

A universal and versatile route for selective covalent tethering of single-site catalysts and functional groups on the surface of ordered mesoporous carbons

Madhura Joglekar¹, Svitlana Pylypenko², Megan M. Otting¹, Justin S. Valenstein and Brian G. Trewyn^{1}*

¹Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO, USA²Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO, USA

Email: btrewyn@mines.edu

Supporting Information

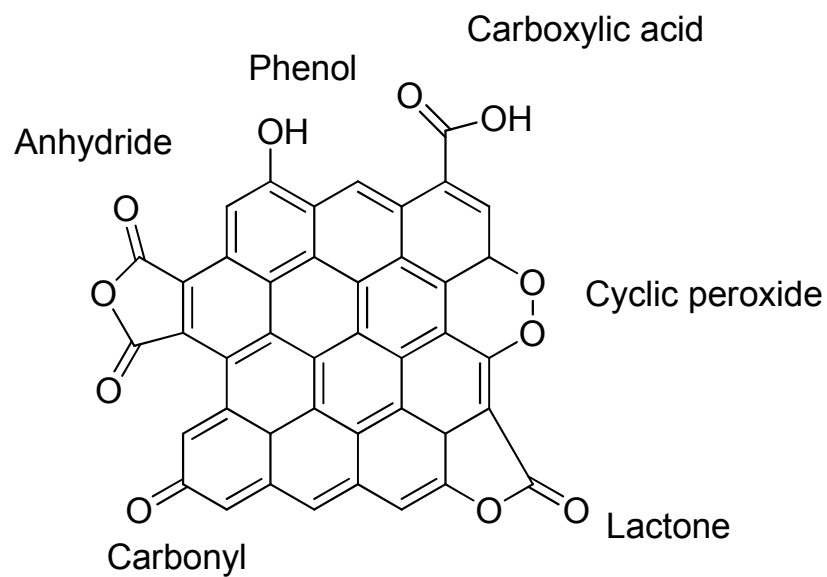


Figure S1: Various functional groups generated when ordered mesoporous carbons (OMCs) are treated with strong oxidants such as hot, concentrated nitric and sulphuric acid. This decreases the selectivity of functionalization of the OMC surface.

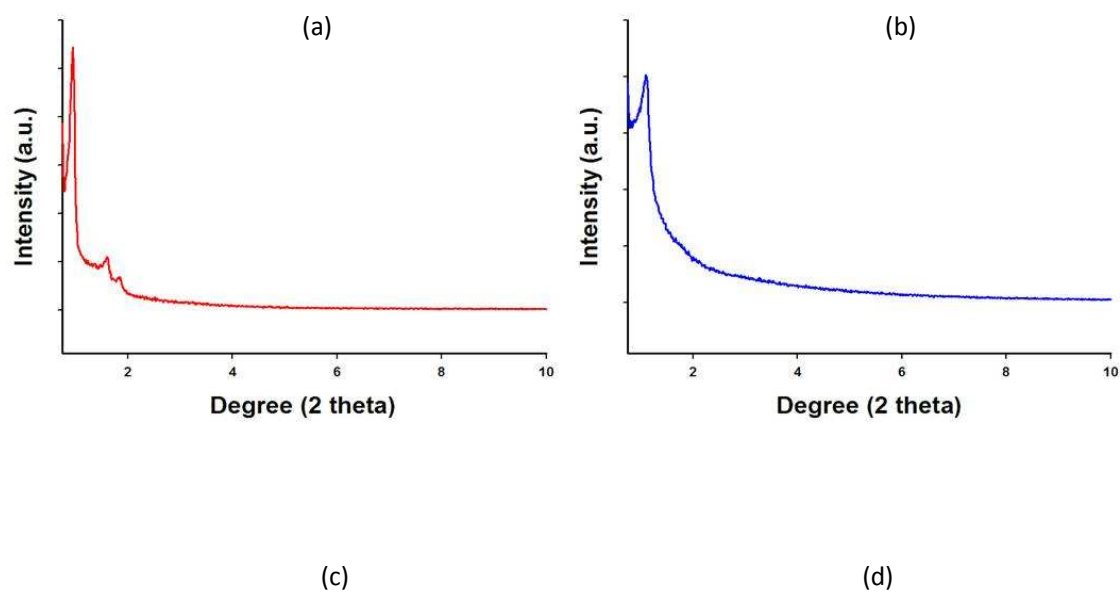


Figure S2: X-ray diffraction patterns of (a) *I*-MSN (red), (b) OMCs (blue). The 100, 110 and 200 peaks are visible for *I*-MSN which suggests 2D hexagonal arrangements of pores. Only 100 peak is visible for OMCs suggesting some degree of disorder along the other two planes.

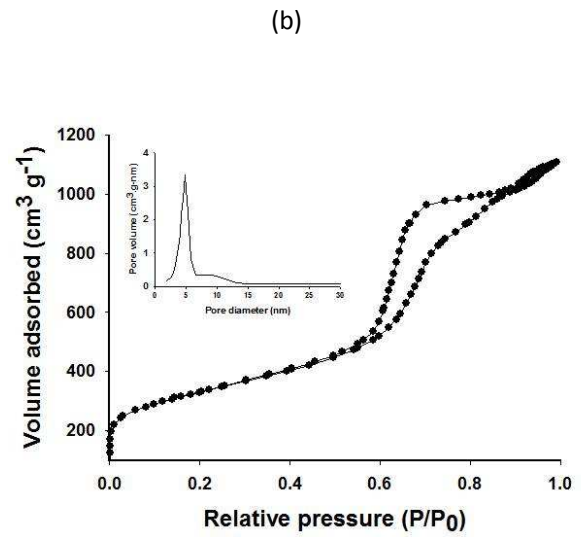
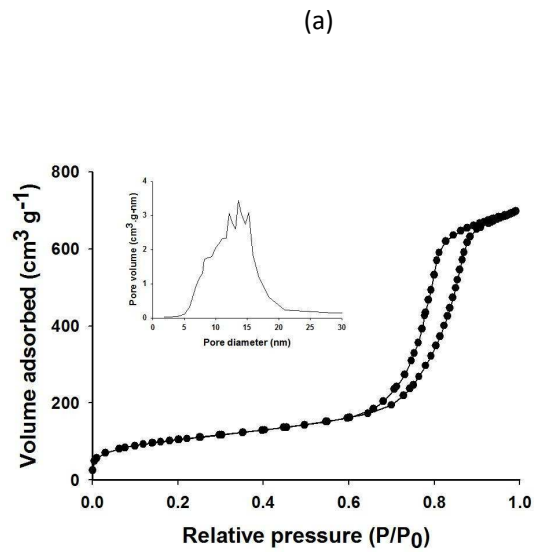
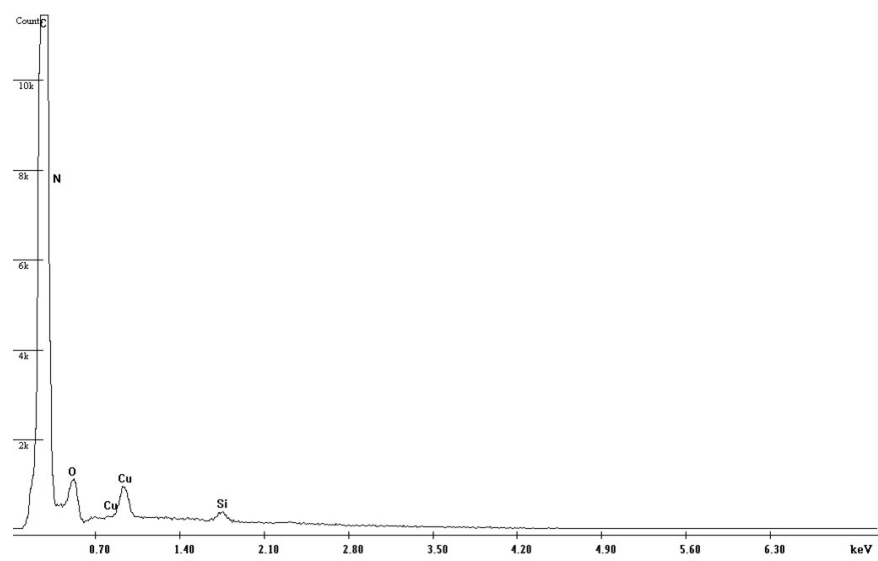


Figure S3: Linear plot of nitrogen sorption isotherms and pore size distributions of (a) *I*-MSN (b) OMCs

Table S1: Characteristics of OMCs as determined from nitrogen sorption measurements

Sample	Surface Area (m ² g ⁻¹)	Pore Size (nm)	Pore Volume (cm ³ g ⁻¹)
OMCs	912.0	5.2	1.2

(a)



(b)

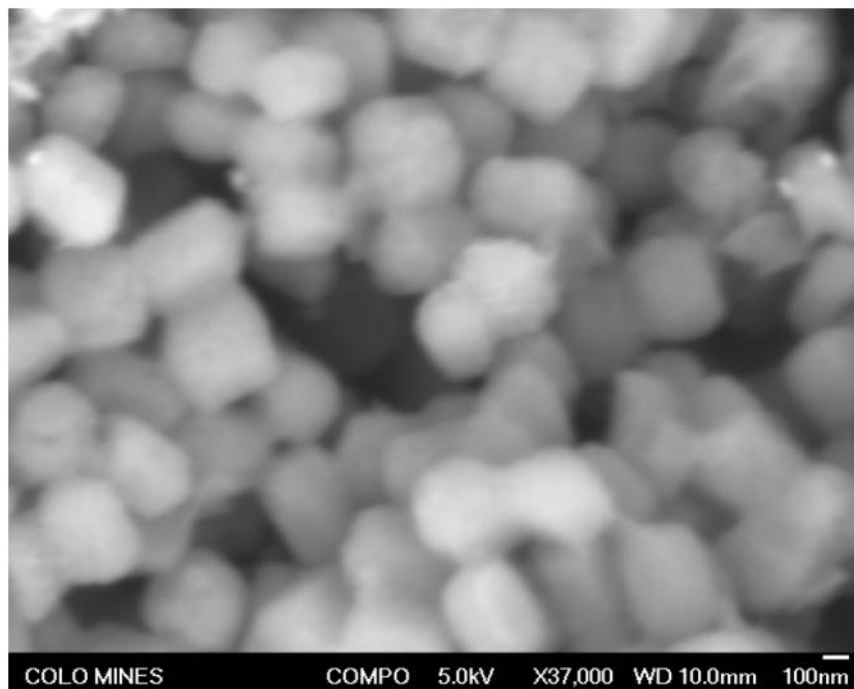


Figure S4: (a) Energy dispersive spectrum of OMC-Bpy-Cu showing the elemental composition of the catalyst. (b) Backscattered image of OMC-Bpy-Cu showing homogeneous distribution of copper on the surface. Very few areas have bulk copper.

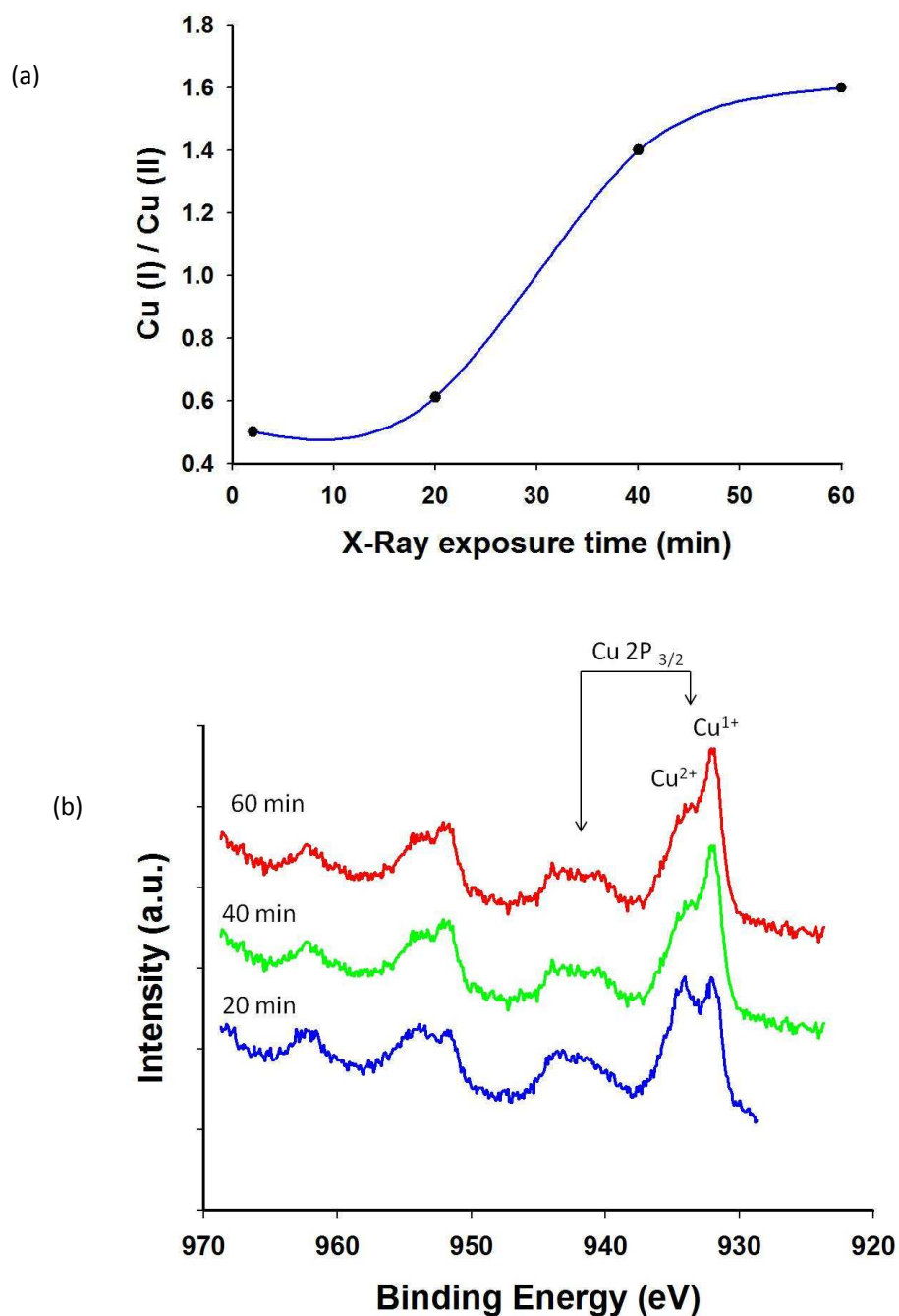


Figure S5: (a) Plot of ratio of Cu (I)/Cu (II) to X-ray exposure time as determined from XPS studies showing negligible change in the amount of Cu (I) after exposure for 2 and 20 min. (b) X-ray photoelectron spectra determined at various acquisition times of 20 min (blue), 40 min (green) and 60 min (red). The change in the peak intensity of Cu (I) is clearly visible with prolonged exposure time.

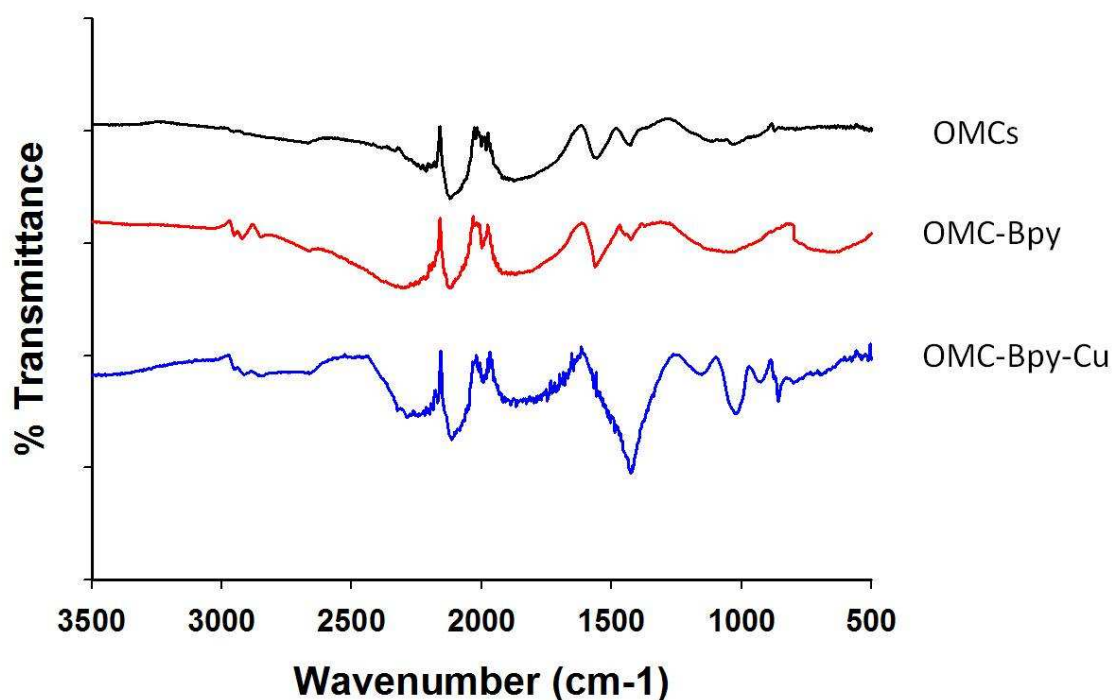


Figure S6: FTIR spectra of the as-synthesized OMCs (black) from the *I*-MSN template, OMC-Bpy (red) and OMC-Bpy-Cu (blue) after coordination with copper. The spectra have been baseline corrected and the low signal/noise ratio is due to the strong absorbance of OMCs. The spectra after functionalization with 2,2'-bipyridine appears similar to OMCs since the nitrogen atom in bipyridine behaves similar to a substituted carbon atom in benzene. However, after coordination with copper in the OMC-Bpy-Cu sample, new bands appear at 1423 cm⁻¹ and 1024 cm⁻¹ in the fingerprint region indicating a change in the chemical composition on the surface of OMCs. Given the strong absorbance of the OMC solid support, it is difficult to interpret these vibrations in FTIR.

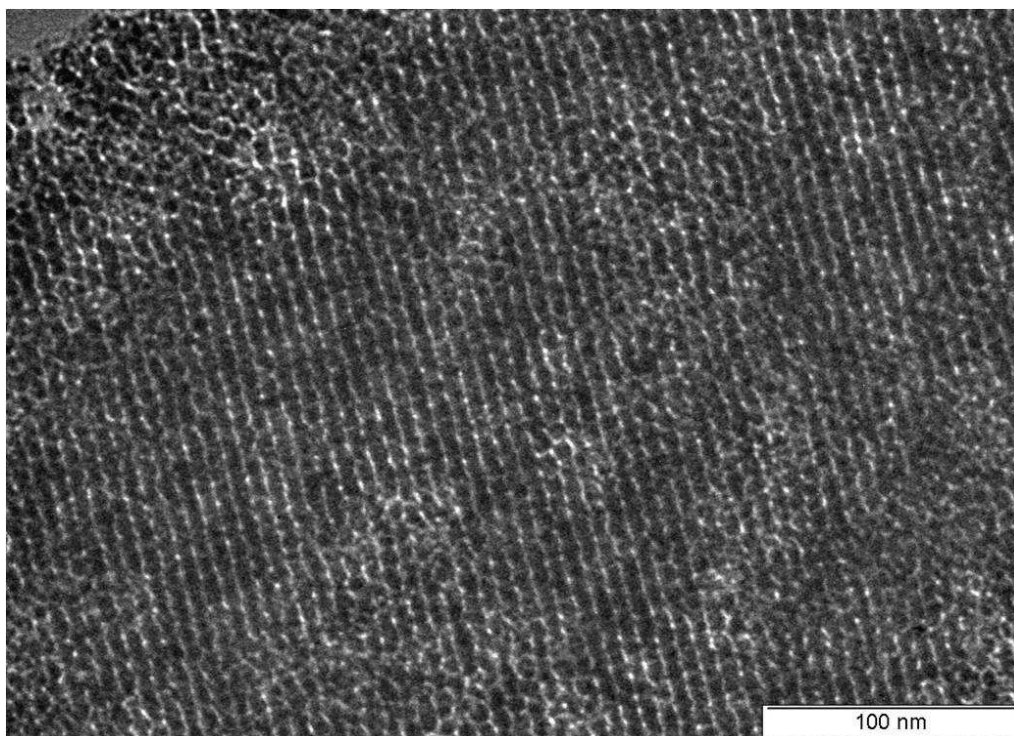


Figure S8: High magnification transmission electron micrograph of OMCs showing the arrangement of pores.

Determination of the amount of 2,2'-bipyridine tethered onto the surface of OMCs using titration curve

The exact molarity of HCl after titration with standardized NaOH = 0.011 M

The volume of 0.011 M HCl corresponding to the second equivalence point was used for the calculation of the amount of base since it correlates to the protonation of both the bipyridinic nitrogen atoms.

At equivalence point

Moles of HCl = Moles of base

$$M_1 \times V_1 = M_2 \times V_2$$

$$0.011 \text{ M} \times 23.25 \text{ mL} = M_2 \times 50 \text{ mL}$$

V_1 = Volume of HCl corresponding to second equivalence point

V_2 = Volume of KCl containing 50 mg OMC-Bpy

$$M_2 = 5.115 \times 10^{-3} \text{ M}$$

$$M_2 = 5.115 \times 10^{-3} \times 156.19 \text{ g L}^{-1} \text{ (Molar mass of 2,2'-bipyridine} = 156.19 \text{ g mol}^{-1}\text{)}$$

$$M_2 = 0.799 \text{ g L}^{-1}$$

Accordingly, 50 mL KCl solution containing 50 mg OMC-Bpy contains 0.039 g base (2,2'-bipyridine).

Hence, 1000 mg OMC-Bpy sample contains 0.799g base.

However, for every 2,2'-bipyridine moiety tethered on the surface of OMCs, two HCl molecules are required for neutralization. So the actual concentration of base on the surface is 0.399g per gram OMCs i.e 2.56 mmol base per gram OMCs.