Triethanolamine (TEA) aqueous solution as an Electrolyte promoter in CO\textsubscript{2} photoelectro-conversion under simulated solar irradiation assisted by Cu-doped graphene-Titania Catalyst

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Abstract

Copper doped graphene-TiO\textsubscript{2} nanocomposite were prepared via sol-gel process and embedded onto ITO coated glass films using electrophoretic deposition technique. The catalyst films were used for photoelectrocatalysis (PEC) of CO\textsubscript{2} induced under simulated solar irradiation. Triethanolamine (TEA) aqueous solution was used as an electrolyte in this experiment. CO\textsubscript{2} capture in the electrolyte solution plays vital role in the PEC process and in this case, the effect of TEA was investigated. Although the absorption rate of CO\textsubscript{2} is lower in TEA solution than primary or secondary amines, CO\textsubscript{2} loading was found higher in the solution. Less reactivity of TEA towards CO\textsubscript{2} was also observed. The impedance results showed that, increased concentration of TEA in aqueous solution helps to reduce charge transfer resistance and thus facilitates CO\textsubscript{2} reduction process.

Introduction

Along with some major greenhouse gases such as methane, carbon dioxide (CO\textsubscript{2}) is also of concern nowadays because of its high stability in nature and heat trapping property in the environment, thus acting as heat sink. Researchers have been working on rapid and effective conversion of atmospheric CO\textsubscript{2} for energy, chemicals and environmental sustainability. But increasing population, deforestation, burning of fossil fuels and high energy demands for driving modern civilization are contributing to increase atmospheric CO\textsubscript{2} day by day [1]. One of the most modern technologies proposed by the researchers for the mitigation of atmospheric CO\textsubscript{2} is photoelectrocatalysis (PEC) process of CO\textsubscript{2}. Reduced charge recombination, efficient photo conversion and recycling capability are the major advantages of PEC process. A lot of research works are being carried out to establish CO\textsubscript{2} photoconversion technology for an industrial revolution. The main challenges to attain desired results are to find suitable semiconductor photoelectrode with appropriate band energies, electrolyte media for high CO\textsubscript{2} absorption and optimum process conditions [2].

Titania (TiO\textsubscript{2}) semiconductor nanomaterials have already showed high photocatalytic performance. Modification of TiO\textsubscript{2} with various metals and non-metals were carried out in recent days to increase performance. Recently, graphene, a crystalline state of carbon, showed high photocatalytic performance when incorporated with TiO\textsubscript{2} nanomaterials.

In this work, Cu-doped graphene-TiO\textsubscript{2} nanocomposite thin film were prepared for photoelectrocatalysis of CO\textsubscript{2} and aqueous triethanolamine (TEA) solution was used as electrolyte. It is expected that, higher concentration of TEA in aqueous solution helps to facilitate CO\textsubscript{2} conversion reaction by reducing charge transfer resistance.
Experimental procedure

(a) nanocomposite preparation. Cu doped graphene-TiO$_2$ nanocomposite was prepared via sol-gel processing. Precise weighted amount of copper nitrate pentahemihydrate and fine graphene powder was added with DI water, absolute ethanol and 8 ml of acetic acid to prepare solution A. Solution B was prepared with 20 ml of tetra-n-butyl ortho titanate (analytical grade) and 80 ml of absolute ethanol. Solution A was added dropwise to solution B while it was under vigorous stirring. A homogeneous solution thus obtained was further stirred continuously for 30 minutes and kept for 48 hours until gel formation. A thick gel was obtained and it was dried at 100°C overnight. The coarse dry sample was milled and calcined at 550 ºC under air for 4 hours. The atomic ratio in the doped sample was kept 1% for both Cu and graphene content.

(b) Electrode preparation. In this part of experiment, electrophoretic deposition was carried out at a constant voltage of 60 V as the optimum potential in 0.01 mg/ml water suspension of aforementioned composite material. Indium tin oxide (ITO) coated glass substrates were used as anode and cathode. The substrates were connected to a regulated DC power supply. Prior to the deposition process, the ITO substrates were washed with acetone, dehydrated alcohol and finally with distilled water.

Results and discussion

From the SEM image in Fig. 1, it could be observed that the nanocomposite coating on ITO substrate was homogeneous. Layered particles with high surface area were also observed (inset). Particle size variation found which ensures the influence of doping process.

Fig. 1: SEM image of Cu doped TiO$_2$ nanocomposite thin film.

Photoelectrocatalysis experiment was conducted in a cubic quartz reactor using a three electrode system (Fig. 2). A standard calomel electrode (SCE) was used as a reference and platinum was used as counter electrode. A 150 W solar simulator was used as a light source.

Fig. 2: Photoelectrocatalysis of CO$_2$ in TEA aqueous electrolyte solution.
TEA aqueous solution of 5%, 10% and 20% (by volume) were used as electrolyte. The result in Fig. 3 shows, 5% TEA solution gained higher charge transfer resistance whereas 10% and 20% TEA solution obtained lower resistance respectively. The reaction is proposed as,

\[
\text{CO}_2 + \text{N}(\text{CH}_2\text{CH}_2\text{OH})_3 + \text{H}_2\text{O} \leftrightarrow (\text{CH}_2\text{CH}_2\text{OH})_3\text{NH}^+ + \text{HCO}_3^- \quad (1) \quad [3]
\]

The reaction in Eq. 1 is a pseudo-first order reaction. In fact, tertiary amine does not react directly with CO\(_2\) and the reaction rate is very slow. With the increase of TEA concentration, CO\(_2\) loading is also increased. Thus the reaction goes forward and protonation occurs with time. This facilitates CO\(_2\) reduction in the solution. Furthermore, HCO\(_3^-\) is not very stable in TEA the solution. This phenomenon makes CO\(_2\) reduction process easier.

![Graph showing concentration effect of TEA aqueous solution on photoelectrocatalysis of CO\(_2\)](image)

**Fig. 3:** Concentration effect of TEA aqueous solution on photoelectrocatalysis of CO\(_2\) (EIS responses in Nyquist plot).

**Conclusion:**

TEA as a tertiary amine, does not react with CO\(_2\) directly. Unlike primary and secondary amine, TEA produces bicarbonates rather than carbamate ions. Although bicarbonates need higher potential to reduce, free CO\(_2\) increases with the increase of TEA concentration in the solution. TEA solution, being less reactive, could resist unwanted reactions as well as decomposition products [4]. Thus, TEA could be an effective solution component for efficient CO\(_2\) photoreduction process.

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