Supplementary Information

Hollow Carbon Spheres and a Hollow Carbon Sphere/Polyvinylpyrrolidone Composite as Ammonia Sensors

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Synthesis of the SiO_2 spheres and the HCSs

A modified Stober method[1] was used to synthesize the SiO_2 spheres by mixing 180 mL of ethanol, 126 mL of distilled water and 10 mL of NH_4OH and stirring the solution for 10 min. Then 32 mL of TEOS was added *rapidly* and the mixture was stirred for 1 h. The solution was centrifuged at 4500 rpm for 20 min and the product was dried at 80 °C for 12 h and the obtained powders were calcined at 600 °C for 6 h. Carbonization of the SiO_2 spheres was carried out by a bubbling method using toluene as the carbon source and argon as the carrier gas in a chemical vapor deposition reactor at 900 °C for 1 h[2]. The carbonized silica was then etched with 10 % HF for 24 h at room temperature and dried to give the pristine hollow carbon spheres (HCSs). Annealed HCSs were obtained by annealing 5 mg of pristine HCSs in air at 300 °C for 4 h.

Characterization of the SiO_2 and HCSs

The morphological features of the SiO_2 and the hollow carbon spheres were ascertained by transmission electron microscopy (TEM) using a FEI Technai G2 spirit electron microscope operating at 120 KV. A sample specimen was prepared by dispersing a small amount of sample in 1 mL of ethanol. The mixture was sonicated for 20 min to form a homogeneous solution. One drop of the SiO_2 or HCS suspension was placed onto a carbon coated copper grid and allowed to dry before taking the images using a microscope. The thermal stability of the SiO_2 and HCSs was investigated by thermal gravimetric analysis (TGA) conjugated with a weight loss derivative curve (DTG) using a Perkin Elmer Pyris 1 TGA. About 10 mg of each sample was placed in a ceramic pan that was placed in the instrument furnace and heated to 900 ^{0}C at a rate of 10 ^{0}C/min under air. The N_2 adsorption and desorption isotherms of the HCSs were taken at 77 K using a Micrometrics Tristar 3000 instrument. The samples were degassed at 250 ºC in N_2 for 4 h. The specific surface area was calculated by the BET method from N_2 adsorption data. Raman spectroscopic analysis was done to determine the degree of graphitization of the HCSs using a Jobin-Yvon T6400 micro-Raman spectrometer equipped with a liquid nitrogen cooled charge coupled device detector and a laser excitation wavelength of 514.5 nm.

Preparation of HCS solutions using a surfactant dispersion method

Two solutions of the pristine HCSs were prepared by dispersing 2 mg separately in 1 mL of deionized H_2O. Similarly, 2 mg of annealed HCSs was dispersed in 1 mL of deionized H_2O. In order to promote a good dispersion of all the carbon nanostructures in water, a surfactant assisted method was used as previously reported[3]. To each solution, was added 5 mg of CTAB and the subsequent solutions were sonicated at 60 °C for 30 min. The dispersions were then sonicated at 0 °C for a further 30 min. The samples were then left for 2 days at 0 °C (below the Kraft temperature of CTAB, 25 °C)[4]. The amount of surfactant and the time that the samples were kept at the low temperature was optimized for each nanostructure. The supernatant (500 µL) of the pristine and annealed HCS solution was extracted and referred to as pristine HCSs and annealed HCSs respectively. A PVP solution was prepared by dissolving 25 mg of PVP (M_W = 30 kDa) in a 0.2 mL of deionized H_2O, followed by stirring for 30 min at 50 °C. The HCS/PVP composite dispersion was prepared by mixing a pristine HCS supernatant dispersion (250 µL) with a PVP solution (50 µL) followed by sonication for 30 min at room temperature.

The three different sensors were exposed to ammonia vapours to determine their response and sensitivity. The concentration of ammonia vapours (C) was determined from the volume of ammonium hydroxide added using the equation below, as reported elsewhere [5];

$$C\ (ppm) = \frac{2.46(Vd)}{V_s M_w} \times 10^7 \qquad \textbf{(1)}$$

where V represents the volume added in µL, d is the density of ammonia in gmL^{-1}, V_s is the volume of the chamber in mL (in this case 2400 mL) and M_w is the molecular weight of ammonia solution in gM^{-1}. Different NH_4OH volumes were added (1 µL to 4 µL in steps of 1 µL) corresponding to 74 ppm, 147 ppm, 221 ppm and 295 ppm ammonia vapour concentration respectively.

Morphology and thermal stability of the SiO_2 spheres

The TEM micrographs of the SiO_2 show that the spheres exhibit a spherical morphology with an average diameter size of 212 ± 17 nm (Fig. S1a). In the TG-DTA curves of the SiO_2 spheres, a first derivative peak was observed between 40 °C and 200 °C, which can be attributed to the loss of adsorbed water and ethanol molecules (Fig. S1b). From 250 °C to 380 °C, a considerable weight loss was observed due to the removal of organic residues and further polymerization of the silica network (removal of OH from Si-OH) [6].

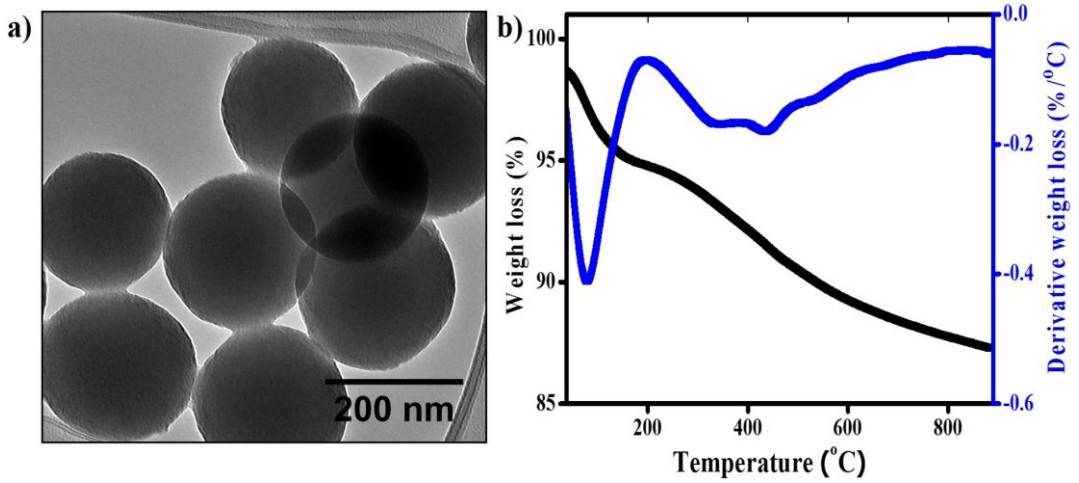

Figure S1. The pristine SiO_2 spheres. (a) TEM image and; (b) TG-DTG curves, respectively.

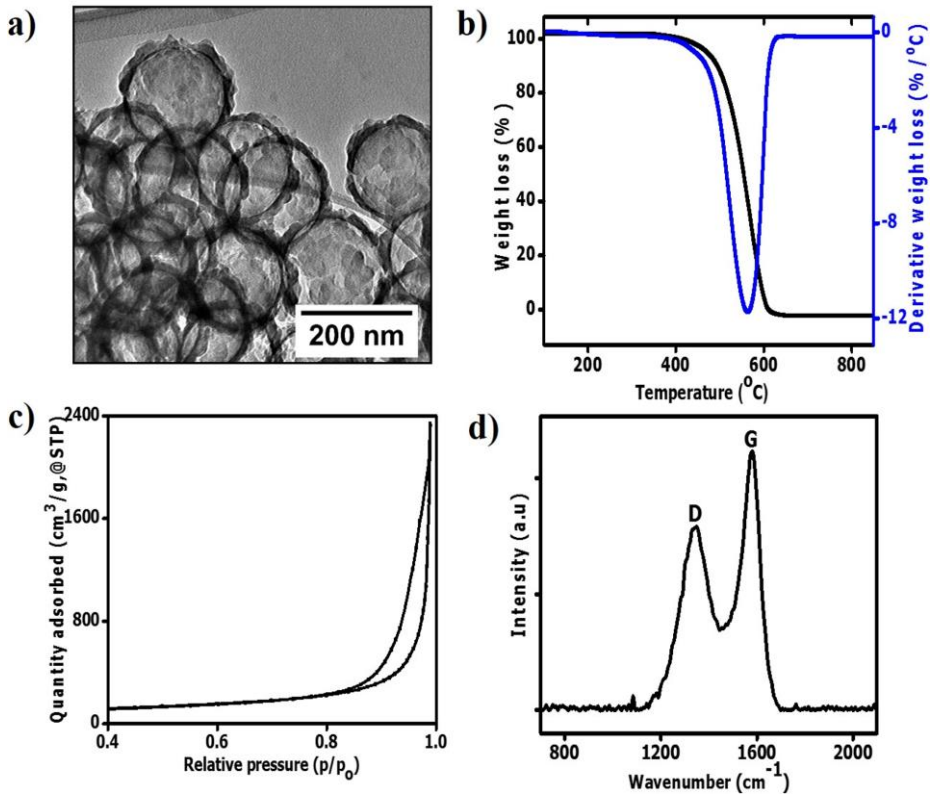

Figure S2. The characteristics of the annealed HCSs. (a) TEM image; (b) TG-DTG curves; (c) N_2 adsorption and desorption isotherms and (d) Raman spectrum, respectively.

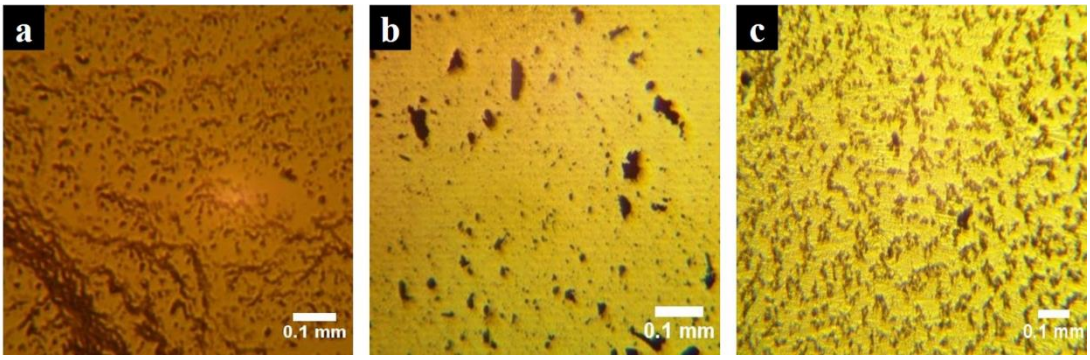

Figure S3. Optical images of dispersed spheres in CTAB solution (a) pristine HCSs, (b) HCS/PVP and (c) annealed HCSs, respectively.

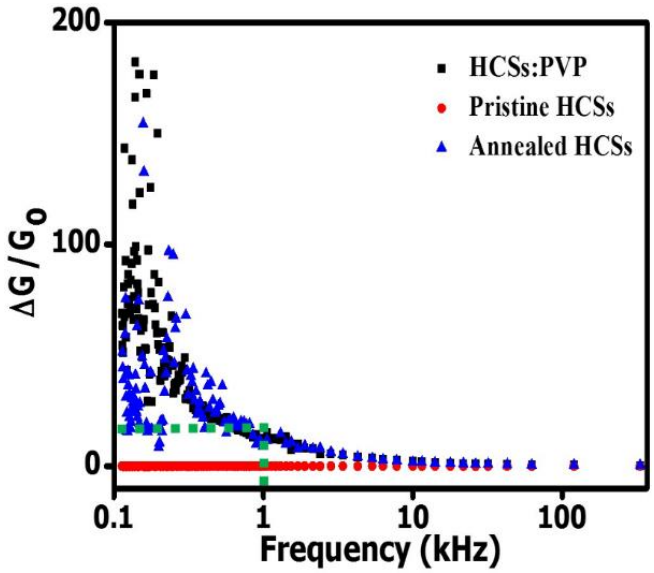

Figure S4. Response of pristine HCSs, HCS/PVP composite and annealed HCSs based sensors as a function of frequency. Ammonia concentration: 74 ppm; RH: 50 %.

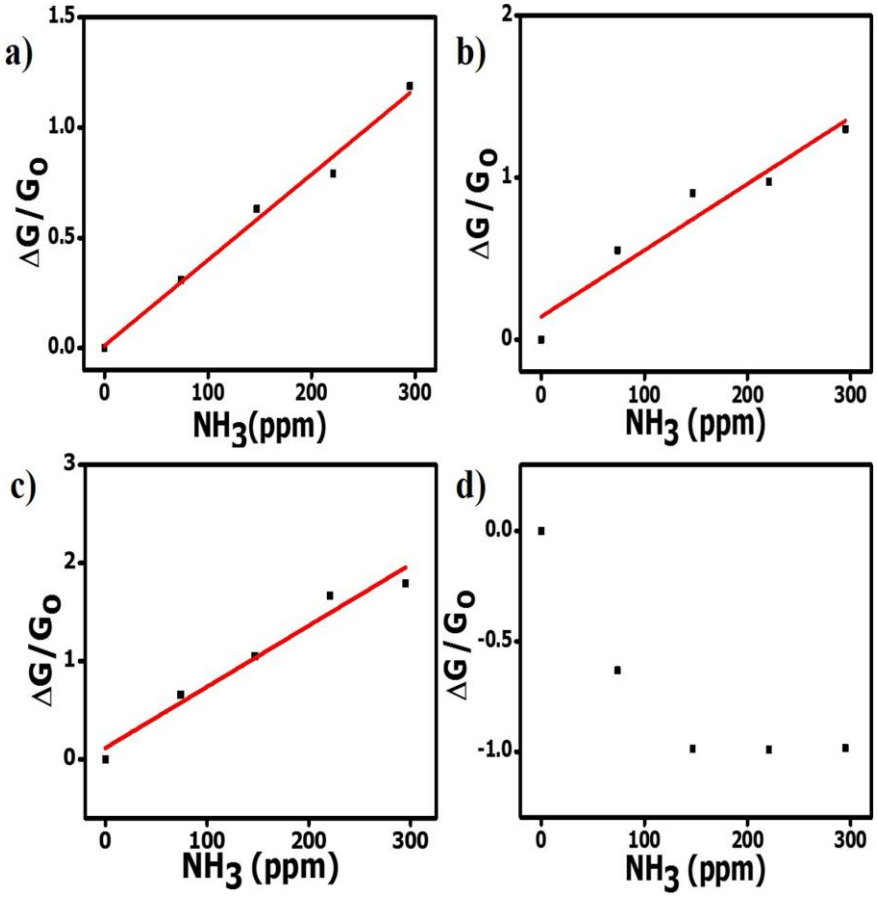

Figure S5. The ammonia sensitivity curves in pristine HCSs at different relative humidity. (a) 33% RH; (b) 59% RH; (c) 75% RH and; (d) 97% RH, respectively. The lines are drawn to aid the eye.

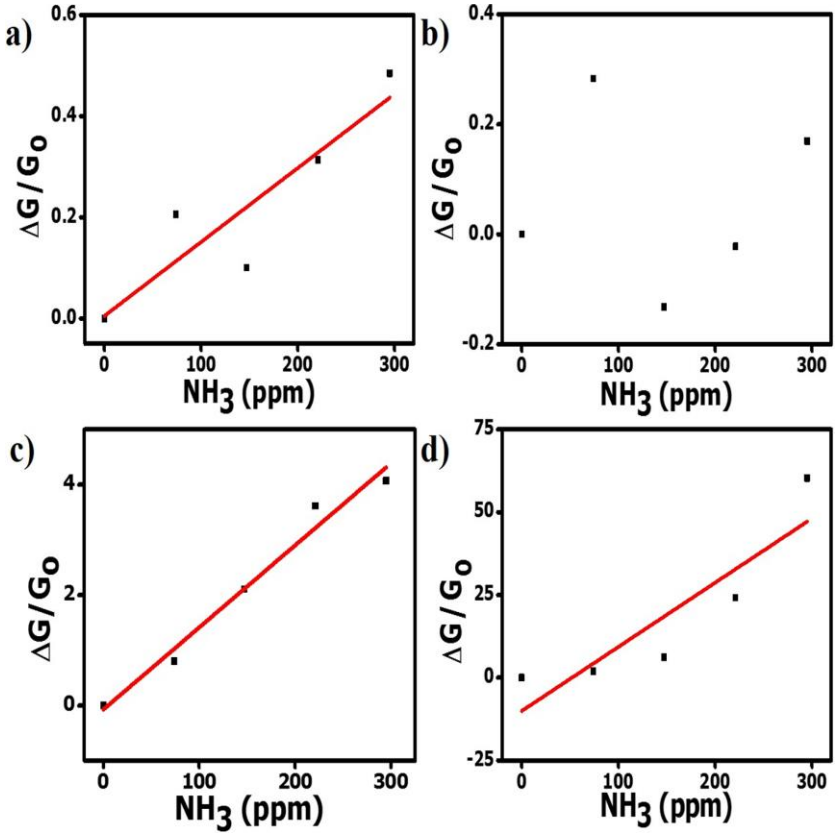

Figure S6. The ammonia sensitivity curves in the HCS/PVP composite at various relative humidity. (a) 33% RH; (b) 59% RH; (c) 75% RH and; (d) 97% RH, respectively. The lines are drawn to aid the eye.

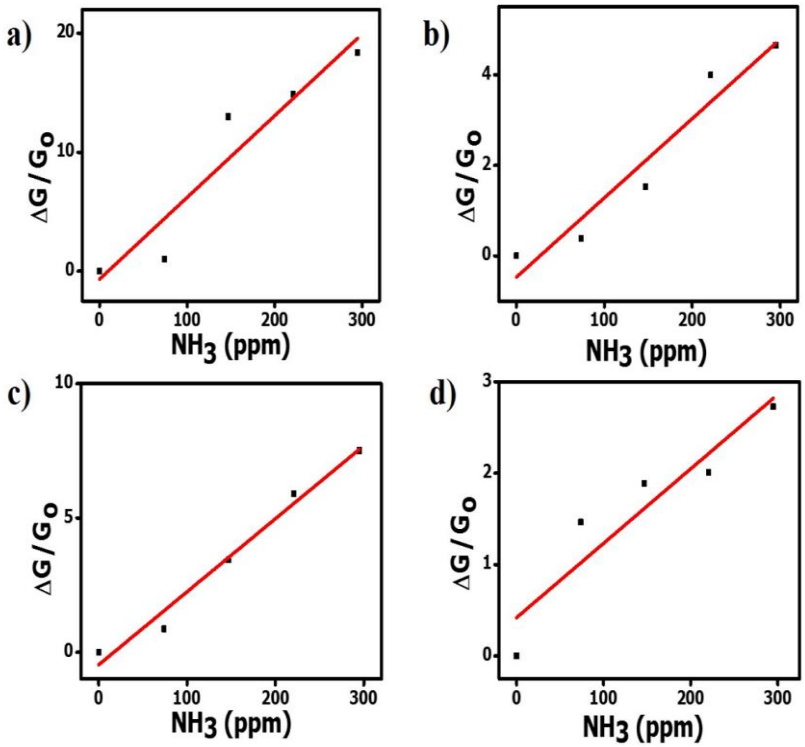

Figure S7. The ammonia sensitivity curves in the annealed HCSs at various relative humidity. (a) 33% RH; (b) 59% RH; (c) 75% RH and; (d) 97% RH, respectively. The lines are drawn to aid the eyes.

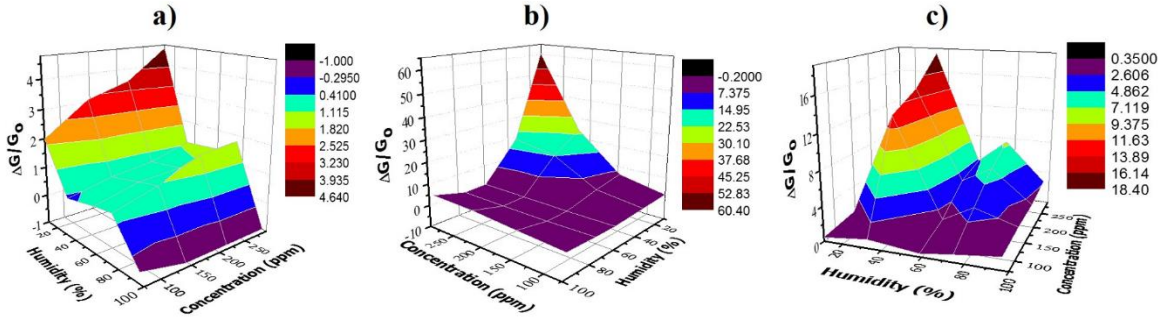

Figure S8. Surface plot showing the response for ammonia and different RH for (a) pristine HCSs, (b) HCS/PVP and (c) the annealed HCSs, respectively.

References

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6. G. E. Maciel, *Journal of the American Chemical Society*, 1996, **118**, 401-406.