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# Carbon dioxide adsorption and cycloaddition reaction of epoxides using chitosan–graphene oxide nanocomposite as a catalyst

Santosh Kumar<sup>1,2,\*</sup>, Mohmmad Y. Wani<sup>1</sup>, Joonseok Koh<sup>2</sup>,  
João M. Gil<sup>3</sup>, Abilio J. F. N. Sobral<sup>1,\*</sup>

1. Chemistry Center, Department of Chemistry, University of Coimbra, Coimbra 3004-535, Portugal  
 2. Department of Organic and Nano System Engineering, Konkuk University, Seoul 143-701, Republic of Korea  
 3. CFisUC, Department of Physics, University of Coimbra, Coimbra 3004-516, Portugal

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## ABSTRACT

One of today's major challenges is to provide green materials for a cleaner environment. We have conducted studies on carbon dioxide (CO<sub>2</sub>) adsorption and conversion to valuable products by an ecofriendly approach based in chitosan/graphene oxide (CSGO) nanocomposite film. Rheological behavior indicates that the CSGO has a better solvation property than the pure chitosan. An adsorption capacity of 1.0152 mmol CO<sub>2</sub>/g of CSGO nanocomposite at 4.6 bar was observed. The catalytic behavior of the CSGO nanocomposite in the presence of tetra-*n*-butylammonium iodide (*n*-Bu<sub>4</sub>NI) as co-catalyst was evaluated for the cycloaddition of CO<sub>2</sub> to epoxides, to give cyclic carbonates, in the absence of any solvent. These results strongly suggest that the CSGO nanocomposite may open new vistas towards the development of ecofriendly material for catalytic conversion and adsorption of CO<sub>2</sub> on industrial scale.

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## Introduction

Burning of fossil fuels has caused a steady increase in atmospheric carbon dioxide concentration which is considered to be the most important provider to the increase in atmospheric temperatures in the 21st century (Kintisch, 2008). In response to this, and growing needs of modern society and rapid industrial development, it is necessary to design environmentally friendly and low-cost CO<sub>2</sub> storage methods and CO<sub>2</sub> conversion catalysts. Graphene has attracted great interest for its potential use in various applications, such as hydrogen storage (Kumar et al., 2014; Ma et al., 2009; Srinivas et al., 2010; Yuan et al., 2011), carbon dioxide capture

(Balasubramanian and Chowdhury, 2015; Kumar et al., 2015c; Liu et al., 2015; Shen et al., 2015) and solar energy (Dai, 2013; Lightcap and Kamat, 2013; Tu et al., 2013). Graphene oxide (GO) possesses various reactive functional groups such as hydroxyl, epoxy, and carboxylic groups (Kumar and Koh, 2014). GO-based materials have attracted wide and intense interest for energy and environment related applications due to its excellent chemical stability, environmental friendliness and abundance. GO can be readily functionalized, which renders it useful in a wide range of synthetic transformations (Fan et al., 2015; Su and Loh, 2013; Zhang et al., 2014). Graphene has been suggested for storage of different gases in theoretical studies and its CO<sub>2</sub> adsorption capacity was

\* Corresponding author. E-mail: [santoshics@gmail.com](mailto:santoshics@gmail.com) (Santosh Kumar), [asobral@ci.uc.pt](mailto:asobral@ci.uc.pt) (Abilio J. F. N. Sobral).

demonstrated at  $-78.15^{\circ}\text{C}$  temperature, which has not much practical application (Ghosh et al., 2008). Therefore, there is a need to investigate and improve the  $\text{CO}_2$  adsorption and conversion ability of graphene based materials.

$\text{CO}_2$  is a thermodynamically stable molecule due to the negative adiabatic electron affinity and large ionization potential, thus making its conversion into useful products difficult under normal conditions. The formation of cyclic organic carbonates using  $\text{CO}_2$  as a renewable carbon feed stock is a highly vibrant area of research. Since these organic carbonates are useful building blocks and nontoxic reagents. Several different catalysts have been designed for the conversion of  $\text{CO}_2$  to useful products such as cyclic carbonates (Kumar et al., 2015c; Wani et al., 2016). Cyclic carbonates can be used as electrolytes in lithium ion batteries, as precursors for pharmaceutical intermediates, raw materials for plastics, and as environmentally friendly nonprotic solvents (Fujita et al., 2014).

Chitosan (CS) is a biopolymer, used in biomedical and industrial applications due to its biodegradability, biocompatibility and low cytotoxicity (Chattopadhyay et al., 2013; Dang and Leong, 2006; Dutta et al., 2013; Fan et al., 2013; Garg et al., 2013; Jayakumar et al., 2010; Kumar et al., 2010, 2015a, 2015b; Kumar and Koh, 2013; Muzzarelli, 1977; Srivastava et al., 2011; Wan Ngah et al., 2011). Recently, we have studied the carbon dioxide capture on a porous CS derivative (Kumar et al., 2016; Silva et al., 2013). Chitosan-graphene oxide organic aerogels for  $\text{CO}_2$  capture and effect of pyrolysis on chitosan-graphene oxide hybrid aerogels have also been studied (Alhwaige et al., 2013). However, to the best of our knowledge,  $\text{CO}_2$  adsorption and conversion on chitosan/graphene oxide (CSGO) nanocomposite films have not yet been reported. Pure CS polymer is not efficient for adsorption applications. We have demonstrated that dispersing GO into a CS matrix in the form of nanocomposite film leads to higher  $\text{CO}_2$  adsorption and improves its catalytic performance for cycloaddition of  $\text{CO}_2$  to epoxides. The preparation and applications of GO hydrogels and their composites are becoming a rapidly growing area in modern chemistry (Li and Shi, 2014). Herein, we report the development of CSGO nanocomposite for  $\text{CO}_2$  adsorption and chemical conversion to cyclic carbonates.

## 1. Materials and methods

### 1.1. Materials

CS with a degree of deacetylation (DD) of 79% was purchased by Sigma-Aldrich Chemical Co. (Germany). Graphite, 30% hydrogen peroxide, potassium permanganate, hydrochloric acid, sulfuric acid, glacial acetic acid, tetra-*n*-butylammonium iodide, propylene oxide, 2-(chloromethyl)oxirane and styrene oxide were purchased from Sigma-Aldrich Co. (Germany). All chemicals were used without further purification. Double distilled water was used to prepare experimental solutions.

### 1.2. Characterization

Fourier transform infrared (FT-IR) spectra of the compounds were recorded on a FT-IR (300E, Jasco, Japan) using an attenuated total reflectance method for films. X-ray diffraction measurements

were performed using a (D/Max2500VB+/Pc, Rigaku, Japan) with a  $\text{Cu K}\alpha$  radiation source (wavelength  $\lambda = 0.154 \text{ nm}$ ) at a voltage of 40 kV and a current of 50 mA. The scanning rate was  $3^{\circ}/\text{min}$  and the scanning scope of  $2\theta$  was from  $2$  to  $45^{\circ}$ . The surface morphology was analyzed by high resolution transmission electron microscope (HR-TEM, JEM3010, Jeol Ltd., Japan). The scanning electron microscope (SEM) images were measured with a scanning electron microscope (Vega3 SB, TESCAN, USA). The Brunauer-Emmett-Teller (BET) specific surface area of the CSGO was determined using a sorption analyzer (ASAP 2000, Micromeritics, Co., USA). The sample was degassed at  $200^{\circ}\text{C}$  until absolute pressure stabilizing below 25 mm Hg with  $\text{N}_2$  gas as the adsorbate. Percentage of porosity of CSGO was measured by Porosimeter (AutoPore IV Mercury, Micromeritics, USA). Density of CSGO was measured by AccuPyc 1330, Micromeritics, USA.

### 1.3. Synthesis of CSGO

GO was prepared by the oxidation of graphite using a modified Hummer's method (Hou et al., 2011; Hummers and Offeman, 1958). GO can be easily dispersed in water and forms a stable colloidal dispersion. The CSGO nanocomposite film was prepared according to our previous work (Kumar and Koh, 2014). CS (200 mg) was dissolved in 10 mL of 1.5% aqueous acetic acid and stirred for 20 hr at room temperature to prepare a clear solution. The GO powder (90 mg) was dispersed in 2 mL of distilled water and sonicated for 30 min until a homogeneous solution was formed. After that GO was added to CS solution at  $35^{\circ}\text{C}$  for 2 hr. The blended solution was poured in petri dish for a desired thickness and was dried at room temperature for about 36 hr. The film was carefully separated from petri dish.

### 1.4. Rheological measurements

Rheological measurements were performed using a rheometer (HAAKE MARS III, Thermo Scientific, Australia), with automatic gap setting and with a cone and plate geometry. The temperature control ( $\pm 0.1^{\circ}\text{C}$ ) was achieved using a Peltier unit. The rheological properties of the CS and CSGO hydrogels were determined through oscillatory measurements. An amplitude sweep (1–100 Pa) at fixed frequency (1 rad/sec) was firstly performed to make sure that the selected stress (20 Pa) is within the linear viscoelastic region. Then an oscillatory frequency sweep (0.01–10 rad/sec), at  $25^{\circ}\text{C}$ , was performed to measure  $G'$  and  $G''$ , the storage and loss modulus, respectively.

### 1.5. Carbon dioxide adsorption study

A volumetric Sieverts system was used for the analysis of  $\text{CO}_2$  sorption (Kumar et al., 2016; Silva et al., 2013). To derive the adsorbed quantities from pressure and temperature data we used the Benedict-Webb-Rubin equation of state on dedicated developed software, which includes corrections for pressure transducer calibration and small temperature variations. The sample chamber volume was measured by expanding helium gas at room temperature from the calibrated reference volume to the previously evacuated sample chamber. Prior to analysis, samples were outgassed at  $150^{\circ}\text{C}$  for 1 hr under vacuum, separately. The sample dry masses (0.0337 g for

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