## Supporting Information

Graphene oxide immobilized copper phthalocyanine tetrasulphonamide: first heterogenized homogeneous catalyst for dimethylcarbonate synthesis from CO$_2$ and methanol.

Subodh Kumar, Pawan Kumar and Suman L. Jain**
Chemical Sciences Division
CSIR-Indian Institute of Petroleum, Dehradun-248005 (India)

Email: Suman@iip.res.in

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1. Materials

Graphite flakes, triethylamine (99%), copper phthalocyanine (≥80%) were procured from Sigma Aldrich. Potassium permanganate (99.0%), sodium nitrate (99.0%), concentrated sulphuric acid, hydrogen peroxide (30%), hydrochloric acid, chloroacetic acid, thionyl chloride, chlorosulfonic acid (99%), dehydrated methanol, diethyl ether, dimethyl carbonate, DCC and HPLC grade water, were indentied from MERCK India. All chemicals were used as received and no further purification was done.

2. Techniques used

High Resolution Transmission Electron Microscopy (HR-TEM) image was recorded on FEI-TecnaiG² Twin TEM working at an acceleration voltage of 200 kV. For TEM analysis very dilute aqueous suspension of samples was deposited on carbon coated TEM grid. The structural and phase properties of synthesized materials was characterized by X-ray diffraction pattern using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu Kα radiation (λ= 0.15418 nm) with a scan rate 10°/min. The analysis was done by taking samples in glass slide and drying. FTIR spectra of synthesized catalyst were recorded on Perkin–Elmer spectrum RX-1 IR spectrophotometer. Raman spectra of materials were collected at room temperature using a Raman Microprobe (HR-800 Jobin-Yvon) with 532 nm Nd-YAG excitation source. A Perkin Elmer lambda-19 UV-VIS-NIR spectrophotometer was used to determine the optical absorption of the samples in the wavelength range of 200–900 nm with resolution of 1 nm using BaSO₄ as reference material. Thermal degradation pattern (TGA) for evaluation of chemical nature of material was obtained on a thermal analyzer TA-SDT Q-600 between temperature range was 40
to 900 °C with heating rate was 10 °C/min under nitrogen flow. The Brunauer–Emmett–Teller (BET) surface area and other surface properties like pore diameter and pore volume of obtained samples were measured with an ASAP2020M apparatus Micromeritics ASAP2010 working in liquid nitrogen at 77 K. The yield of product during photoreaction was determined by GC-MS (Model No. ) and GC-FID. Metal content of catalysts were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc, USA). For ICP-AES samples were prepared by digesting calculated amount of samples with minimum amount of HNO₃ for oxidizing carbonaceous material and then volume was made upto 10 ml by adding water.

3. Synthesis of graphene oxide (GO)

Graphene oxide was synthesized by following Modified Hummer’s method¹. In a round bottom flask, 1 g graphite flakes and 0.75 g sodium nitrate was taken and placed in an ice bath for maintaining the temperature below 5 °C. After that concentrated sulphuric acid (34 ml) was added with stirring. To this solution 4.5g KMnO₄ was added slowly and the resulting mixture was kept for stirring for 5 days. To the reaction mixture 50 ml dilute H₂SO₄ (5 wt%) was added and heated at 90°C with stirring. Next to this step 2.7 ml 30 wt% H₂O₂ solution was added to reaction mixture and stirred for 2h at room temperature. The obtained graphene oxide sheets was washed with H₂SO₄ (3 wt%), H₂O₂ (0.5 wt%), H₂O₂ (0.5 wt%), and HCl (3 wt%) by centrifugation. Finally washing was done with distilled water until the pH of solution became neutral dried.

4. Synthesis of carboxylated graphene oxide
The synthesized GO was dispersed in distilled water under sonication to make a 2 mg/ml suspension of GO. Then 1.2 g NaOH and 1.2 g chloroacetic acid was added to this suspension and sonicated for 3 h for converting –OH and epoxide groups in –COOH groups by attachment of –CH₂COOH linker. After sonication dil. HCl was added until solution for making solution neutral. Finally obtained GO-COOH was separated by centrifuge and washed 3 times with distilled water and dried under vacuum. The detailed experimental procedure is given in literature².

5. Immobilization of CuPc-tetrasulphonamide to carboxylated GO

Immobilization of CuPc-tetrasulphonamide is done according to the literature³. In a round bottom flask 200 mg GO-COOH was taken and 1ml DMF and excess of thionyl chloride was added. The obtained mixture was heated to 65 °C for 12 h for converting –COOH groups to –COCl groups. Unreacted thionyl chloride was removed by distillation under reduced pressure to obtain GO-COCl 1 which was finally washed with THF (three times) and dried under vacuum for 12 h. For the immobilization, 50 mg of CuPc-(SO₂NH₂)₄ prepared as given in literature⁴ and 200 mg GO-COCl were added to a round bottomed flask and refluxed in DMF at 130 °C for 24h in the presence of triethyl amine (1 ml) under nitrogen. After cooling, the heterogeneous material i.e. GO-CuPc(SO₂NH₂)₄ 2 was collected by centrifugation and washed with ethanol until color of washing disappear and dried. Copper content of synthesized catalyst as determined by ICP-AES analysis was found 2.4 wt%.

6. General Experimental Procedure for DMC synthesis

In a typical reaction, GO-CuPc(SO₂NH₂)₄ (0.2 g) and methanol (6 ml, ) were charged into the 15 ml high pressure reactor without using any additional solvent. The reactor was sealed and purged
with carbon dioxide to replace all others gases. Reactor is then charged with CO$_2$ until 25 bar pressure reached. The reaction mixture was stirred for 2.5 h at 110 °C. After this, the reactor was placed into ice water and CO$_2$ was released slowly passing through a cold trap containing ethanol. After depressurization, the reaction mixture was transferred in a beaker and the catalyst was separated by centrifugation. Reaction mixture was then analyzed by GC equipped with a flame-ionized detector and a capillary column. The crude product was purified by distillation; the product dimethyl carbonate was obtained as transparent clear liquid in 13.3% yield. To study the reusability of the catalyst, the recovered GO-CuPc(SO$_2$NH$_2$)$_4$ catalyst was washed using ethanol and then dried under vacuum for 2 h at 50 °C before reuse

7. Adsorption Desorption Isotherm of GO and GO-CuPc(SO$_2$NH$_2$)$_4$

Adsorption desorption isotherm of GO and GO-CuPc(SO$_2$NH$_2$)$_4$ as shown in Fig S1a, was of Type IV so the material was mesoporous in nature according to IUPAC classification. Surface area as calculated by BET ($S_{BET}$) for GO and GO-CuPc(SO$_2$NH$_2$)$_4$ was found to be 80.24 m$^2$.g$^{-1}$ and 22.65 m$^2$.g$^{-1}$ respectively. Further pore size distribution of GO as shown in Fig S1b has most of the pores having diameter of approximately 3.54 nm while for GO-CuPc(SO$_2$NH$_2$)$_4$ different types of pore originated in the region of 4.12 nm, 12.5nm and 27.4nm. This change in pore size distribution was assumed due to the intercalation of CuPc(SO$_2$NH$_2$)$_4$ between GO’s sheets.
Fig S1: Adsorption desorption isotherm and pore size distribution of; a) GO; b) GO-CuPc(SO$_2$NH$_2$)$_4$

8. UV-Visible spectra of CuPc(SO$_2$NH$_2$)$_4$, GO, GO-CuPc(SO$_2$NH$_2$)$_4$

Electronic spectra (UV/Vis) of CuPc(SO$_2$NH$_2$)$_4$, GO and GO-CuPc(SO$_2$NH$_2$)$_4$ is shown in Fig. S2. As shown the spectra of copper phthalocyanine tetrasulphonamide shows two intense characteristics Soret and Q band at 309 nm and 672 nm respectively (Fig S2 a). In case of graphene oxide a intense peak at $\lambda_{max}$ 230 nm due to $\pi\rightarrow\pi^*$ transition of sheets of aromatic system and a shoulder at $\lambda_{max}$ 300 nm is due to $n\rightarrow\pi^*$ transition of oxygen carrying groups to $\pi^*$ orbitals of ring system (Fig. S2b), it is in accordance to the previously reported literature. In GO-CuPc(SO$_2$NH$_2$)$_4$ the peak of GO is showing red shift, a peak at 230 nm is disappeared and a new intense peak observed at 305nm is probably due to the utilization of epoxide groups in bond formation so the planer $\pi$ aromatic system of ring became distorted (Fig. S2c). Due to this deformation $\pi\rightarrow\pi^*$ transition became weak and $n\rightarrow\pi^*$ transitions strongly appear. Further increase of area under curve in GO-CuPc(SO$_2$NH$_2$)$_4$ shows that due to attachment of phthalocyanine visible light absorptivity of GO get increased.
**Fig S2:** UV-Visible spectra of; a) CuPc(SO$_2$NH$_2$)$_4$; b) GO; c) GO-CuPc(SO$_2$NH$_2$)$_4$

**References**


