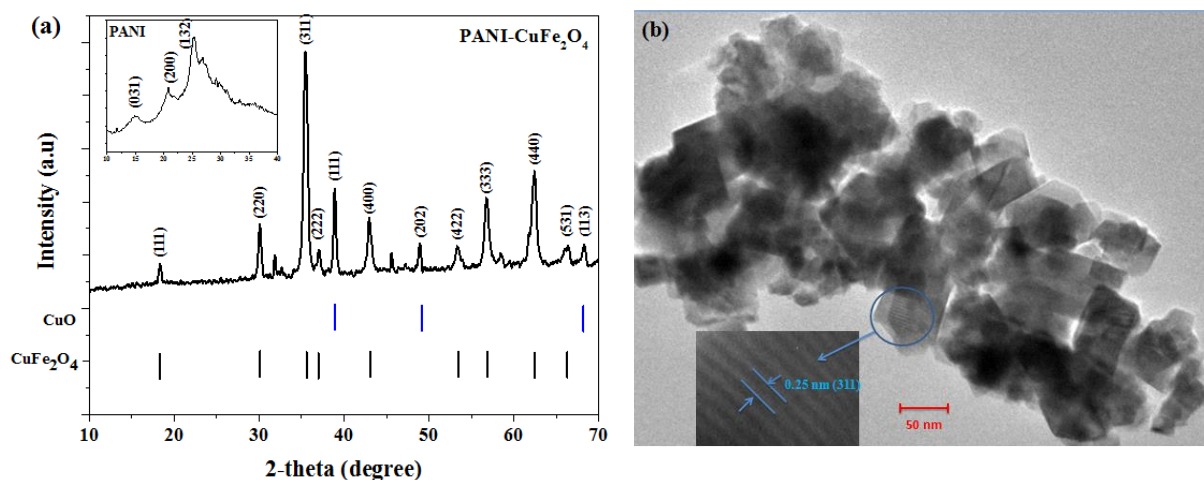

Figure 1. XRD pattern of hybrid PANI-$CuFe_2O_4$ and PANI (inset) and (b) HR-TEM image of PANI-$CuFe_2O_4$.

2.2. Photoelectrochemical activity of the synthesized catalysts

Current density-potential behaviour of the as-prepared photocatalyts under dark and light on condition (both N_2 and CO_2 saturated) was determined through the LSV (Figure 2a and 2b). From figure 2a, it is found that small amount of cathodic current was produced for all electrodes which may be associated with the water-proton reduction reaction [23].
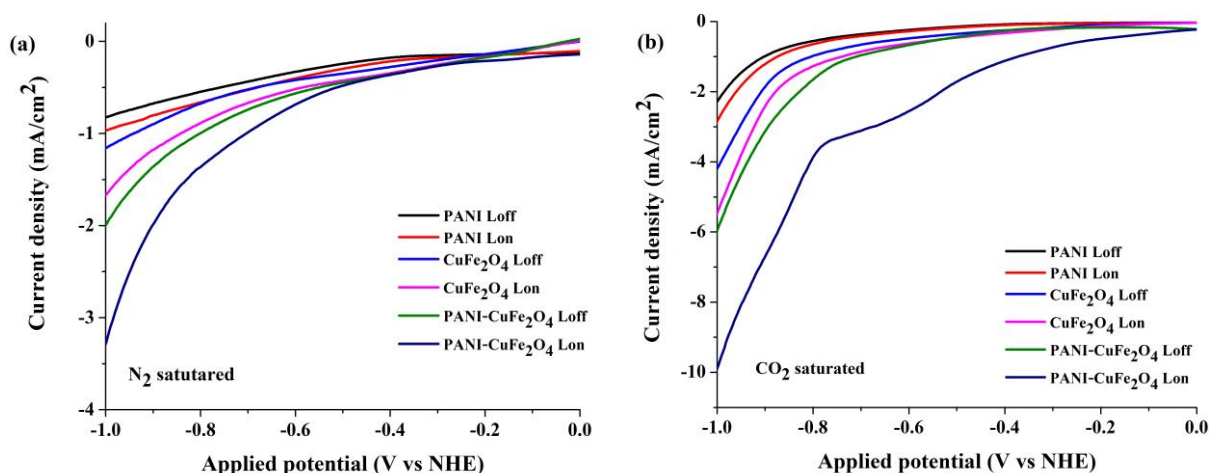
Figure 2. LSV of $CuFe_2O_4$, PANI and PANI-$CuFe_2O_4$ in (a) N_2 saturated and (b) CO_2 saturated 0.1M $NaHCO_3$ aqueous solution under 470 nm cut-off filter.

But under light irradiation in CO_2 condition the observed cathodic current for each electrode was higher than dark condition indicate that the electrodes were strongly affected by light exposure and were associated with CO_2 reduction. A remarkable cathodic current (9.97 mA/cm^2) was observed for PANI-$CuFe_2O_4$ electrode during light irradiation compared to dark condition (5.97 mA/cm^2). During light exposure the photogenerated electrons may be produced in the CB of the low band gap $CuFe_2O_4$ semiconductor leaving behind holes (h$^+$) in the VB in $CuFe_2O_4$. The photogenerated electrons available in CB of $CuFe_2O_4$ could transfer to the CB of PANI resulting in higher photocatalytic activity for the generation of photocurrent. Under light exposure, the hybrid catalyst PANI-$CuFe_2O_4$ produced almost double cathodic current (9.97 mA/cm^2) from $CuFe_2O_4$ (5.28 mA/cm^2) and three times higher than PANI (2.97 mA/cm^2) indicating that the synergistic effect was happened when PANI was incorporated with $CuFe_2O_4$.
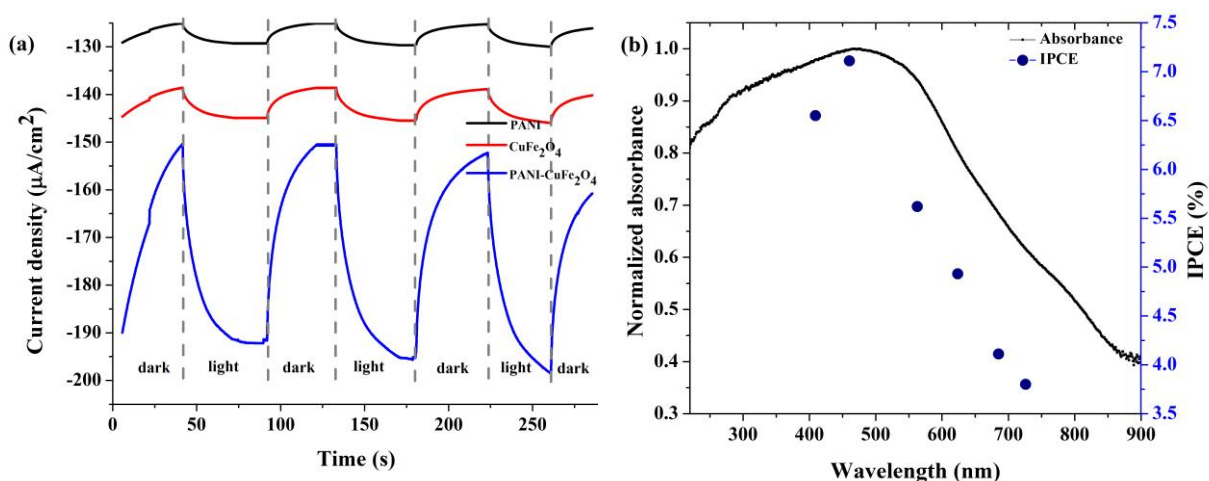

Figure 3. Chronoamperometry in CO_2 saturated 0.1M $NaHCO_3$ aqueous solution under 470 nm cut-off filter at an applied potential -0.4 V vs NHE and (b) IPCE action spectrum along with UV-visible spectroscopy of PANI-$CuFe_2O_4$.

The photocurrent generation under light on condition was also measured by chronoamperometry experiments (Refer figure 3a). From figure 3a, it is clear that, in presence of light, photogenerated currents in PANI-$CuFe_2O_4$ hybrid catalyst (42.4$\mu A/cm^2$) was significantly higher than its individual components. The hybrid PANI-$CuFe_2O_4$ catalyst can produces almost ten times higher than PANI (4.6 $\mu A/cm^2$) and seven times higher than $CuFe_2O_4$ (6.3 $\mu A/cm^2$) photocurrent under light illumination. The enhanced IPCE activity for different monochromatic light irradiation (420-730 nm) was estimated followed by our earlier work [17] and was found as 7.11 % for 470 nm cut-off filter. The results showed that IPCE value initially increased up to 470 nm wavelength light irradiation and then decreased and reached minimum value for 730 nm wavelength light irradiation (3.8 %) (Refer figure 3b) and the result is consistent with the UV-visible results. The IPCE results indicate that the hybrid catalyst was able to absorb visible light leading to e^-/h^+ generation and charge transfer in the photocathode electrolyte interface to derive PEC CO_2 reduction. The presence of high mobility of charge carriers and CO_2 capturing material PANI ensure the efficient charge separation and visible light harvesting capacity of the hybrid catalyst.

The EC and PEC CO_2 reduction was carried under 470 nm cut-off filter at -0.4 V vs NHE for 4 h. During PC CO_2 reduction the cell was disconnects with potentiostat but others condition was maintained same like EC and PEC CO_2 reduction. The liquid products of the sample of each experiment (PC, EC and PEC CO_2 reduction) was collected at different time intervals and analyzed in where methanol was found as sole product. The rate of formation of methanol during all system was initially increased and found maximum at 1h after that the rate was gradually deceased and reached steady state almost (Refer figure 4a). The rate of methanol formation for first hour was found as 8.1, 27.8 and 49.2 μmole $g^{-1}.h^{-1}$ for PC, EC and PEC CO_2 reduction respectively. The quantum efficiency(QE) and Faradaic efficiency (FE) for methanol formation during PEC CO_2 reduction in PANI, $CuFe_2O_4$ and the hybrid PANI-$CuFe_2O_4$ were calculated and the results is shown in figure 4b. The QE and FE results showed that the hybrid PANI-$CuFe_2O_4$ catalyst possessed higher efficiency (23.9 % and 73% for QE and FE respectively) than its individual components indicate that during PEC CO_2 reduction both the photogenerated electrons from PC system and external electrons form EC system were effectively used for methanol production selectively.
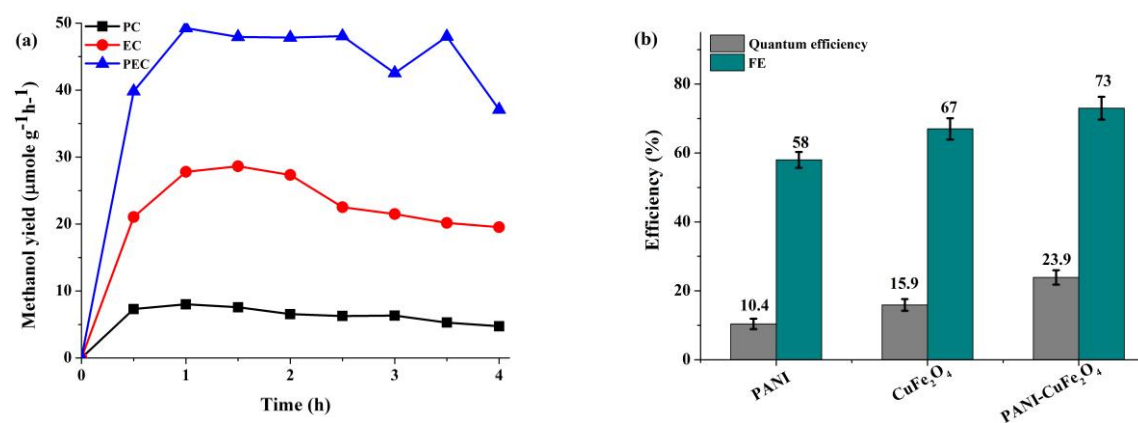

Figure 4. (a) Methanol formation rate during PEC CO_2 reduction in hybrid PANI-$CuFe_2O_4$ and (b) Quantum efficiency and Faradaic efficiency of methanol formation during PEC CO_2 reduction in PANI, $CuFe_2O_4$ and PANI-$CuFe_2O_4$ hybrid catalyst at -0.4 V vs NHE.

3. Conclusion

PANI-$CuFe_2O_4$ hybrid catalyst has been successfully prepared and characterized. The distribution of the $CuFe_2O_4$ nanoparticles over PANI matrix is revealed by TEM. PEC CO_2 reduction activity results demonstrated that the methanol was formed with a high selectivity with 73 % FE. The superior

performance of the catalyst can be ascribed to its unique hetero-architectures that can effectively use the photogenerated electrons along with external electrons during PEC CO_2 reduction.

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