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Supporting Information

Binder free graphene-single-wall carbon nanotube hybrid papers for the removal of polyaromatic compounds from aqueous systems

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Preparation of purified GnP-SWCNT hybrid papers

The experimental setup is shown in **Fig. S1**. 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 (37.5% Sigma-Aldrich) for 17 hours, a non-oxidative acid treatment applied to remove metal particles (**Fig. S2**). 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), as depicted in **Fig. S3**. 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 (**Fig. S2**). For comparison, free-standing papers were also prepared with the same amount of adsorbent using 33.8mg 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.

Characterization

The as-prepared SWCNT and hybrid papers were characterized by electron microscopy and Raman spectroscopy prior to adsorption. Morphologies of the papers were checked using a field emission scanning electron microscope (FE-SEM, Hitachi S-900) operated at 2 kV. Raman spectroscopy was performed at room temperature from 1000 to 3000 cm^{-1} using a JY-Horiba Labram spectrophotometer equipped with a 632.6 nm He/Ne laser as the excitation radiation.

Adsorption studies

Solution phase adsorption studies were performed in quartz cuvettes by submerging the dried papers (0.5 mg) in 3.5 mL of PBA (97% Sigma-Aldrich) solution at a fixed temperature of 20°C. For the kinetic studies, three concentrations (5.0, 10.0 and 15.0 µg/mL) of PBA were prepared in a 1% (v/v) ammonium hydroxyde (NH₄OH, 30% Sigma Aldrich) aqueous solution which had a pH of 10. The quartz cuvettes were placed on an orbital shaker (Chang Bioscience, KJ-201BD) continuously operated at four different rotation speeds (0, 60, 120 and 180 rpm). The PBA concentration was determined by optical absorption spectroscopy at the maximum absorption peak for PBA ($\lambda = 341$ nm) using a measured extinction coefficient from Beer's law analysis equaling 0.110 mL.µg⁻¹.cm⁻¹. Optical absorption measurements were taken in 15 minute increments for 3 hours using a Perkin-Elmer Lambda-900 UV/Vis/NIR spectrophotometer. The adsorption values, q , were computed using a mass balance on the PBA in the bulk solution, arising from the established relationship between measured absorbance values and solution concentration. By subtracting the solution concentration at any time from the initial solution concentration and multiplying by the cuvette volume, the mass of PBA adsorbed onto the surface of the carbon nanomaterials was deduced. For long time experiments, five concentrations (5.0, 7.0, 10.0, 13.0 and 15.0 µg/mL) of PBA were prepared in a 1% (v/v) ammonium hydroxyde aqueous solution which had a pH of 10. The samples were stored at room temperature on the orbital shaker continuously operated at either 0 or 120 rpm. Analysis were taken daily and the equilibrium was ascribed to the time beyond which no appreciable changes in the mass of PBA adsorbed to the carbon nanomaterials as measured by optical spectroscopy.

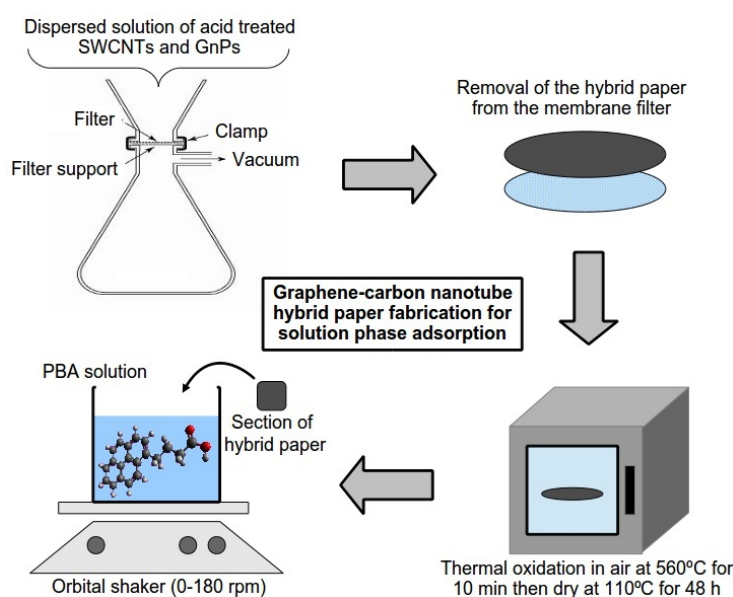


Figure S1. Process chart of the free-standing GnP-SWCNT hybrid paper fabrication.

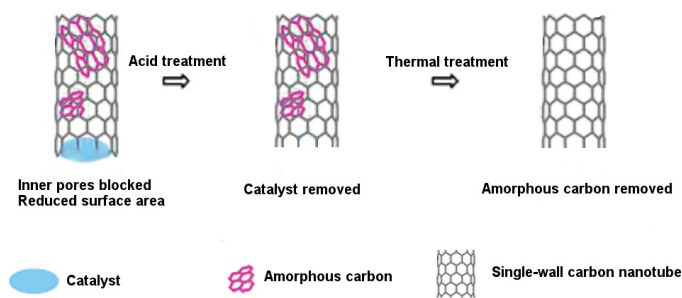


Figure S2. Adsorption properties as affected by the carbon-nanomaterial purification

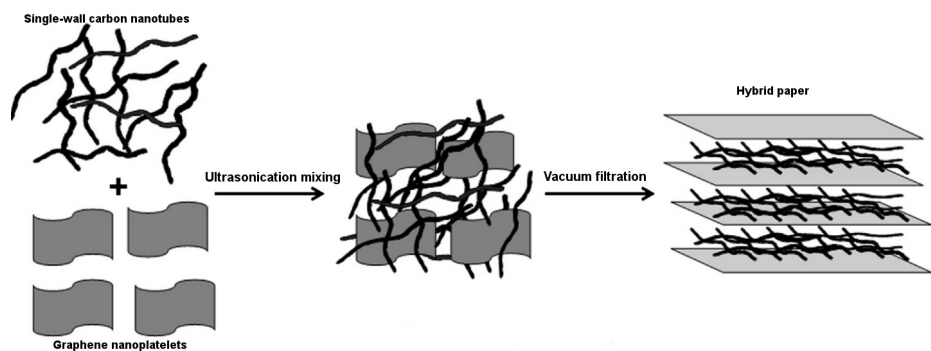


Figure S3. Schematic diagram of the fabrication of GnP-SWCNT composite papers by vacuum filtration.