Supporting Information for:

Aerosol synthesis of phase-controlled iron-graphene nanohybrids through FeOOH nanorod intermediates

X. S. Lv,^{a,b,†,*} Y. Qiu,^{a,†} Z. Y. Wang,^a G. M. Jiang,^b Y. T. Chen,^a X. H. Xu,^c R. H. Hurt^{a,*}

^a School of Engineering, Brown University, Providence, Rhode Island 02912

^b Engineering Research Center for Waste Oil Recovery Technology and Equipment, Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, China

^c Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, People's Republic of China.

[†] These authors contributed equally to this work.

* Corresponding author: lyuxiaoshu@zju.edu.cn; Robert_Hurt@brown.edu





Figure S1 TEM images of the aerosol synthesis products using various iron-based precursor nanoparticles: (a) Fe_3O_4 NPs, (b) Fe^0 NPs, with the two insets showing the bare precursor NPs before encapsulation. Image in (a) shows aggregation and some unencapsulated Fe_3O_4 NPs when using Fe_3O_4 NPs as precursors. Image in (b) shows unsuccessful encapsulation (nearly empty nanosacks) when Fe^0 NPs are used as precursors. Although Fe_3O_4 NPs are colloidally unstable, their positive surface charge in acidic solution leads to association with the negatively charged GO, and facilitates to disperse the unstable NPs in GO suspension and subsequently encapsulate them inside the sacks. For Fe^0 NPs, magnetic force, bigger particles size, and weaker adhesion with GO (due to low positive surface charge) may result in lager aggregates that cannot be nebulized, thus lead to totally unsuccessful encapsulation.



Figure S2 Comparison of the Teflon filter membrane after collection of nanosack samples at different furnace temperatures with FeOOH/GO as precursors (left and right filters) or GO alone (middle filter).



Figure S3 (a) TEM image and (b) XRD pattern of bare FeOOH nanorods after aerosol-phase synthesis process in absence of GO nanosheets. Without GO, the nanorod morphology of FeOOH was maintained if the furnace temperature was below 300° C. XRD pattern shows that no reduction of FeOOH nanorods occurred in this process; while FeOOH is converted to Fe₃O₄ in the presence of GO under the same condition. That suggests that GO/rGO serves as a carbothermic reducing agent for the conversion of FeOOH to Fe₃O₄.





(b)

Figure S4 Comparison of TEM images (a) solid Fe₃O₄-rGO nanosacks, which are fabricated under 300°C; (b) hollow Fe₃O₄-rGO nanosacks, which are fabricated under 500°C.









(c)

Figure S5 (a) SEM image, (b) TEM image and (c) XRD pattern of FeOOH-rGO nanosacks after annealing at 800 °C in N_2 atmosphere for 2 hrs. Typical Fe⁰ peak at 44.5° proves the carbothermal reduction of FeOOH by rGO sacks, and larger Fe⁰ spherical NPs due to sintering and partial fusion at excessively high temperature.



(b)

Figure S6 TEM and SEM images of (a) bare FeOOH nanorods and (b) FeOOH-rGO nanosacks before and after H_2 reduction at 600°C.



(b)



Figure S7 TEM images of empty rGO nanosacks under different magnification.

Figure S8 X-ray photoelectron spectroscopy (XPS) of (a) extracted Fe^{0} -rGO nanohybrids after reaction; (b) Cr $2p_{2/3}$ photoelectron peaks. The appearance of Cr and O peaks in Fig. S8(a) indicates that parts of Cr species may be adsorbed on the surface of Fe^{0} -rGO nanohybrids as Fe/Cr (oxy)hydroxides. Also, the Cr $2p_{2/3}$ region could be decomposed into three peaks at 576.2 and 577.2 eV of Cr(III) and 578.4 eV of Cr(VI), implying reducibility of Fe^{0} -rGO nanohybrids.

Figure S9 HRTEM image of Fe^0 NPs inside Fe^0 -rGO nanosacks produced through annealing in N₂ at 800 °C for 2 hr. A carbon coating on Fe^0 particles was clearly observed, that may protect encapsulated Fe^0 NPs.

Figure S10 (a) Vibrating sample magnetometry of fresh prepared bare Fe^0 NPs and Fe^0 -rGO nanosacks at room temperature; (b) the change of saturation magnetization as a function of air exposure time at room temperature. After exposure to air, these samples may lose some values in magnetic moment due to surface oxidation, thus the changes of saturation magnetization value (M_s) demonstrate the degree of oxidation. Here, M_s value of Fe^0 -rGO nanosacks decreased from 126.6 to 113.4 emu/g-Fe, a 10.4% magnetic moment loss after 3 days exposure; while bare Fe^0 NPs had a much faster magnetic moment loss (about 41.4%), implying slower oxidation of Fe^0 with carbon coating.

It is important to note that, although both stored in aerobic environment, there are some differences between powder samples for Cr(VI) removal recycling test and VSM, the former one is stored in sealed and relatively dry condition, while the later one is open environment.

Adsorbents	Initial pH	Adsorption Capacity $(mg g^{-1})$	Ref
Fe ⁰ -rGO nanohybrids	5.0	344.8	This work
Fe ⁰ -Fe ₃ O ₄	3.0/8.0	100/29.4	1
Fe ⁰ -graphene	4.25	162.6	2
Fe ⁰ -Fe ₃ O ₄ /graphene	3.0/8.0	101/66.2	3
Fe ⁰ - reduced graphene oxide	5.0	187.16	4
Cellulose-supported Fe ⁰	3.0	562.8	5
Fe ⁰ -graphene	7.0	21.72	6
Sepiolite-supported Fe ⁰	6.0	43.86	7
SDS-modified Fe ⁰	3.0	264.55	8
Cherry leaf extracts support Fe ⁰	2.5	904.1	9

Table S1 Cr(VI) adsorption capacities of various Fe⁰ nanoparticles-based adsorbents.

Adsorption capacities of all above adsorbents were calculated by Langmuir isotherm model. Adsorption capacity of Fe⁰-rGO nanosacks in this study is higher than most of the listed adsorbents under same or even lower initial pH.

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