

# Magadiite templated high surface area graphene-type carbons from metal-halide based ionic liquids

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## Experimental Section

### General

All reagents were purchased from Sigma Aldrich in the highest purity available and used as is without further purification. 3-butyl-1-methyl-1H-imidazol-3-ium bromide, Bmim[Br],<sup>1</sup> and 3-butyl-1-methyl-1H-imidazol-3-ium chloride, Bmim[Cl]<sup>1</sup> were synthesized according established literature procedures and dried under high vacuum prior to use. Metal halide based ionic liquids, namely Bmim<sub>2</sub>[MnCl<sub>4</sub>],<sup>2</sup> Bmim[FeBrCl<sub>3</sub>],<sup>3</sup> Bmim[FeCl<sub>4</sub>],<sup>4</sup> Bmim<sub>2</sub>[CoCl<sub>4</sub>],<sup>2</sup> Bmim<sub>2</sub>[NiCl<sub>4</sub>],<sup>2</sup> were synthesized following established literature procedures.

To form the starting material for carbonization, an equivalent weight of the appropriate ionic liquid and Magadiite (1/2.5 wt. ratio) were combined in a glass vial and sonicated for 12 hours. For comparison, Magadiite was sonicated with Bmim[Br] in ethanol (1:2:2 wt.) for the same amount of time. Carbonization was carried out in a horizontal quartz tube furnace under a 4% H<sub>2</sub>/Ar atmosphere, 10°C/min heating rate, at 900°C for 2 hours. Approximately 500mg of the obtained carbon-silicate nanocomposites were then stirred in 20ml of aqueous 4M ammonium hydrogen difluoride solution for 24 hours. The final graphene-type carbons were dried overnight at 80°C under vacuum.

### References:

- 1) Burrell, A. K.; Del Soto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449-454.
- 2) Zhong, C.; Sasaki, T.; Jimbo-Kobayashi, A.; Fujiwara, E.; Kobayashi, A.; Tada, M.; Iwasawa, Y. *Bull. Chem. Soc. Jpn.* **2007**, *12*, 2365-2374.
- 3) Gao, J.; Wang, J.-Q.; Song, Q.-W., He, L.-N. *Green Chem.* **2011**, *13*, 1182-1186.
- 4) Hayashi, S.; Hamaguchi, H. *Chem. Lett.* **2004**, *33*, 1590-1591.

### Characterization

Nitrogen adsorption isotherms were measured at -196°C using TriStar 3000 volumetric adsorption analyzer manufactured by Micromeritics Instrument Corp. (Norcross, GA). Before adsorption measurements the finely ground carbon powders were degassed in flowing nitrogen from one to two hours at 200°C.

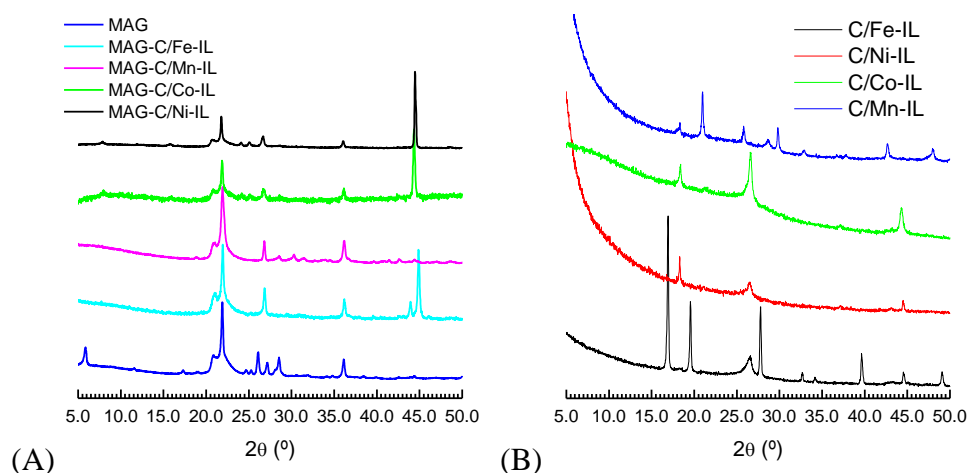
The TG measurements for carbon-silicate nanocomposite materials were performed using a high resolution mode of the TA Instruments TGA 2950 thermogravimetric analyzer. The TG profiles were recorded up to 800°C in flowing air using a heating rate of 10°C min<sup>-1</sup>.

For TEM characterization, carbon powders were dispersed in ethanol using ultrasonic bath. The final suspensions were transferred to lacy carbon coated 200-mesh copper TEM grids and dried in ambient air prior to electron microscopy analysis. Specimens were then characterized using a Hitachi HD-2000 operating in STEM mode using a secondary electron (SE) and/or bright-field STEM detector operating at 200 kV. EDX spectra and SEM images were collected using Energy-dispersive X-ray spectroscopy (EDX) measurements were acquired with a JEOL-6060 scanning electron microscope using the electron energy of 15 kV.

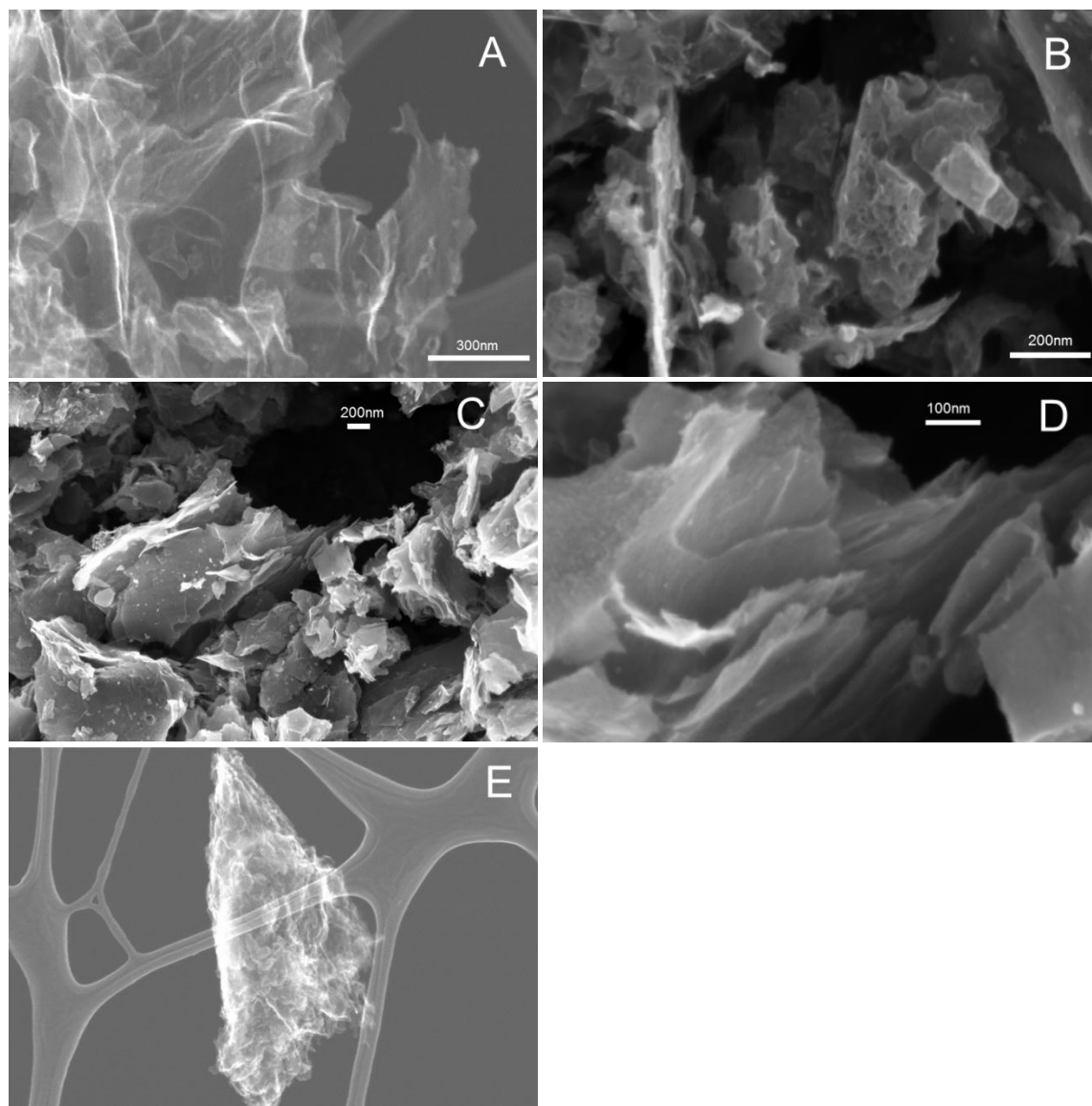
The powder XRD patterns were recorded on a PANalytical. Inc. X'Pert Pro (MPD) Multi Purpose Diffractometer with X'Celerator detector and Cu K $\alpha$  radiation (0.1540 nm), using an operating voltage of 40 kV and 40 mA, and 0.01° step size

( $5.00^\circ < 2\theta < 50.00^\circ$ ). Microscope glass slides were used as sample supports for all measurements. The samples were manually ground prior to the XRD analysis and all measurements were performed at room temperature.

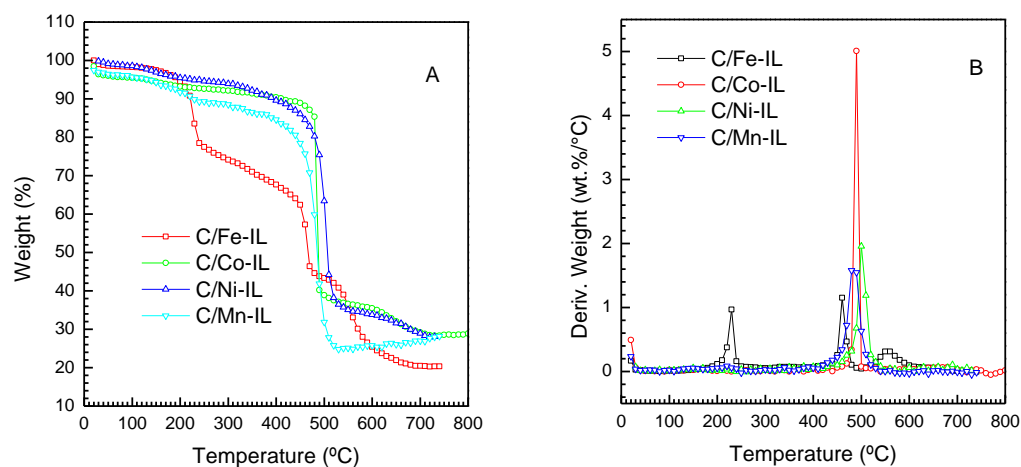
Raman spectra were collected using a Renishaw system 1000 Raman spectrometer equipped with an integral microscope (Leica DMLMS/N). Excitation was provided by a 25-mW He-Ne laser (Renishaw) and the 632.8 nm excitation beam was focused onto the sample with a 50 $\times$  objective; the laser power at the sample was approximately 0.2-0.5 mW for carbon onions and carbon black and 2mW for nanocomposites. An edge filter removed the Rayleigh scattered light, while a holographic grating (1800 grooves/mm) permitted a spectral resolution of  $\sim 1 \text{ cm}^{-1}$ . A silicon wafer with a Raman band at  $520 \text{ cm}^{-1}$  was used to calibrate the spectrometer and the accuracy of the spectral measurements was estimated to be better than  $1 \text{ cm}^{-1}$ .



**Figure S 1** – Powder XRD patterns for Magadiite-Carbon nanocomposites (A), and graphenetype carbons after Magadiite etching (B). The silicate pattern indicated the presence of both Magadiite  $\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot 10\text{H}_2\text{O}$  (JCPDF 421350) and Cristobalite (JCPDF 4-8-7639), MAG-C/Fe-IL contained carbon (JCPDF 4-6-5764) and  $\text{SiO}_2$  (JCPDF 4-12-1126), similar to MAG-C/Ni-IL  $\text{SiO}_2$  (JCPDF 4-7-2134). For MAG-C/Mn-IL,  $\text{SiO}_2$  (JCPDF 39-1425) and  $\text{MnSiO}_3$  (JCPDF 12-432) were identified, whereas for MAG-C/Co-IL, only  $\text{SiO}_2$  phase (JCPDF 61-35) could be identified. The following phases were identified for the silicate-free materials: carbon (JCPDF 41-1487) and  $(\text{NH}_4)_3\text{FeF}_6$  (JCPDF 4-14-9602) for C/Fe-IL, carbon (JCPDF 23-64) for C/Ni-IL, carbon (JCPDF 4-6-5764) and  $\text{Co}(\text{OH})_2$  (JCPDF 4-15-4721) for C/Co-IL,  $\text{NH}_4\text{MnF}_3$  (JCPDF 18-114) and  $\text{SiO}_2$  (1-77-8642) for C/Mn-IL.



**Figure S 2** - SEM images of C/Mn-IL (A), of C/Ni-IL (B), of C/Co-IL (C and D), and STEM image in SE mode of C/IL (E).



**Figure S 3** – TG (A) and DTG (B) profiles of graphene-type carbons from metal halide-ionic liquids in air, after Magadiite dissolution.