Chemical Communications Supporting Information

pH-driven physicochemical conformational changes of single-layer graphene oxide

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Contents

Experimental details

pH changes

SLGO was purchased from CheapTubes Inc and cleaned according to a previous methodology to ensure no residue acid and fulvic acids were present.[1] 2 M solutions of HCl

and NaOH were used for rapid adjustment of pH and for precise control buffered solutions were used to obtain pH 3 (10mM formic acid / ammonium formate), 4.75 (10 mM acetic acid / ammonia acetate), 7 (1 mM and 10 mM sodium dihydrogenphosphate / disodium hydrogenphosphate), 9.24 (10 mM ammonia / ammonia chloride) and 12 (10 mM sodium hydroxide).

SLGO (3 mg) was added to each solution (40 ml) and sonicated for 5 mins. Samples were withdrawn from the supernatant dispersion 2 mins after standing and dropped onto TEM grids and allowed to dry in air. In all samples where a buffer was added, SLGO sedimented from solution on standing up to one week. Only SLGO in pure water remained as a stable dispersion over extended periods.

Silver capture

Using solutions made above, silver nanoparticles (4mg, 98 % Sigma Aldrich 125 mesh) were added and sonicated for 1 min. SLGO (4 mg) was added and the mixture sonicated for a further 5 mins. Similarly, samples were taken from the dispersion 2 mins after standing, dropped onto TEM grids and allowed to dry in air.

Buckypaper composites

Multi-walled carbon nanotube buckypaper was fabricated according to a previously published article. Typically MWCNTS (100 mg) were sonicated in methanol (40 ml) until a fine dispersion was obtained. The mixture was placed between two polypropylene frits (70 micron pore size) sat inside a syringe column and slowly compressed to remove methanol. The MWCNT compression was pushed out of the syringe housing and allowed to dry in air to yield thick buckypaper. SLGO (10 mg) was sonicated in water (40 ml at pH 7) until fully suspended. Buckypaper was added to the dispersion and HCl (2 M) was added drop-wise

until the pH reached 1. The buckypaper was removed from solution and rinsed gently with water (pH 7) and then allowed to dry. This method was repeated, but prior to removal the pH was subsequently adjusted to 14 with drop-wise addition of NaOH (2 M), and then rinsed and dried in a similar fashion.

Results & discussion

The aromatic network of the graphene sheets in SLGO is interspersed with oxygen-containing groups. The nature and arrangement of these groups have been ascertained from solid state NMR, micro-Raman and XPS analysis, which showed the occurrence of carboxylic, alcohol, hydroxyl / phenolic, lactone, ester, epoxy and ketone groups[2]. An alternative method of determining the type of oxygen-containing acidic groups on carbons is using acid-base (Boehm) titrations[3], which can also be used to directly assess the chemical reactivity of SLGO through hydrazine reduction, amidation or esterification, etc.[1] Samples were stirred in the appropriate base for 24 hours prior to separation (membrane filter) and subsequent titration, which facilitated the comparison with acid-oxidised carbon nanotubes.

Therein, acid-oxidised carbon nanotube frequently possess surface-immobilised lattice fragments or fulvic acids that are only removed in alkaline solution. However, SLGO was not found to leach any fragments (fulvic acids or smaller oxidative fragments) unlike acid-oxidised carbon nanotubes[4] or SLGO in other investigations[5]. Herein, it is deduced that SLGO preparation procedures can be quite different and will yield SLGO sheets with different chemical and thermal stabilities and behoves the necessity of extensive checks, i.e. base washing, prior to their use. Furthermore, the different degrees of oxygen functionality, which may also include the presence of lattice vacancies and variable sizes of non-functionalised regions, will contribute to the widely varying morphological changes observed between two samples of SLGO from the same supplier.

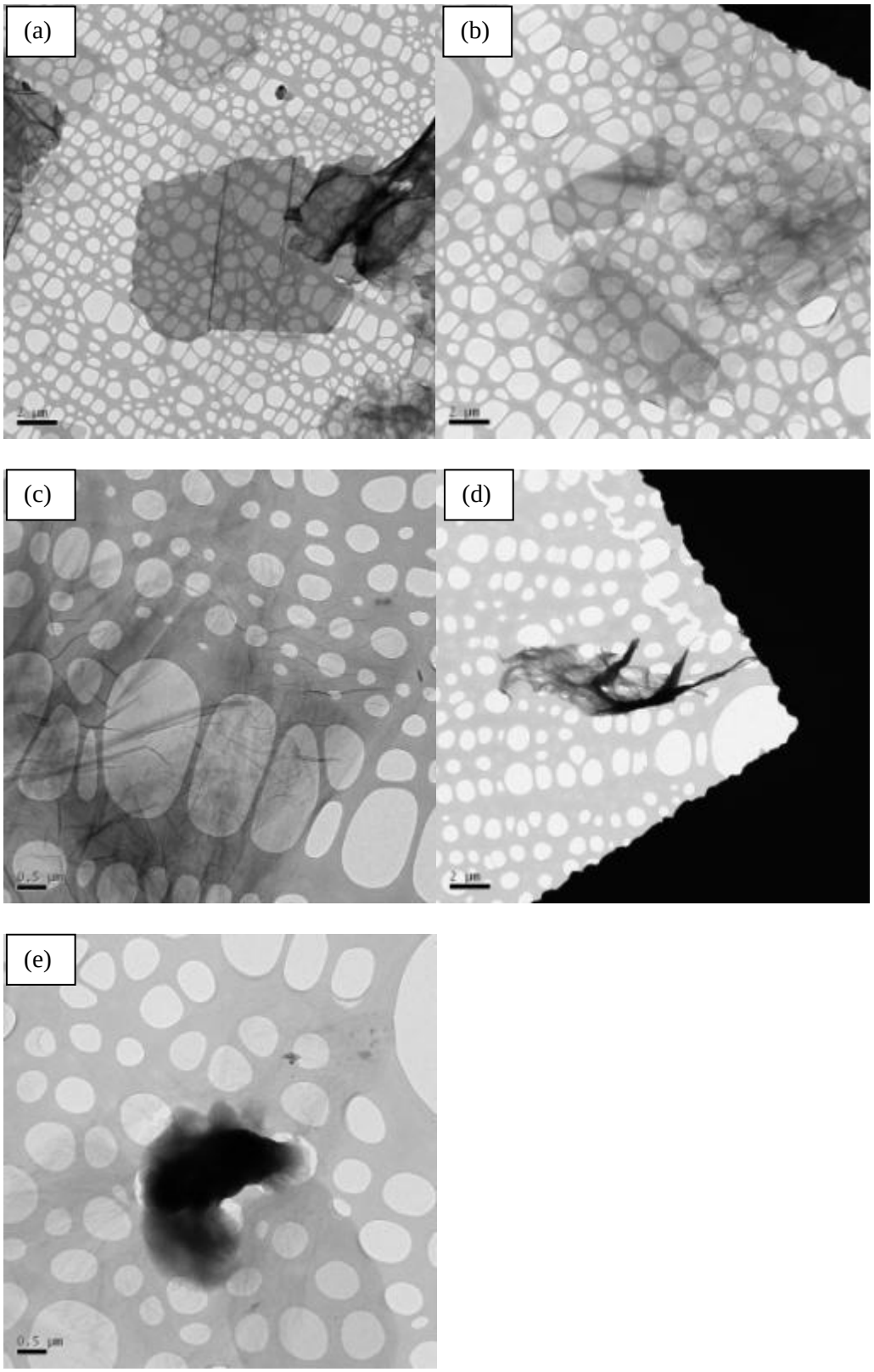


Fig. S1. TEM images of SLGO at pH (a) 3, (b) 5, (c) 7, (d) 9 and (e) 12 in 10 mM buffered solution.

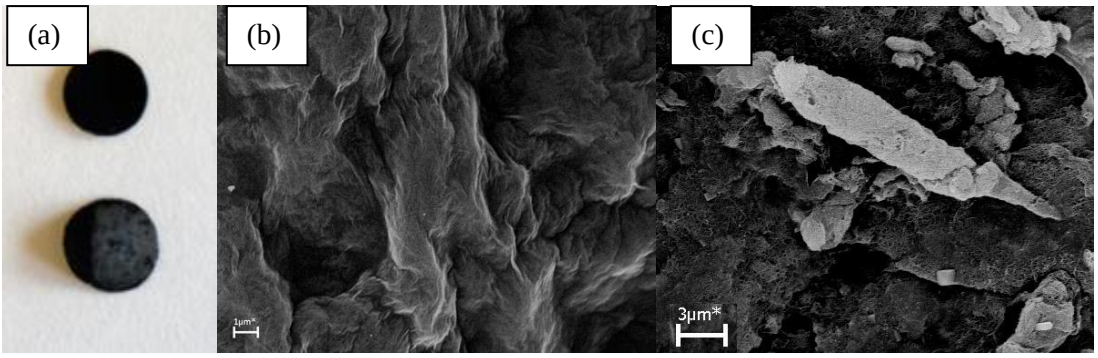
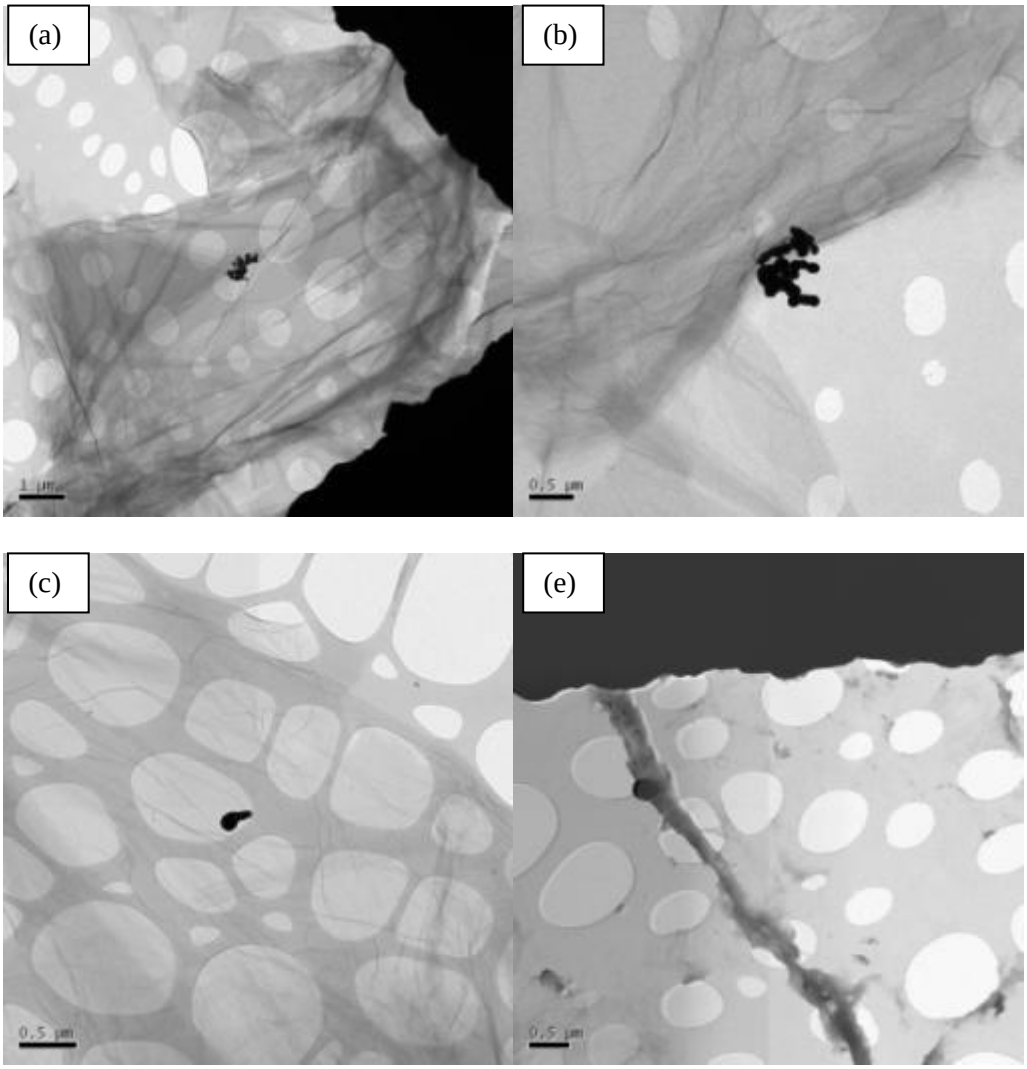


Fig. S2. (a) MWCNT buckypaper uncoated (top) and coated (bottom) with SLGO; SEM images of (b) SLGO coating the surface of MWCNT buckypaper at pH 1 and (c) SLGO remaining stably adsorbed to the surface at pH 14, although the individual sheets have folded.



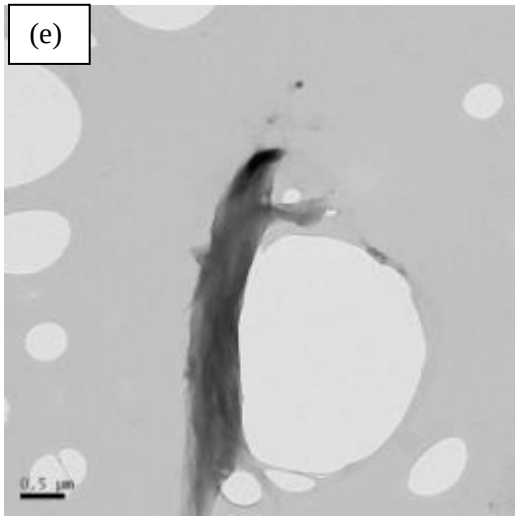


Fig. S3. TEM images of SLGO in the presence of AgNPs at pH (a) 3, (b) 5, (c) 7, (d) 9 and (e) 12 in 10 mM buffered solution.

References

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