Environmental Science: Nano

Supporting Information

Enhanced adsorption of carbon nanocomposites exhausted with 2,4-dichlorophenoxyacetic acid after regeneration by thermal oxidation and microwave irradiation

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Preparation of purified GnP-SWCNT hybrid papers

First, 22.5 mg of single-wall carbon nanotubes (SWCNTs, 90wt%, Cheap Tubes) and 11.3 mg of graphene nanoplatelets (GnPs, 99.5%, XG Sciences, Grade M-25) were soaked in hydrochloric acid (HCl, 37.5% Sigma-Aldrich) for 17 hours, a non-oxidative acid treatment applied to remove metal particles. The mixture was then filtered over an aqueous membrane (90 mm, 113 Whatman) and thoroughly washed with deionized water. After dispersing the dried mixture into N,N-dimethylacetamide (99% Sigma-Aldrich) by ultrasonication for 45 minutes, the hybrid papers were prepared using vacuum filtration onto a 47 mm PTFE membrane (0.5 μm, Zefluor). Prior to filtration, the PTFE membrane was rinsed with methanol (99% BDH Chemicals) to allow easy release of the paper from the membrane filter. The resulting papers were then thermally oxidized in air at 560°C for 10 min in a muffle furnace (Thermo-scientific, Thermolyne 1300) to remove amorphous carbon. For comparison, free-standing papers were also prepared with the same amount of adsorbent using 33.8 mg of SWCNTs. The papers were cut into smaller sections (0.5 cm^2) and weighed on a ultra-microbalance (Mettler-Toledo, XS204) with each section weighing 0.5 mg. All papers were finally dried at 110°C for 48 hours to remove moisture.

Acid/base titration

The content of basic oxygen surface groups was evaluated by a typical Boehm titration. The

titration was conducted by adding 5 mg of nanocomposites into a vial containing 20 mL of 0.1 M solution of hydrochloric acid (HCl, Sigma-Aldrich). Pristine nanocomposites and hybrids recovered after one saturation/regeneration cycle were both investigated. The vial was sealed and placed on an orbital shaker (Chang Bioscience, KJ-201BD) operated at 180 rpm for 24 hours at 20ºC. Then, the total basicity was estimated by titrating directly triplicate samples of 5 mL of the solution against 0.1 M sodium hydroxide (NaOH, BDH Chemicals), where the pH was monitored using a pH meter (Mettler Toledo, FG2). Since the adsorbent papers were stable in acidic/basic solutions ranging from pH=1 (HCl) to 13 (NaOH), there was no need of filtration to remove the carbon nanomaterials, thus avoiding the possibility that acid adsorbed onto the filter. The results are depicted in Fig. S1. It can be seen that more HCl reacted with the basic sites of the regenerated nanocomposites compared with the pristine ones, hence indicating that the regeneration process increases the presence of basic groups on the adsorbent surface.

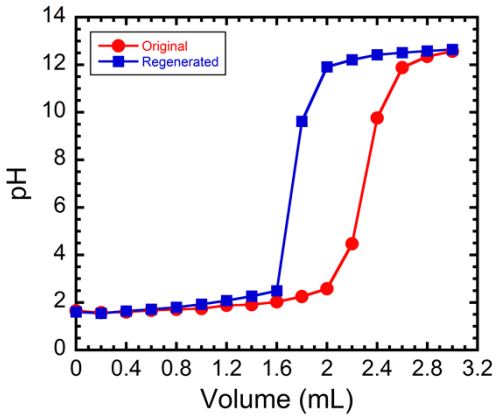

Fig. S1. Titration curves for HCl direct titration plotted versus titrant volume showing the amount of carbon basic surface functionality of the original nanocomposites and those recovered after the first saturation/regeneration cycle.

Raman spectroscopy

In order to examine the effect of the recycling process on the nanocarbon structure, Raman

spectroscopy was performed on SWCNT papers both before and after the first adsorption/regeneration cycle of the adsorbate. Typical Raman spectra of the SWCNT papers are presented in Fig. S2 using a JY-Horiba Labram spectrophotometer equipped with a 632.6 nm He/Ne laser as the excitation radiation. It can be seen that the integrated intensity ratio between the D and the G band (I_D/I_G), corresponding to the graphitization degree of the nanocarbon structure, increased from 0.24 to 0.54 after the first cycle. This suggests that the desorption process induces significant structural modifications in the SWCNT papers.

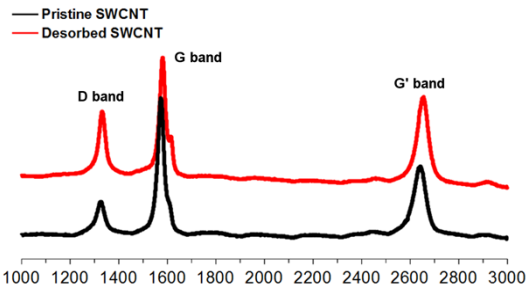

Fig. S2. Raman spectra of SWCNT papers before and after the first adsorption/regeneration cycle of the adsorbate.