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Photo-catalytic Reduction of CO_2 to Ethanol

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ABSTRACT

We report here photo-catalytic reduction of CO_2 to ethanol by Cu_2O nano catalyst dispersed onto p-type Si-wafer. The catalyst was synthesized by simple hydrothermal reaction of Cu(I) -acetate salt. The purified catalysts were characterized by AFM, TEM and XPS. A boron doped Si-wafer was spin coated with a thin film of aqueous dispersions of the catalyst for photo-reduction of CO_2. We observed signature of ethanol in NMR analysis of photo-reduction products. The mechanism of ethanol formation has been discussed.

1. Introduction

During the recent years, there is an increasing interest [1-9] in the development of photo-catalysts and electro-catalysts for CO_2 reduction. Carbon dioxide is a greenhouse gas and causes global warming to a large extent. Natural photosynthetic pathway or carbon pathway [2] is not capable of restoring the ecological CO_2 balance because of rapidly increasing global carbon emission. Thus, CO_2 utilization through its photo-chemical or electro-chemical reduction [1-8] to alcohol or hydro-carbon is an additional effective path in restoring CO_2 balance. But major bottleneck of CO_2 reduction reaction is that it is thermodynamically non spontaneous reaction and kinetically difficult because of requirement of high activation energy. In natural photosynthetic dark reaction, free energy released by conversion of ATP to ADP and reducing molecule NADPH are used to fix and reduce CO_2 to carbohydrate. The enzyme Ribulose Bisphosphate Carboxylase (RuBPCO) acts as catalyst. In laboratory experiments with CO_2 reduction using sun light or electrical energy, it is reported [2,8,9] Cu_2O is an efficient catalyst for such reduction. This is because of its unique band gap energy (2.2 eV) matches absorption of visible light and CO_2 molecules are easily adsorbed onto crystal lattice of Cu_2O. Calculated values of heat of adsorption show favourable interactions between CO_2 molecules and Cu_2O. Apart from these, high optical absorption coefficient and simplicity in preparation of Cu_2O make it an attractive candidate for photo-voltaic application.

In this paper, we report our works on one step hydrothermal method of preparation of copper –oxides nano particles and their catalytic activity towards photo reduction of CO_2.

2. Experimental Methods

2.1 Materials

$CuSO_4$, $5H_2O$, NaOH (Sigma-Aldrich) and AcOH, HCl (technical grade, Fisher Scientific) were used as supplied. Hydrothermal reaction was carried out in a hard glass 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 system was used to obtain DI water of resistivity 17.9MΩ-cm. Fisher scientific digital vortex mixer was used to mix reagents for reaction.

2.2 Methods

We have modified the literature [10] protocol of preparing copper (I)-oxide nanoparticles. Exactly 300 mg of $CuSO_4$, $5H_2O$ was dissolved in 30 mL of 10% AcOH solution followed by hydrothermal reaction at 300 °C for 1.5 hr followed by adjustment of pH to 7.4. This dispersion was dialysed against DI water, centrifuged and dried under vacuum. It is proposed that cupric acetate undergoes reduction and decomposition under hydrothermal condition forming Cu and Cu_2O.

2.3 AFM Images

Silicon wafer (boron doped) was purchased from Nova electronic materials water dispersed sample was spin coated and dried in vacuum. 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 k Hz). AFM images were recorded at room temperature.

2.4 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.

2.5 XPS Images

X-Ray Photoelectron Spectroscopy (XPS) was performed 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 and 30% Lorentzian line shape was used.

2.6 NMR Spectroscopy

NMR spectra were recorded with a Varian Gemini-500 (500 MHz for 1H) or spectrometer with D_2O as solvent. After photo-catalytic reduction of saturated CO_2 solution the silicon wafer coated catalyst was taken in vial and washed with D_2O to leach out the products.

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2.7 Fabrication of Catalyst Coated Si-wafer and Photo Reduction Setup

A 1cm² silicon wafers was cut and cleaned with dilute HCl, water and ethanol followed by air drying. Chitosan coated copper nano particles disperser in water was spin coated at exact same condition as the AFM samples were prepared. In a 10 ml cylindrical vessel measured amount of Na_2CO_3 was taken then HCl was injected for full neutralization of Na_2CO_3 inside. Silicon wafers coated with catalyst and were placed carefully in the CO_2 saturated solution. The whole set up was kept for 8 hr under direct sun-light. A control experiment was performed wrapping the container with a black paper.

3. Results and Discussion

The AFM image (Fig. 1) clearly shows mono dispersed nano formation. The particles are dispersible in water. The particle sizes vary from 40-250 nm. This is been confirmed from TEM image latter. The particles are almost spherical.

From TEM image (Fig. 2), presence of copper nanoparticles are seen with calculated d spacing values of 4.2 Å, exactly matching with Cu_2O, 111 planes. It is worth mentioning that 111 plane is best for catalytic activity in CO_2 reduction reaction facing up in our case. The diameters of the Cu_2O nano particles varied from 50-250 nm indicating formation of nearly mono dispersed nanoparticles of Cu_2O.

The XPS spectra (Fig. 3) shows presence of different mixed valent copper both Cu^+ and Cu^{2+} copper oxide samples. The presence of 934 ev peak is characteristic to Cu(I) whereas the peak at 936 ev together with shake up peaks indicates presence of Cu(II) peaks as well as acetate coatings.

The acetate coated copper catalyst solution was drop casted on to the Si-wafer. It nicely stuck to the wafer. The copper nanoparticles are well dispersed as seen in AFM images. After exposing the catalysts coated Si-wafer dipped in CO_2 saturated solution to direct sunlight for 8 hours and analyzing the products by NMR (Fig. 4), we get an indication of formation ethanol as major photo-reduction products of CO_2.

It may be mentioned that Liu *et al* [11] also observed exclusive formation of ethanol as photo-catalytic reduction product using $BiVO_4$ as photo- catalyst. Xia *et al* [12] studied photo-reduction of CO_2 with multi walled CNT-TiO_2 composites catalyst and noted that ethanol is a major product when the catalyst was prepared by sol-gel technique but formic acid was formed as major product with catalyst prepared by hydrothermal method. We have also observed [13] formation of formic acid with Cu_xO catalyst prepared using depolymerized chitosan. In fact, different photo-reduction products like methane, methanol, ethanol, formic acid, ethane etc. are obtained [14, 15] depending on nature of catalysts, their size, shapes and reaction conditions particularly pH of the solution.

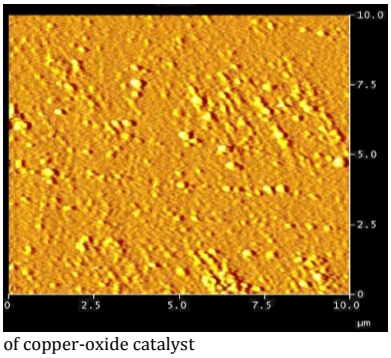

Fig. 1 AFM image of copper-oxide catalyst

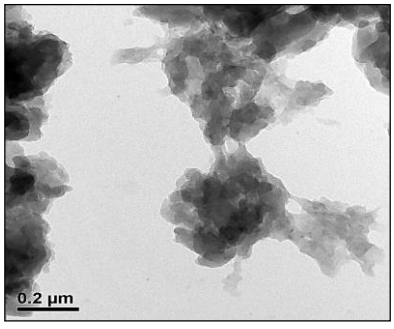

Fig. 2 TEM image of copper-oxide catalyst

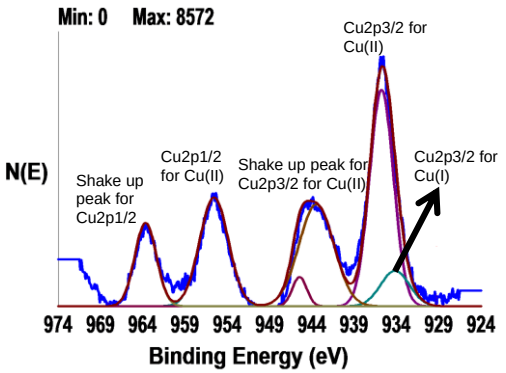

Fig. 3 XPS image of the prepared Cu-oxide catalyst.

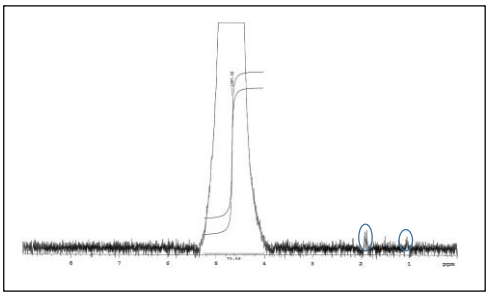

Fig. 4 NMR of the products leached in D_2O

Admittedly, the quantum yield of such conversion is extremely small but the signature of ethanol is indicated from simple NMIR analysis. It may be mentioned that the reaction was carried out under moist condition, there are huge noise peaks in this simple NMR product analysis method.

We propose formation of ethanol according to the following scheme [13]:

This is initiated by water splitting reaction [9] and formation of CO_2 radical ion onto catalyst surface by electronation.

$$CO_2\,(ad) + e\,(CB) = {}^{\bullet}CO_2^-$$
$${}^{\bullet}CO_2^- + H^{\bullet}\,(ad) = CO\,(ad) + OH^-$$
$$CO\,(ad) + e\,(CB) = {}^{\bullet}CO^-$$
$${}^{\bullet}CO^- + H^{\bullet}\,(ad) = {}^{\bullet}C + {}^{\bullet}OH$$

Formation carbonaceous deposit onto catalyst surface supports this scheme.

$${}^{\bullet}C + xH^+ + xe = {}^{\bullet}CH_x$$
$${}^{\bullet}CH_2 + {}^{\bullet}CH_2 + H^+ + e = {}^{\bullet}C_2H_5$$
$${}^{\bullet}C_2H_5 + {}^{\bullet}OH = C_2H_5OH$$

${}^{\bullet}OH$ radicals are formed at the hole sites of semiconductor.

4. Conclusion

We have synthesized Cu_2O nano photo-catalyst by simple hydrothermal method and demonstrate that it reduces CO_2 with ethanol as major product. We have explained the formation of ethanol by well-known carbon radical formation path.

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