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Chitosan coated copper-oxides nano particles: A novel electro-catalyst for CO₂ reductionSrijita. Basumallick^{a,b,c} and Swadeshmukul.Santra^{b,c}Received 00th January 2012,
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We report here a simple one-pot method of synthesis of copper-oxide based novel film forming electro catalyst for CO₂ reduction. Water dispersible chitosan (CS)-CuO/Cu₂O (Cu_xO) nano composites of diameter 10-20 nm was obtained by hydrothermal reactions of CS, CuSO₄.5H₂O and tartaric acid (TA). Here, TA acts as a multifunctional reagent as depolymerizer of CS, ionic cross linker of depolymerised CS and complex forming ligand with Cu²⁺ ions. These CS coated Cu_xO nanoparticles were characterized by HRTEM, UV-VIS, AFM, FTIR and XPS. An ultra thin film of composite catalyst was deposited onto a Pt electrode by drop cast technique and applied to study CO₂ reduction by cyclic voltametric technique. The voltammogram shows a reduction peak at -0.665 V vs. RHE at pH 5.3 with a short hydrogen evolution tail indicating its better performance in terms of retarding H₂ evolution reaction. This has been explained proposing a model of protonated CS on to electrode surface that repels incoming H⁺ ion at the electrode-electrolyte interface. This is the first time we are reporting a film forming copper-oxide based nano composite material for efficient electro-catalytic reduction of CO₂ in aqueous solution.

Introduction

During the recent years, there is an increasing interest¹⁻¹⁰ in the development of photo-catalysts and electro-catalysts for CO₂ reduction. Carbon dioxide is a greenhouse gas and a major contributor of global warming. Natural photosynthetic pathway or

carbon pathway¹¹ is not capable of restoring the ecological CO₂ balance because of rapidly increasing global carbon emission. Thus, CO₂ utilization through its photo-chemical or electro-chemical reduction¹⁻¹⁰ is an additional effective path in restoring CO₂ balance. But major bottleneck of CO₂ reduction reaction is that it is an uphill reaction and kinetically difficult because of requirement of high activation energy. In natural photosynthetic dark reaction¹¹ free energy of cleavage of phosphate bond of ATP and reducing molecule NADPH are used to fix and reduce CO₂ to carbohydrate. The enzyme Ribulose Bisphosphate Carboxylase (RuBPCO) acts as catalyst. In laboratory experiments with CO₂ reduction using sun light or electrical energy, it is known oxides of copper;⁵⁻⁷ particularly Cu₂O is an efficient catalyst for such reduction. This is because of its unique crystalline structures^{10,12} where CO₂ molecules get easily adsorbed with favourable heat of adsorption.

In this paper, we intend to focus on chitosan coated nano Cu_xO composite catalyst for CO₂ reduction; we have selected chitosan as it has the ability to form an ultra thin adhesive film¹³ onto electrode surface that will reduce catalyst loading. Chitosan loaded composite electrode has been successfully applied in immobilizing enzyme¹⁴ for bio-fuel cells. Film forming ability of chitosan with linear chain structure has been studied¹³ using solid-state NMR and X-ray diffraction techniques. These studies have revealed that H bonding ability of chitosan along with its strong cross linking ability through its protonated -NH₂ groups with poly-valent anion of a cross linker makes it an unique film forming material.

DFT calculations¹² on CO₂ reduction onto Cu based catalysts revealed different mechanistic paths for such reduction. These calculations have shown¹² possible mechanistic path for multi electron transfer reactions involve in CO₂ reduction.

Recently, Flake et al¹⁵ reported Cu nano cluster loaded ZnO electrode for CO₂ reduction and shown that different reduction products as methane, CO, ethylene, methanol, ethanol, methyl formate are formed as reduction products. Hori et al⁵⁻⁷ have shown CH₄ is the major product of Cu₂O electrode surface. Again, it is reported¹⁵ CO₂ reduction occurs within the potential range -0.6 to -1.4 V vs. Ag/AgCl or -0.065 V to -0.865 V vs RHE at pH 5.3. Usuki

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and his group¹⁶ showed that at low over potential CO₂ reduction leads to formation of formic acid.

Ogura et al¹⁰ in their review article discussed the mechanism of ethylene formation and pointed out that CO₂ is adsorbed onto Cu electrode prior to electro reduction.

In this paper, we report a simple one-pot hydrothermal method of synthesis of chitosan coated nano copper-oxide catalyst and studied their electro-catalytic activity towards CO₂ reduction. Chitosan is an excellent film forming material, it is anticipated CS coated Cu_xO nano composite will be a promising catalytic material for efficient electro-reduction of CO₂. To the best of our knowledge this has not been reported earlier.

Experimental

Materials

Water insoluble low molecular weight Chitosan was purchased from Sigma Aldrich (Saint Louis, Missouri, USA) and used without further treatment. CuSO₄·5H₂O, (technical grade) was purchased from CQ concepts INC (Ringwood, Illinois, USA). NaOH (ACS grade, Amresco Solon, Ohio, USA) and HCl (technical grade, Fisher Scientific.) were used as supplied. Hydrothermal reaction was carried out in a hard glass well stopper bomb keeping in a temperature controlled oven (Thermo electron corporation, Lundeberg/Blue M). A Mettler Toledo, Delta 320 pH meter was used to adjust pH of the solution after calibrating it using HACH pH calibration solutions. Barnsted Nano pure Diamond DI water was used to obtain DI water of resistivity 17.9 MΩcm. Fisher scientific Digital vortex mixers was used to mix reagents for reaction.

Preparation of chitosan coated copper-oxides nano particles by hydrothermal method.

In this preparation of CS coated Cu_xO, we had optimised the reaction conditions for obtaining almost water dispersible (fewer agglomerated particles) product. Here, we took 300 mg of chitosan and 300 mg of tartaric acid that acts as depolymerizer, ionic cross linker and complex forming agent, in a hydrothermal bomb to that 30 ml of DI water was added, mixed well and kept at 150°C under hydrothermal condition for 1.5 hours. After the reaction was over, the solution was cooled to room temperature and 25 ml of (1% w/v) CuSO₄ solution was added to the hydrothermally depolymerized solution and kept under vortex for one hour followed by addition of 1.0 N NaOH drop wise to adjust its pH to 7.4. Then, 5 ml of this solution was added to 25 ml DI water and kept under hydrothermal at 150°C for one hour to convert remaining Cu(OH)₂ completely to Cu₂O/CuO. The final dispersed solution was dialysed centrifuged and dried under vacuum for further studies.

Preparation of control CuO/Cu₂O (without CS)

We followed literature¹⁷ protocol of preparation of copper-oxide nano, dissolving 300 mg of Cu-acetate (in 30 ml of 10% CH₃COOH solution followed by hydrothermal reaction at 150°C for 90 min and pH of the solution was adjusted to 7.4. This dispersion was dialysed against DI water, centrifuged and dried under vacuum. It was proposed that Cu-acetate undergoes disproportionation reaction under hydrothermal condition forming Cu and CuO.

Preparation of control CS solution.

CS solution (1%w/v) in 1% (v/v) HCl was heated at 150°C for 90 min. The pH of the solution was raised to 7.4 by adding 1.0 N NaOH drop wise to this depolymerized CS solution. The final solution was centrifuged and re-dispersed in DI water. The washing procedure was continued for 3 to 4 times. The solution was vortexed for 15 minutes between each centrifuge and washing step. The solid palate was vacuum dried for FT-IR analysis.

Characterization

Ultraviolet-Visible Spectroscopy (UV-VIS): UV-VIS absorption spectra of the prepared catalysts and their controls have been taken in the range 200–800 nm using Varian Cary 300 Bio UV-Vis double beam spectrophotometer in a semi micro quartz cuvette with path length 10 mm.

Fourier Transform Infra-red Spectroscopy (FT-IR): FT-IR technique was used to characterize functional groups present in these four samples. FT-IR spectra were recorded on Perkin Elmer Spectrum 100 ATR FT-IR Spectrometer.

TEM Images: FEI Tecnai TEM with resolution 0.20 nm point to point, 0.102 nm per line was used. The machine was equipped with SEG with hot and cold stages and High angle annular dark field (HAADF) detector using Gatan Image Filter (GIF). The lyophilized catalyst powder was dispersed in ethanol. Au grid with carbon mass was directly dipped in to the solution and after absorption was dried under vacuum for 24 hr to remove any solvent.

AFM Images: Water dispersed sample was spin coated and dried in vacuum onto a silicon wafer (boron doped, purchased from Nova electronic materials). AFM images were recorded on a Veeco Manifold multimode V model (tapping mode) using silicon nitride tip (radius B 50 nm) attached to a cantilever (spring constant=0.032 Nm, oscillating frequency 0-600 kHz). AFM images were recorded at room temperature.

XPS images: X-Ray Photoelectron Spectroscopy (XPS) was done on a Physical Electronics 5400 ESCA spectrometer equipped with a monochromatic Al Ka source operating at 300 W. Vision software provided by the manufacturer was used for data analysis and quantification. A Shirley background was used for quantification and curve fitting of Cu2p, C1s, N1s and O1s spectra. All the spectra were charge referenced to the aliphatic carbon at 285 eV. For curve-fits, 70% Gaussian/30% Lorentzian line shape was used.

Fabrication of Cu-CS composite and control Cu₂O loaded electrodes for CV studies: Catalyst loaded electrodes were prepared by conventional drop cast method. 100 μL of dispersed Cu-CS was added to a 1 cm² cleaned Pt electrode and the water was evaporated under vacuum. Similar procedure was followed to prepare control electrode. For cyclic voltammetry study, the catalyst loaded electrode was used as working electrode coupled with a Pt counter electrode and Ag/AgCl reference electrode. The electrodes were dipped into a solution taken in a beaker containing 10 ml of 0.1 M Na₂SO₄ solution saturated with CO₂, prepared just before the measurement by reaction of 2 ml 0.2 M Na₂CO₃ and 2 ml 0.2 M H₂SO₄. CV was recorded at a scan rate of 200 mVs⁻¹ in the potential window of +0.8 to -2.0 V, the CV diagrams are shown in Fig. 6-7. The potential values are plotted in RHE at pH 5.3 for the sake of comparison with literature data

Results and Discussions

Fig. 1 shows UV-visible spectra of CS coated copper-oxide nanoparticles and their control. A flat absorption peak around 450 nm with minima around 250 nm is seen. This featureless absorption behaviour may be due to presence of both Cu (I) and Cu (II) oxides in the composites. It is interesting to note that the UV spectra of the

control NPs show a sharp absorption peak at 250 nm. This may be attributable to the presence of uncoated Cu (I) oxide in the control.

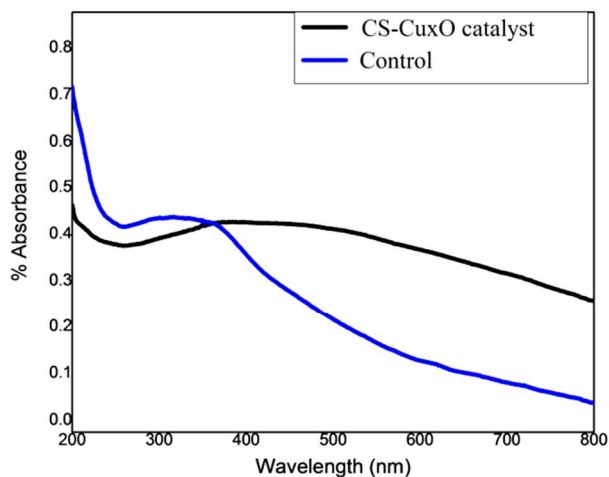


Fig. 1 UV-Vis spectra of CS-Cu_xO composite and control.

IR spectra of these catalysts and their control are shown in Fig 2. These are more or less similar to the reported spectra¹⁸ CS coordinated copper complex. The broad peak around 3400 cm⁻¹ of CS due to -OH and -NH₂ stretching is reduced substantially in the CS coated catalyst due to its low concentration onto NM surface. However, presence of -CH stretching at 2900 cm⁻¹ in the spectra of catalyst clearly indicate that copper oxides NMs are capped with CS. Appearance of a carbonyl peak at around 1659 cm⁻¹ and amide (II) 1503 cm⁻¹ (blue shifted¹⁸ because of capping) as well as characteristic amide (III) at 1356 cm⁻¹, reinforces presence of CS, together with this 1255 cm⁻¹, 1022 cm⁻¹, for glycosidic bond also indicates presence of chitosan. A pictorial representation of the CS coated nano material is shown in Fig 3. It is seen that depolymerized CS will easily bind to metal-oxide nanoparticles by ligand binding mode and will be dispersible in aqueous medium because of presence of hydrophilic groups.

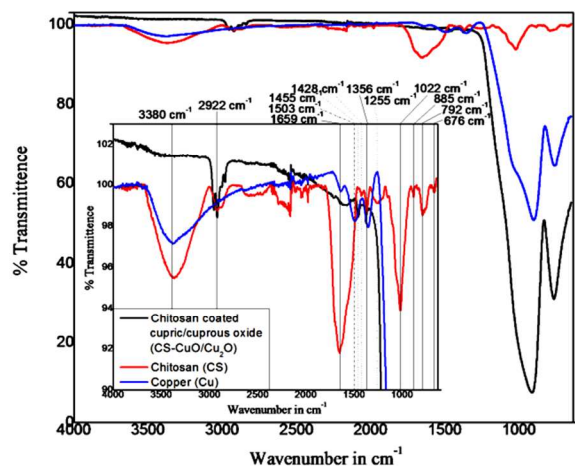


Fig. 2 FTIR spectra of CS-Cu_xO and its control.

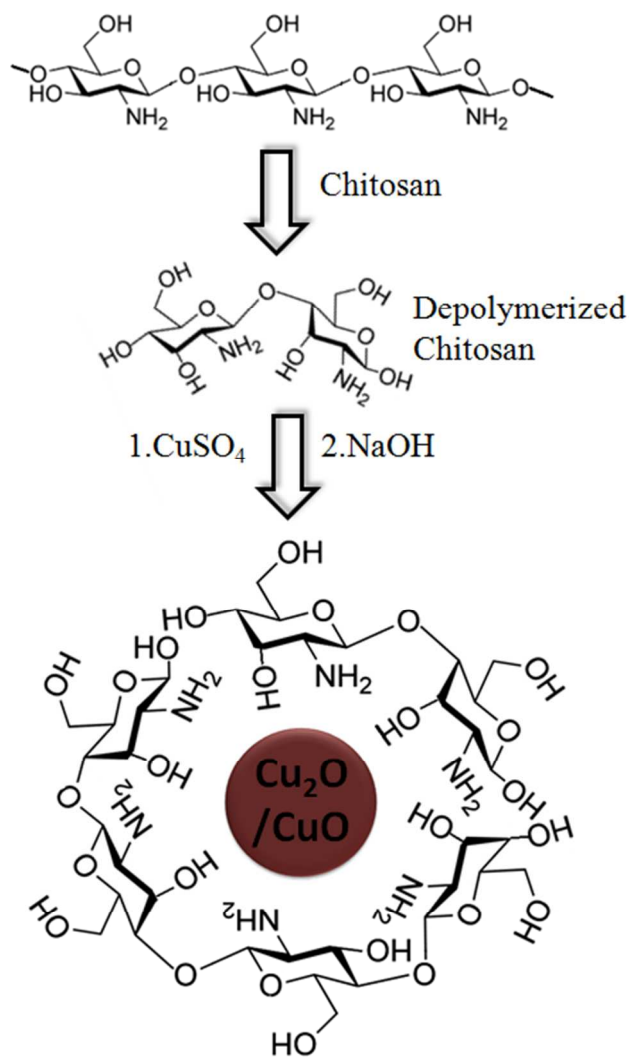


Fig. 3 Schematic representation of chitosan coated CuO/Cu_xO nano particles

AFM images of this catalyst and its control are shown in Fig. 4. It is seen that distinct non agglomerated particles of relatively smaller sizes are formed with catalyst in contrast to catalyst control where particles are mostly agglomerated. AFM image shows these NMs are composed of particles of different sizes as expected from their preparation method.

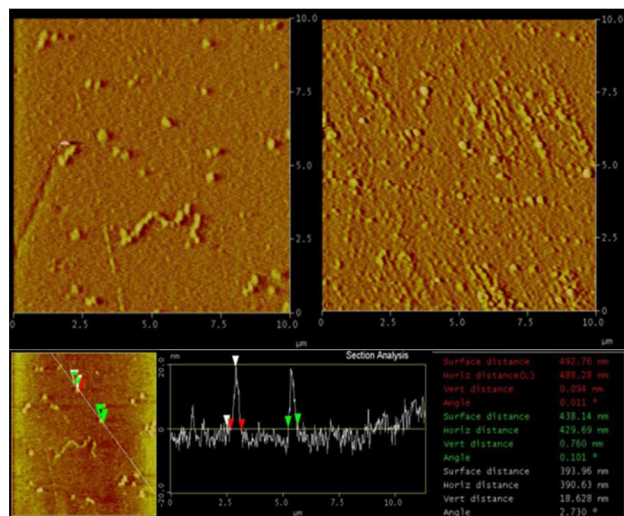


Fig. 4 AFM images of CS-Cu_xO (top left) (particle diameter ~400 nm), thickness of the catalyst film (~18 nm, bottom) and AFM image of the control (top right).

XPS images of CS-CuO/Cu_xO indicate presence of mixed valence states Cu (II) and Cu (I) on the surface. While Cu (I) state is predominating in CS-CuO/Cu_xO catalyst, Cu (II) oxide is present at a larger percentage on the surface of the control sample (Fig. 4). This may be owing to reducing property of CS. The peak at 932 eV and auger parameter 1848 eV is due to Cu 2p_{3/2} and characteristic of Cu (I) state. In survey spectra the peak for N 1s indicates presence of CS. Different functional groups present in chitosan help in coating formation as seen in C 1s as well as O 1s peaks.

HRTEM analysis shows (Fig. S1) formation of nanoparticles of core diameter 10-15 nm with d spacing of 4.2 Å (characteristic of Cu₂O, 111), these crystals also show presence of grain boundaries. Pt crystal with grain boundaries shows higher current density in I/V curve, we anticipate similar behaviour with our catalyst material. Theoretical calculations¹² on CO₂ adsorption onto Cu₂O crystal show most favourable adsorption occurs on 111 plane of Cu₂O crystal. From SAED analysis, we find brightest ring due to 111 planes indicating these nano crystals will adsorb CO₂ easily. The chitosan film embedded Cu₂O catalyst are seen in low magnification (Fig.S1).

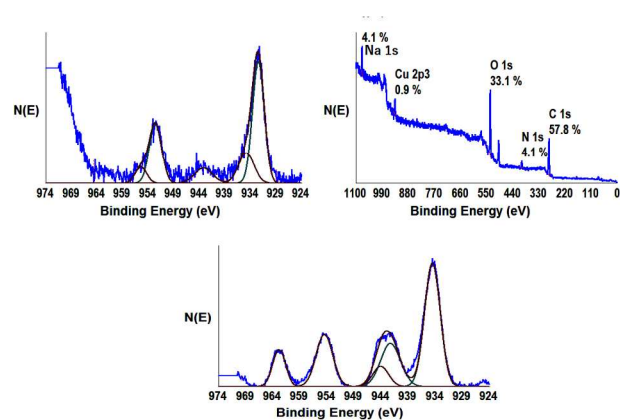


Fig. 5 XPS of CS-Cu_xO (top, left) and Cu_xO, control (bottom), survey scan of CS-Cu_xO (top, right).

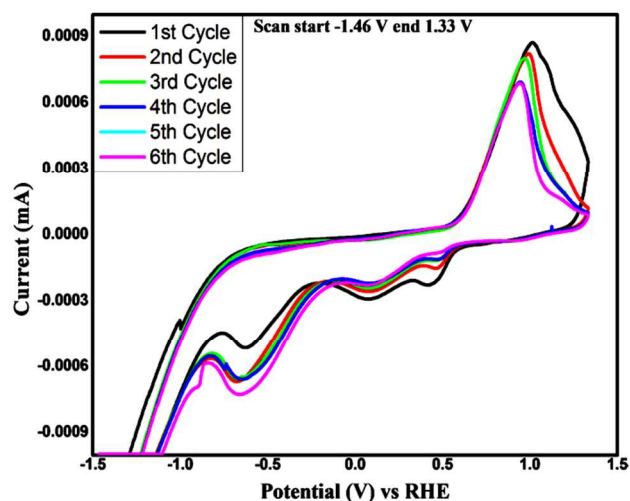


Fig. 6a CV of CO₂ reduction on to Pt|CS-Cu_xO at a scan rate of 200 mVs⁻¹.

Electro-catalytic activities of these CS-Cu oxides catalysts towards CO₂ reduction have been studied by cyclic voltammetry (CV) techniques. Cyclovoltamograms of CO₂ reduction using these catalyst loaded electrodes in 0.1 M Na₂SO₄ solution saturated with CO₂ (pH=5.3) at scan rate of 200 mVs⁻¹ are shown in Fig. 6-7, scan rate is optimised at 200 mVs⁻¹ to obtain significant peak current values and minimize Cu (II) formation during forward scan. A typical CV for this system using control catalyst at a scan rate of 50 mVs⁻¹ is shown in Fig. S2. Interestingly, the current values are reduced almost 10 folds compare to those at higher scan rate (Fig. 7); as a result, some important reduction peak like peak at -0.24 vs RHE of Fig.7 become almost invisible. The appearance of initial small reduction peaks at around 0.535 V and 0.085 V vs RHE at pH 5.3 (Fig.6) are owing to the reduction of Cu (II) to Cu and Cu (II) to Cu (I) respectively. These values are close to the reported values of these redox couples on to Cu powder pasted on graphite electrodes.¹⁹

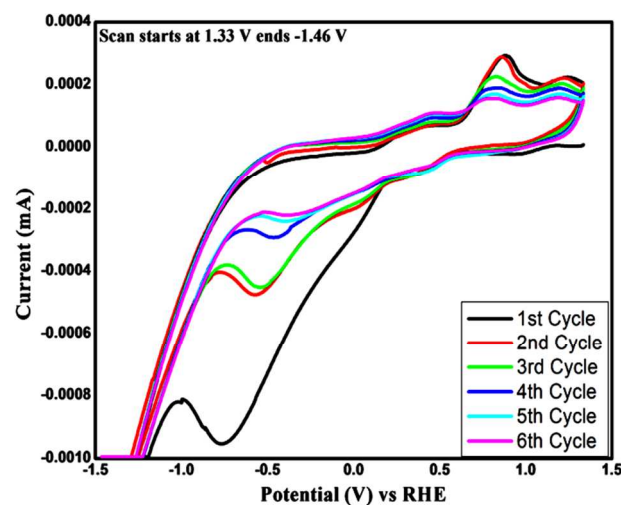


Fig. 6b CV of CO₂ reduction onto Pt|CS-Cu_xO at scan rate of 200 mVs⁻¹.

Cyclic voltammograms of CO₂ reduction using different electrocatalysts including Cu₂O, Cu-ZnO composite have been reported²⁰ earlier that shows a long downward cathodic tail²⁰ due to H₂ evolution reaction (HER) along with a small CO₂ reduction peak. We have also observed similar cathodic tail²⁰ owing to H₂ evolution reaction (HER) with our Cu₂O control without CS (Fig. 7).

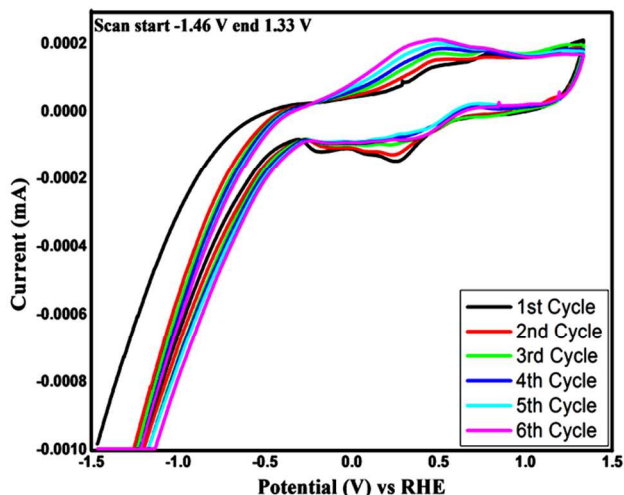


Fig. 7 CV of CO₂ reductions onto Pt/Cu_xO at a scan rate 200 mVs⁻¹.

But with CS composites of Cu_xO, this tail appears (Fig.6) after -0.865 V with a small peak at -0.665 V vs RHE at pH 5.3 attributable to CO₂ reduction. This indicates HER onto CS-Cu oxides composite surface is retarded probably due to protonation of free amino groups of CS which repels incoming H⁺ towards electrode surface as shown in Fig. 8. It is interesting to note that basic features of the cyclic voltammogram remains unaltered after repeating the cycles and changing the scanning directions which indicate that the catalysts are not poisoned by the reduction products. Carpenter et al²¹ reported that an indole based amine acts as a good photo catalyst for conversion of CO₂ to formic acid.

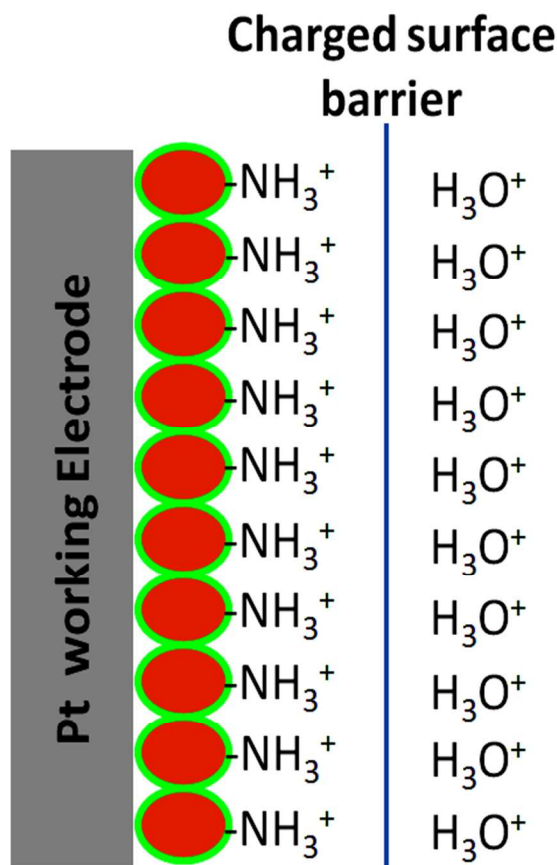
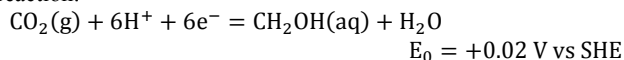


Fig. 8 Schematic diagram showing positively charged barrier formation of CS coated Cu_xO catalyst that retards H₂ evolution reaction.

Flake et al^{15(a)} has reported good Faradic efficiency for CO₂ reduction onto Cu-ZnO surface holding potential at -1.4 V vs Ag/AgCl and in another paper^{15(b)} this group has pointed out that thinner copper-oxide layers are found to improve efficiency of CO₂ electro-reduction to methanol. Ogura et al¹⁰ pointed out that CO₂ reduction starts at -0.6 V vs Ag/AgCl and formation of hydrocarbons like ethylene, methane etc occur at -1.2 V vs Ag/AgCl. It is well reported that CO₂ reduction potential, onset and cathodic peak potential dependent on the reaction conditions^{15(b)} like pH of the solution, composition and morphology of the catalyst²² as these factors mainly dictate the reaction path and products of the reactions. Generally, mixtures of different products as CO, HCOOH, CH₃OH, CH₄, CH₂=CH₂ etc are formed^{5,6,10,15} during such electro reduction process owing to multi steps electro-chemical (EC) and chemical mechanistic paths.¹¹ It is reported¹⁵ CH₃OH is the major reduction product onto Cu₂O surface though it involves six electron transfer reaction.



From Fig. 6, it is seen that CO₂ reduction starts at -0.075 V vs RHE at pH 5.3 or +0.025 V vs SHE with a peak potential at -0.665 V vs RHE, indicating possible formation of mixture of products including methanol as the observed potential is close to the reported value of oxidation potential of methanol onto Cu₂O surface. We have repeated the experiment several times using freshly prepared CS-Cu oxides catalyst and successively using the catalyst coated

electrodes, we got an excellent reproducible results indicating stability of the CS coated catalyst and its control. Here, we have not found any signature of methanol oxidation peak at the anodic scan; this may be due to extremely low methanol concentration on the electrode surface. Methanol formation as a major product of CO₂ reduction onto Cu₂O surface is well reported.^{11,15} and augments our analysis on onset potential of CV experiment

In aqueous environment the H₂ evolution reaction cannot be eliminated.²³ H₂ so formed may undergo dissociative adsorption onto catalytic surface¹¹ promoting chemical reduction path. In our control experiment with Cu_xO prepared using literature protocol, we found a small peak at -0.24 V vs RHE that is because of electro-reduction of adsorbed CO₂ in a different path as suggested by Ogura.¹⁰

Conclusions

In this communication, we have prescribed a simple method of one-pot synthesis of 10-20 nm sizes CS coated CuO/Cu₂O nano electro-catalyst for CO₂ reduction. We have demonstrated for the first time that CS-Cu_xO nano composite is an ultra thin film forming electro-catalyst for CO₂ reduction in aqueous media and it retards hydrogen evolution reaction. This suggests CS-CuO/Cu₂O is a new thin film forming composite electro-catalyst for efficient CO₂ reduction.

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Notes

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