Fabrication of Visible-Light Responsive CQDs/Cu_2O Nanocomposite for CO_2 Photoreduction

Tharani Kulandaivalu[a], Suraya Abdul Rashid[a,b*], Nordin Hj Sabli[b], Tongling Tan[a]

[a]*Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*
[b]*Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*
**Corresponding Author's Email: suraya_ar@upm.edu.my*

Abstract: Semiconductor-carbonaceous integrated materials are gaining a vast demand in photocatalytic reactions for their facscinatng combined features to attain promising photocatalytic results. In this work, blue-fluorescent carbon quantum dots (CQDs) were synthesized via a facile top-down hydrothermal method using EFB biochar of oil palms as the carbon source. The CQDs were incorporated together with copper (I) oxide (Cu_2O) *via* a simple wet impregnation method to form CQDs/Cu_2O nanocomposite. High resolution transmission electron microscopy (HRTEM) confirmed the successful deposition of CQDs onto the surface of Cu_2O nanoparticles. The CQDs/Cu_2O nanocomposite showed a considerable improvement in the CO_2 photoreduction with an enhancement of 54% compared to the pure Cu_2O, due to the retardation of the recombination of charge carriers.

Keywords: *carbon quantum dots; copper (I) oxide; photocatalyst; CO_2 photoreduction*

INTRODUCTION

The increasing level of CO_2 emission from various human activities have lead to world's concern global warming. Photocatalytic reduction of CO_2 to simple hydrocarbon fuels is one of the promising strategies to reduce the concentration of CO_2 in the earth's atmosphere. Cu_2O is a potential photocatalytic material for its non-toxicity and photosensitivity to the visible light region of solar spectrum [1]. However, it suffers from fast recombination rate of electron-hole pairs due to the lower band gap energy (~2.02 eV) [2]. Meanwhile, CQDs are the newly discovered carbon nanomaterial of size less than 10 nm [3].They acted as a good electron mediator when CQDs coupled with semiconductors such as TiO_2, SiO_2 and ZnO were able to mitigate the recombination rate of charge carriers of these semiconductors for a greater photoactivity [4], [5]. This induces the designation of CQDs/Cu_2O nanocomposite photocatalyst in this work, using a simple wet impregnation method. The feasibillity of the developed photocatalyst was tested for CO_2 photoreduction under visible light irradation in a self-designed photoreactor conneted to an online gas chromatograph (GC). This photocatalyst demonstrated a considerable improvement to reduce CO_2 to ethane (C_2H_6) than that of pure Cu_2O under visible light irradiation. This suggests that CQDs/Cu_2O can serve as a promising photocatalyst, mainly due to the presence of CQDs to alleviate recombination of electron-hole pairs.

MATERIALS AND METHODS

Materials and chemicals

Copper (I) oxide nanopowder (Cu_2O) was obtained from US Research Nanomaterials, Inc. Deionized water was used throughout the experiment.

Preparation of CQDs/Cu_2O nanocomposite

In a typical process, 0.2 g of commercial Cu_2O nanopowder was dispersed in 10 ml of deionized water with the aid of a sonicator. About 2 ml of solution containing CQDs (2 mg/ml) which was prepared from EFB biochar of oil palm, *via* a top-down hydrothermal reaction was transferred into the dispersed Cu_2O solution. This mixture was magnetically stirred for 4 hours at room temperature and aged overnight. The mixture was finally washed with ethanol and deionized water several times before oven-dried at 80 °C for 12 hours to obtain the CQDs/Cu_2O nanocomposite. The morphology of the CQDs/Cu_2O nanocomposite was studied using HRTEM (Tecnai TF20 X-Twin FEI Company). The CO_2 photoreduction reaction was carried out in a self-designated reactor connected to an online GC, using halogen lamp as the visible light source.

RESULTS AND DISCUSSION

Morphological properties and photocatalytic study of CQDs/Cu_2O photocatalyst

Fig. 1 (a) displays a typical HRTEM micrograph of CQDs/Cu_2O nanocomposite where CQDs with quasi-spherical shape can be seen to be uniformly distributed uniformly distributed within Cu_2O. The higher resolution image from Fig. 1 (b) showed lattice spacing of 0.21 nm which corresponds to the (100) planes of graphitic carbon (d_{100}=0.213 nm) [6]. This confirms the presence of CQDs in the composite. Fig. 1 (c) shows the test results of the control experiments where (1) blank tests with no light and no catalyst, (2) reaction in the dark in the presence of photocatalysts, (3) photoreaction in the absence of photocatalyst where no considerate amount of product gases were detected by GC throughout the reaction period. This strongly implies that the product gases evolved were solely from the photoreduction of CO_2 and photocatalyst and light source are crucial for the occurrence of this reaction. However, with the presence of both catalyst and visible light source, CO_2 was successfully reduced to C_2H_6 where CQDs/Cu_2O photocatalyst showed a superior photoactivity than that of pure Cu_2O with the total of 103.64 μmol/$g^{catalyst}$ of C_2H_6 generated for 6 hours of continuous light illumination. This yield shows 54% of enhancement than the pure Cu_2O with total amount of C_2H_6 produced about 67.33 μmol/$g^{catalyst}$ for the same reaction time. This improvement of photoactivity of CQDs/Cu_2O suggests that CQDs were able to reduce the recombination rate of charge carriers, thus providing more electrons for the reduction of adsorbed CO_2 species on the surface of catalyst [7].

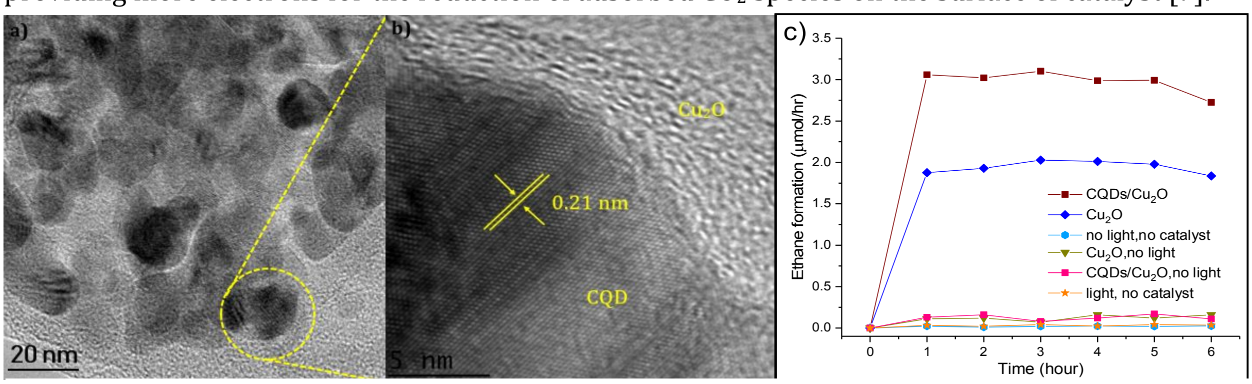

Fig. 1 (a), (b) HRTEM images of CQDs/Cu_2O, C_2H_6 formation from CO_2 photoreduction using Cu_2O and CQDs/Cu_2O photocatalysts

CONCLUSIONS

CQDs were prepared from EFB biochar of oil palms and were decorated onto pure Cu_2O using a simple wet impregnation method. The CQDs/Cu_2O nanocomposite photocatalyst was able to reduce CO_2 to C_2H_6 under visible light irradiation with an improvement in the photocatalytic activity of up to 54% compared to that of pristine Cu_2O. This demonstrated that incorporation of CQDs with Cu_2O was able to retard the recombination of the photogenerated charge carriers. The considerable enhancement in the photoactivity of the nanocomposite describes the importance of the CQDs to maximize the photoactivity of a reaction.

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