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## The potential of a graphene-supported porous-organic polymer (POP) for $CO_2$ electrocatalytic reduction<sup>+</sup>

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A one-pot, bottom-up assembly of a pyrimidine-containing porousorganic polymer (PyPOP) was conducted to homogenously deposit the PyPOP atop unmodified graphene sheets, affording a composite material PyPOP@G. The PyPOP demonstrated an appreciable affinity toward CO<sub>2</sub> capture but was found to be largely insulating, hindering its usage in potential electrochemical conversion of CO2. However, its composite with graphene was found to be microporous, with maintained affinity toward CO<sub>2</sub> and furthermore demonstrated significant electrochemical activity toward CO<sub>2</sub> reduction (5 mA cm<sup>-2</sup> at -1.6 V), not observed in either of its two components separately.

The current interest in technologies to capture and sequester CO<sub>2</sub> emissions has stimulated interest in materials capable of both CO<sub>2</sub> capture and catalytic transformation.<sup>1,2</sup> The bottomup approach of constructing microporous solids with high surface area enabled scientists to access tailorable platform materials. Fine tuning of these materials through judicious selection of the building blocks resulted in demonstrated performance for heterogeneous catalysis.<sup>3,4</sup> Of particular interest are materials acting as non-noble metal-based heterogeneous catalysts for catalytic conversion of CO<sub>2</sub> into feedstock reagents.<sup>5,6</sup> Recently, catalytic moieties like metallo-salens were successfully incorporated into the backbone of microporous solids, facilitating catalytic conversion of CO2 into cyclic carbonates under thermal conditions.<sup>7,8</sup> However, the vast majority of such microporous solids have poor electrical conductivity, hindering access to the rich arena of electrochemical processes. Several attempts have recently been made to enhance the electrical properties of these materials.9-13 Such attempts afforded materials for application in catalytic oxygen reduction,<sup>14,15</sup> supercapacitors,<sup>16,17</sup> as well as energy storage.<sup>18</sup>

Porous organic polymers (POPs) are an emerging class of microporous solids with robust carbon backbones, accessible through various synthetic techniques. They are currently drawing wide attention for CO<sub>2</sub> capture, storage, and sequestration.<sup>19-22</sup> Graphene (G), with its superior properties including mechanical strength and thermal and electrical conductivity, has also attracted attention for various applications.<sup>23-25</sup> As POPs and graphene constitute two distinct solids with highly contrasting synthesis and chemical functionality, an approach to merge the realms of both into a composite material for application in CO<sub>2</sub> capture and/or conversion is of interest. As both solids are virtually insoluble in all common solvents, the approach described here relies on bottom-up assembly of POPs from their soluble molecular precursors atop non-modified graphene. For synthesis of POPs, the Sonogashira-Hagihara (SH) cross coupling reactions were successfully utilized to construct a large family of such microporous solids from judiciously selected molecular building blocks (MBBs).26

Herein, we describe a synthetic strategy to construct a novel composite material targeting CO<sub>2</sub> capture and conversion. Two essential components were incorporated in the design of this solid; namely, a pyrimidine-based POP (PyPOP) that demonstrated a microporous character and good affinity to  $CO_{21}^{20}$  and graphene, with its known desirable electrical conductivity.

In a one-pot reaction, the bottom-up synthesis of the PyPOP was conducted through an SH cross coupling reaction, in the presence of dispersed, non-modified graphene. This reaction resulted in the homogenous deposition of the PyPOP on top of graphene sheets, referred to here as PyPOP@G, Scheme 1. The Fourier-transform infrared spectroscopy (FT-IR) conducted on the PyPOP@G confirmed the presence of the PyPOP in the composite, ESI.† The FT-IR spectrum of the PyPOP@G showed several peaks characteristic of the PyPOP, including the internal  $\nu_{C \equiv C}$  stretching at 2215 cm<sup>-1</sup>, pyrimidine  $\nu_{C \equiv N}$  stretching at 1564 cm<sup>-1</sup> and absence of the terminal  $\nu_{C-H}$  stretching found at  $\sim$  3200 cm<sup>-1</sup> for the starting triethynylbenzene. Further characterization for the composition of the product composite included elemental analysis, indicating significant changes



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Scheme 1 The one-pot, bottom-up, synthesis of the PyPOP@G. C (orange), N (blue), H (white), G (green hexagons).

to C and N contents for the PyPOP@G as compared to the PyPOP. The observed trend of increased C content and decreased N content, when comparing the PyPOP to the PyPOP@G, is expected due to incorporation of purely carbon-based G into the matrix of the PyPOP. The elemental analysis results, shown in the ESI,† indicated the following composition for graphene C, 94.3% and for PyPOP (PyPOP@G): C, 71.55% (76.4%); H, 2.66% (2.95%); N, 21.14% (6.64%). Additional characterization of the PyPOP and the PyPOP@G was conducted through thermogravimetric analysis (TGA, ESI<sup>+</sup>). The TGAs revealed the thermal stability of the PyPOP up to  $\sim$  350 °C, after which noticeable and gradual weight loss was observed due to the thermal degradation of the polymer. The same behavior was also observed for the composite. In the TGA for PyPOP@G, a noticeable weight loss of  $\sim$  5 wt% was observed below 100 °C. This change can be ascribed to loss of adsorbed moisture inside the pores of the PyPOP. The TGA for G demonstrated a minor weight loss of  $\sim 5$  wt% when heated up to 900 °C (ESI<sup>†</sup>). The uniform coverage of G by the PyPOP was evident from the transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images for PyPOP@G, Fig. 1. Further characterization studies including solid-state NMR spectroscopy and energy-dispersive X-ray analysis (EDX) are provided in the ESI,† and they confirmed the construction of the targeted material.

As it was previously demonstrated that the PyPOP, with its abundant basic binding sites of aromatic pyrimidine rings, has a favorable binding energy toward  $CO_2$ ,<sup>20</sup> we opted to explore its behavior toward  $CO_2$  sorption once composited with the graphene. N<sub>2</sub> sorption isotherms were measured for both the PyPOP and the PyPOP@G to establish their microporosity.



Fig. 1 TEM (left) and SEM (right) images of the PyPOP@G indicating homogenous coating of the graphene by the PyPOP.

Both were found to be microporous with comparable apparent surface area, as calculated using the Brunauer–Emmett–Teller (BET) model, Fig. 2 (BET surface area of 664 m<sup>2</sup> g<sup>-1</sup> and 582.7 m<sup>2</sup> g<sup>-1</sup>, respectively). The surface area of the graphene used in this study was also measured (BET surface area of 445 m<sup>2</sup> g<sup>-1</sup>), Fig. 2. Overlaying the three isotherms facilitated the comparison which revealed that the isotherm of the composite occurred midway between the two isotherms for the PyPOP and G, as might be expected for coating the less porous G with the more porous PyPOP. Furthermore, the surface area of the composite (582.7 m<sup>2</sup> g<sup>-1</sup>) closely matched the weighted average of the surface areas of its two components, 586 m<sup>2</sup> g<sup>-1</sup>, as calculated using the total yield of the composite; 26 wt% was assigned to the starting amount of G and 74 wt% to the PyPOP in the composite. We applied the non-local density functional



Fig. 2 (top) N<sub>2</sub> gas sorption isotherms for the PyPOP, graphene, and PyPOP@G (closed symbols for adsorption and open symbols for desorption), and (bottom) the corresponding PSD histograms (\* denotes most significant changes).

theory (NLDFT) model of carbon finite pores to the adsorption points in the three samples to calculate the corresponding pore size distribution (PSD), Fig. 2. The PSD histograms demonstrated close resemblance between the PyPOP and the PyPOP@G, which is in further agreement with the BET surface area findings discussed above. In the PSD histograms, a noticeable difference between the PyPOP and PyPOP@G is the small shrinkage of the pores at ~6 Å and the absence of pores at ~25 Å in the composite. This change could be ascribed to subtle structural changes upon deposition of the PyPOP on the G sheets. Close inspection of the N2 sorption isotherms indicated the presence of H2-type hysteresis in the N<sub>2</sub> isotherm for the PyPOP, which was not observed for the PyPOP@G; potentially indicating rigidification of the PyPOP structure once in contact with the G sheets. The observed hysteresis for the PyPOP can be ascribed to a degree of structural flexibility, *i.e.* breathing of the material upon N<sub>2</sub> uptake, or alternatively can be ascribed to interparticle condensation.<sup>26,27</sup> The isosteric heat of adsorption  $(Q_{st})$  for CO2 into the PyPOP and the PyPOP@G was also measured through variable temperature CO2 sorption isotherms, ESI.† Both solids demonstrated nearly identical Q<sub>st</sub> for CO<sub>2</sub> adsorption ( $\sim$  40 kJ mol<sup>-1</sup> at initial loadings), further confirming that CO<sub>2</sub> adsorption in the composite takes place predominantly within the pores of the POP. Considering the above findings, it appears that graphene has imparted structural rigidity to the composite, while the PyPOP participated largely as the active medium for gas sorption. Thus effective synergism of properties arose from the successful conformal merge between the two components.

To investigate the potential of the above prepared composite for catalytic electrochemical reduction of CO<sub>2</sub>, linear sweep voltammetry (LSV) experiments were conducted under specific reaction conditions utilized previously (0.1 M KHCO<sub>3</sub> solution saturated with CO<sub>2</sub>).<sup>28</sup> The PyPOP was tested under such conditions and was found to be largely insulating while a good potential-current response was observed for the PyPOP@G. This result highlights the enhanced conductivity of the composite due to the presence of the graphene. In the LSV experiment shown in Fig. 3, the first run was commenced in N<sub>2</sub> saturated solution, to help decipher proton reduction reaction from a potential CO<sub>2</sub> reduction one. A large reduction peak was observed with an onset potential of -430 mV, and a second reduction wave at -1.38 V. The first reduction peak at -430 mV was assigned to an oxygen reduction process. This assignment was further confirmed by the absence of this cathodic peak in the second run, commenced immediately after the first run, indicating depletion of oxygen trapped within the pores of the composite during the electrode preparation. The reduction wave in the second run appeared unchanged at its corresponding potential and was then assigned to a proton reduction process. When the solution was then saturated with CO<sub>2</sub> through bubbling for 30 minutes (pH 6.73), the LSV experiment demonstrated one major reduction wave with a potential onset of -1.18 V, signifying electrochemical reduction of CO2. This potential shift was also accompanied by increased cathodic current density in the scanned potential window down to -1.6 V, as compared to



Fig. 3 LSV for the PyPOP@G and G as the active material in CPE, 0.1 M KHCO<sub>3</sub>, saturated with CO<sub>2</sub>, the inset is for PyPOP@G under N<sub>2</sub> saturation and CO<sub>2</sub> saturation conditions.

the behavior in N2 saturated solution. The CO2 electroreduction on the PyPOP@G is remarkable in terms of the onset potential (-1.18 V) and current density  $(5 \text{ mA cm}^{-2} \text{ at } -1.6 \text{ V})$  even when compared to a recently published Cu foam catalyst  $(\sim 5 \text{ mA cm}^{-2} \text{ at } -1.6 \text{ V } \nu s. \text{ Ag}|\text{AgCl}).^{29}$  Additionally, our observed onset potential compares well with that of a recent covalent-organic framework containing Co-porphyrin that demonstrated superior catalytic activity (onset potential of -420 mV RHE (a) pH 7.2, calculated to be -1.02 V vs. Ag|AgCl (a) pH 6.73 of our solution).<sup>30</sup> Our catalyst compares well also with a recent report that demonstrated CO<sub>2</sub> electrocatalytic reduction behaviour for a metal-organic framework based on Co-porphyrin, with an onset potential of -500 mV vs. RHE in 0.5 M K<sub>2</sub>CO<sub>3</sub> solution.<sup>31</sup> Finally, when graphene was tested under the above conditions, Fig. 3, no significant catalytic behavior was recorded, further supporting the role of the POP in the catalytic process observed. From the above, it is reasonable to assume that the PyPOP imparted binding affinity of graphene toward CO2 and further acted as the catalytic active site for CO<sub>2</sub> electrochemical reduction, while graphene imparted some degree of electrical conductivity to the PyPOP, necessary to conduct the CO<sub>2</sub> reduction effectively. In aqueous solution, it is possible for water molecules to compete for the CO<sub>2</sub> binding sites in N-rich POPs.32 Nevertheless, in the composite described here, the PyPOP maintained appreciable affinity toward dissolved  $CO_{2}$ , facilitating its electrochemical reduction. Moreover, it also appears that cohesion, on the molecular level, between the two components of the composite alleviated the drawbacks from each of the components considered separately, namely the poor conductivity of the polymer and the absence of proper binding sites on the surface of the pristine graphene.

In conclusion, we described a one-pot, bottom-up, pathway for constructing a novel composite material of porous organic polymer atop graphene sheets for application in CO<sub>2</sub> capture and electrocatalytic reduction. The uniformity of the coverage of the graphene by the POP was demonstrated through its TEM images. The gas sorption characteristics and electrochemical activity of the composite were also investigated, demonstrating a true mix of the properties of the two components as a result of efficient compositing. Work is in progress to further investigate the nature of the product(s) in the observed catalytic process. These investigations help guide our future design for platform materials capable of capture and conversion of  $CO_2$  into usable feedstock reagents.

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