

Supplementary Information for

Crumpled Graphene Nanoreactors

Zhongying Wang,^a Xiaoshu Lv,^b Yantao Chen,^a Dan Liu,^a
Xinhua Xu,^b G. Tayhas R. Palmore,^{a, c, d} Robert H. Hurt*^{c, d}

^aDepartment of Chemistry, ^cSchool of Engineering,
^dInstitute for Molecular and Nanoscale Innovation,
Brown University, Providence, Rhode Island 02912
^bDepartment of Environmental Engineering,

Zhejiang University, Hangzhou 310058, People's Republic of China

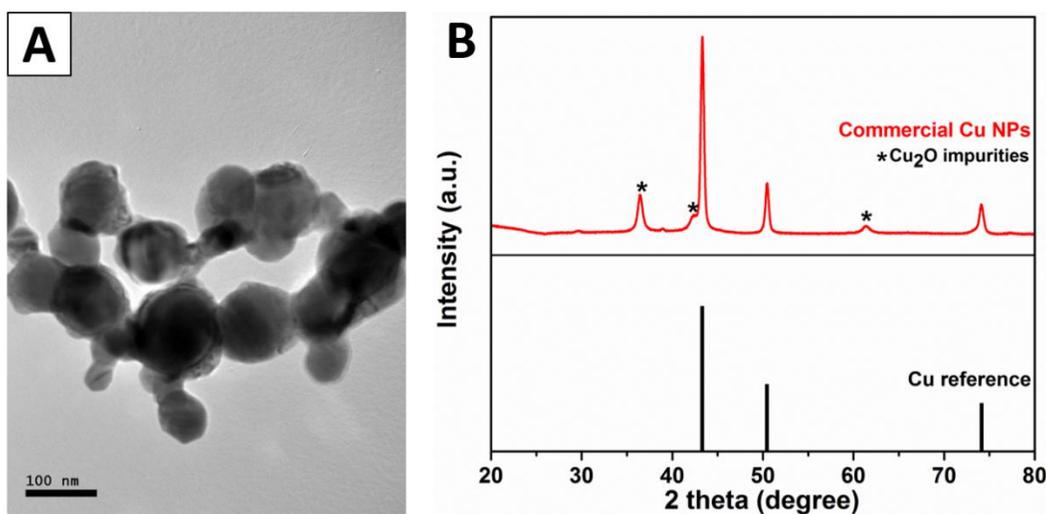


Figure S1. TEM image and XRD spectra of commercial copper nanoparticles (99.9%, US Research Nanomaterials, Inc., USA) used as a reference material.

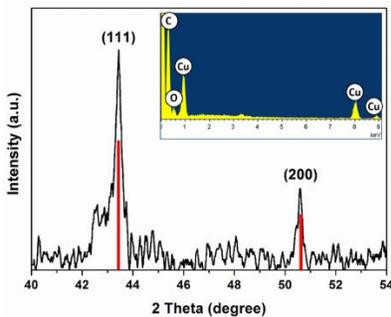


Figure S2. GI-XRD and EDX spectra of Cu/rGO-nanoreactors after electrochemical testing.

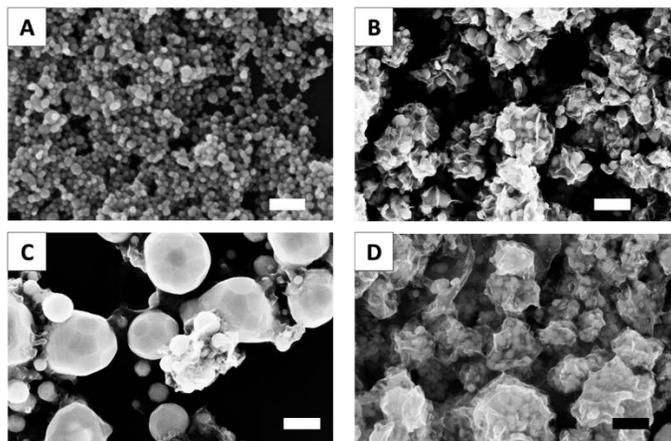


Figure S3. SEM images of as-prepared Ag nanoparticles (A), Ag-rGO nanosacks incubated at 500 °C in 99.99% nitrogen for one hour (B), Ag-rGO nanosacks incubated at 700 °C in 99.99% nitrogen for one hour (C), and Ag-rGO nanosacks incubated at 700 °C in 5/95% H₂/N₂ for one hour (D). All scale bars represent 100 nm.

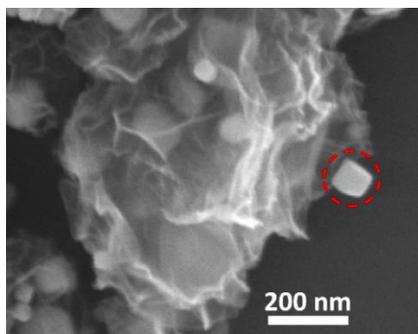


Figure S4. SEM image of Fe-filled graphene nanosacks prepared by chemical reduction of Fe₃O₄-sacks. Unlike the TEM images shown in Fig. 6C, this SEM image clearly reveals the locations of the particles relative to the graphene shell. The vast majority of particles are inside the sack, but the image highlights one outside of the sack (red circle). This pattern is consistent with a previously published theory¹ that describes the structure of filled graphene nanosacks as a function of the electrostatic charges on the different components in the precursor suspension. In this case, the Fe₃O₄ precursor particles have a positive charge in colloidal suspension and attach to the negatively charged GO precursor sheets prior to the drying-induced assembly. In such a case, the very few particles that by chance attach to what becomes the outer surface of the outermost sheet in this multilayer particles will be found on the outside of the sack in the final material, with the vast majority of particle inside, as seen here.

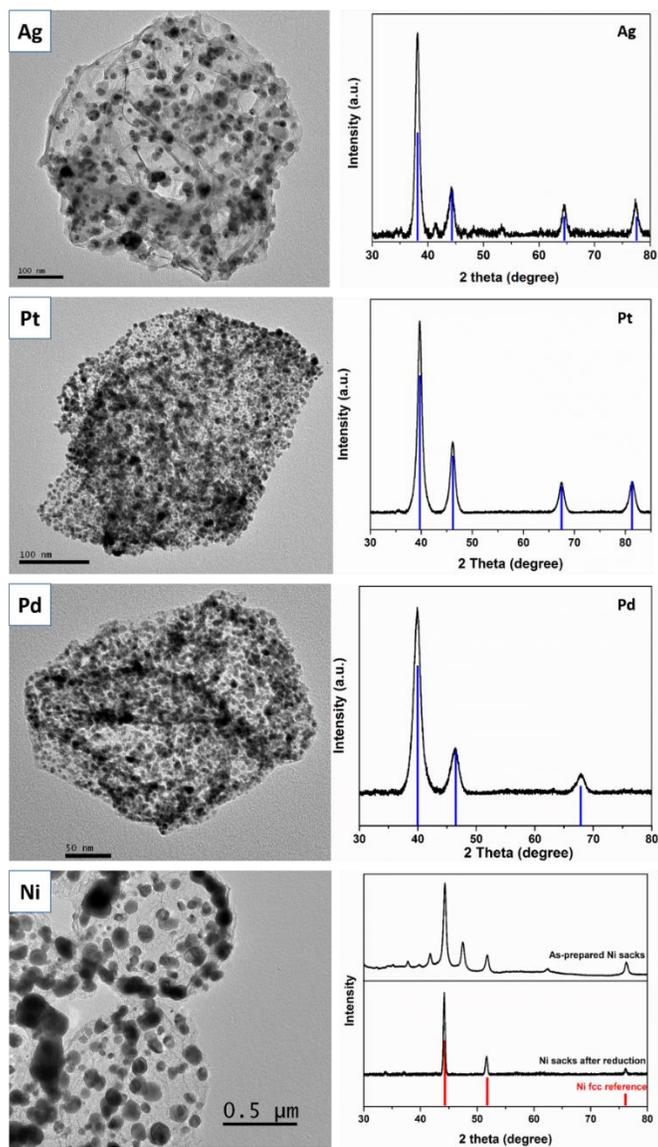


Figure S5. SEM images and XRD spectra of Ag, Pt, Pd and Ni-filled rGO sacks synthesized by adding EDTA at equi-molar concentrations to the metal precursor salt (AgNO_3 , Na_2PtCl_4 , Na_2PdCl_4 and $\text{Ni}(\text{NO}_3)_2$) in the GO suspension. In the cases of Ag, Pt and Pd, metal ions are reduced to zero-valent metal nanoparticles. But zero-valent Ni and nickel oxide mixture are formed in the beginning, after complete hydrogen reduction pure zero-valent Ni nanoparticles are obtained.

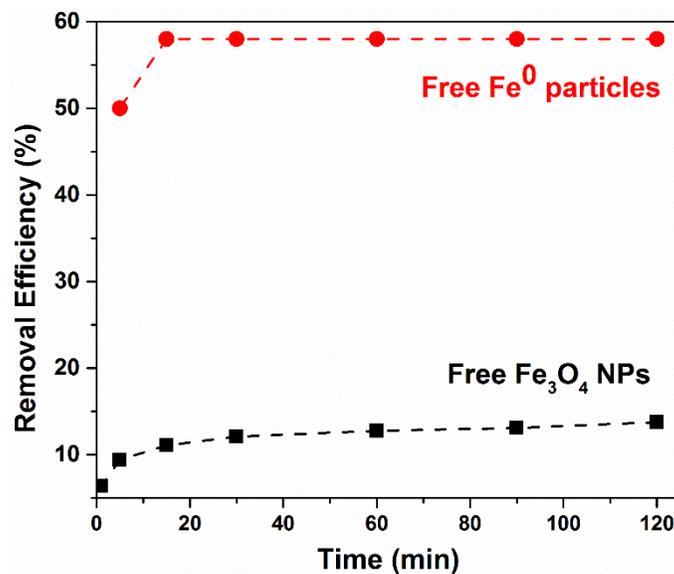


Figure S6. Cr(VI) removal efficiency by free Fe₃O₄ NPs was measured and compared with free Fe⁰ particles on the same experimental conditions. Although Fe₃O₄ is an excellent electronic conductor, only one electron can be given out from one octahedral-shape Fe₃O₄. Within 2 h reaction time, only 13.8% of Cr(VI) is removed by Fe₃O₄. Compared to Fe₃O₄, Fe⁰ is more capable of giving electrons under the same quantity.

Reference

1. Chen, Y.; Guo, F.; Qiu, Y.; Hu, H.; Kulaots, I.; Walsh, E.; Hurt, R. H. Encapsulation of Particle Ensembles in Graphene Nanosacks as a New Route to Multifunctional Materials. *ACS Nano* **2013**, *7*, 3744-3753.