Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information:

Amphiphilic Aminoclay-RGO Hybrids: A Simple Strategy to Disperse High Concentration of RGO in Water

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1. Materials and Characterization techniques:

Aminopropyltrimethoxysilane (APTMS) (Sigma Aldrich), $MgCl_2.6H_2O$ (S D Fine chemicals), ethanol (AR Grade), graphite powder (20 micron) (Sigma Aldrich), $NaNO_3$ (Sigma Aldrich), $KMnO_4$ (S D Fine chemicals), H_2SO_4 (98%, AR grade), $N_2H_4.H_2O$ (99%, AR grade) were used without any further purification.

Powder x-ray diffraction (PXRD) patterns were recorded using Bruker-D8 diffractometer using Cu Kα radiation, (λ=1.54 Å, step size: 0.02, current: 30 mA and voltage: 40 kV). Field-emission scanning electron microscopy (FESEM) images and energy-dispersive analysis of X-rays (EDAX) were obtained by using FEI (Nova-Nano SEM-600 Netherlands) equipment. TEM measurements were performed on a JEOL, JEM 3010 operated at 300 kV. Samples were prepared by placing a drop of dispersion on a TEM grid (holey carbon). Raman spectra were recorded at different locations of the sample using Jobin Yvon LabRam HR spectrometer with 632 nm Ar laser. Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer. 1 mm path length cuvette was used for recording the spectra. The zeta potential measurements were carried out using a NanoZS (Malvern UK) employing a 532 nm laser at a back scattering angle of 173°.

2. Experimental section:

2.1. Preparation of graphene oxide:

Graphene oxide (GO) was obtained from graphite by Hummer's method[1]. In a typical procedure, 23 mL of concentrated H_2SO_4 was mixed with 1 g of graphite and 0.5 g $NaNO_3$ in a 250 mL round bottom flask cooled in an ice bath at 0 °C. 3 g $KMnO_4$ was added slowly to the mixture in small portions with vigorous stirring. Temperature was maintained below 20 °C during this time. The ice bath was then removed and the reaction was brought to 30-35 °C, where it was maintained for 30 min. To this 46 mL water was added slowly causing violent effervescence and rise of temperature to 98 °C. The resultant brown colored suspension was maintained at this temperature for 15 minutes. The suspension was then brought to room temperature and 140 ml water was added. The mixture was then treated with 1 mL of 30% H_2O_2 to reduce any unreacted permanganate. The bright yellow reaction mixture was then

centrifuged at 5000 rpm, washed several times with distilled water until the pH turned neutral. The precipitate was dried at a 60 °C oven.

2.2. Preparation of RGO:

RGO was prepared by the following method. First, 580 mg of GO was dispersed in 200 mL distilled water by sonication. To this suspension 5 mL of hydrazine hydrate was added and refluxed for 10 h. The solution turned clear and black cloudy precipitates of RGO were seen floating. The precipitate was centrifuged at 5000 rpm, washed with distilled water until the pH turns neutral. Final product was dried overnight at 80 °C to get RGO.

2.3. Preparation of aminoclay:

Typically, bulk aminopropyl-functionalized magnesiumphyllosilicate clay was prepared at room temperature by drop wise addition of 1.0 mL (5.85 mmol) 3-aminopropyltrimethoxysilane to an aqueous solution of 0.84 g (3.62 mmol) magnesium chloride in water (25 mL) The solution was left stirring for 24 hours, dried at 60 °C, dispersed in water, reprecipitated from ethanol and dried. The yield of the product was 1.0 g.

2.4. Preparation of aminoclay-GO and aminoclay-RGO hybrids: (In-situ synthesis)

In this method, the aminoclay nanostructures were allowed to form over the surface of GO sheets dispersed in water. In a typical procedure, for preparation of AC-GO-25 (hybrid containing 25 wt% GO) 0.35 g of GO was dispersed in 25 mL water by sonication for 10 min. To the dispersion 0.84 g (3.62 mmol) magnesium chloride was added followed by drop wise addition of 1.0 mL (5.85 mmol) 3-aminopropyltrimethoxysilane. The solution was stirred for 48 hours to form a brown-black slurry, which was dried at 100 °C. The solid thus obtained was dispersed in water (20 mL) and precipitated from ethanol (100 mL). The precipitate was centrifuged and subsequently dried at 60 °C to get the aminoclay-GO hybrid (AC-GO-25).

For preparation of aminoclay-RGO hybrids (AC-RGO-25) 0.35 mL hydrazine hydrate was added to the AC-GO-25 slurry followed by drying at 100 °C. The resultant hybrid was dispersed in water and reprecipitated from ethanol followed by drying to get the aminoclay RGO hybrid. Thus prepared aminoclay GO and RGO hybrids are abbreviated as AC-GO and AC-RGO respectively followed by number which indicate the weight percent of GO or RGO with respect to clay. The amount of GO introduced was varied to get different compositions- AC-GO-7.5, 25, 35 and AC-RGO-7.5, 25, 35.

The hybrids were dispersed in water (0.1 g in 5 mL) by probe sonication for 5 min. For comparison 10 mg of RGO was also dispersed in 5 mL water by sonication. High concentration water dispersion of RGO was prepared by sonicating 30 mg of AC-RGO 25 in 1 mL water.

2.5. Preparation of APTMS functionalized RGO:

To a 0.35 g GO dispersion in 20 mL distilled water 1 mL of APTES was added. The reaction mixture was stirred for 48 h, 0.35 mL hydrazine hydrate was added to it and dried at 100 °C to get APTMS functionalized RGO.

2.6. Etching of clay from RGO-aminoclay hybrid:

The demineralization of a AC-RGO hybrid was done according to a previously reported procedure[2]. In a typical method 0.25 g of AC-RGO 25 was stirred with 30 mL solution of 12% HCl and 13% HF for 12 h.

2.7. Adsorption of biomolecules on GOC and RGC hybrids

Adsorption studies with cytochrome C and (DNA) biomolecules were done at pH 10.3. The reason for choosing these biomolecules is that their soret bands are quite apart (260 nm for DNA and 410 nm for cytochrome C) and don't interfere with one another. Stock solution (1g/L) of both the biomolecules (DNA and cytochrome C) were prepared by dissolving them in tris buffer (0.1M) solution (pH 10.3). For each experiment 20 mg of each hybrid (AC-RGO 7.5, 25, 35) were suspended in 4 mL of the stock solutions. 20 mg of aminoclay and 8 mg of RGO were also suspended in 4 mL of the stock solutions as references. For combined adsorption studies a stock solution containing 1 g/L of DNA and cytochrome C was used. These solutions were allowed to stand for 24 h at 25 °C to attain the equilibrium. After ageing of the solutions they were centrifuged at 10000 rpm and the supernatant liquid was taken for UV-Vis absorption studies to quantify the remaining biomolecule concentration.

For adsorption measurements at pH 5.8 and 7 phosphate buffer solution of pH 7 was prepared and the pH was adjusted by addition of acid as required.

3. Supporting Figures

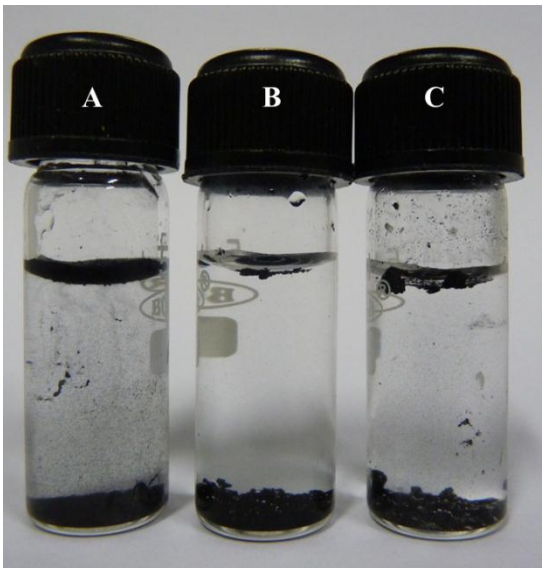

Figure S1. Water dispersion of A) Reduced form of preformed aminoclay-GO hybrid, B) APTMS functionalized RGO, C) Demineralized AC-RGO-25 hybrid just after sonication.

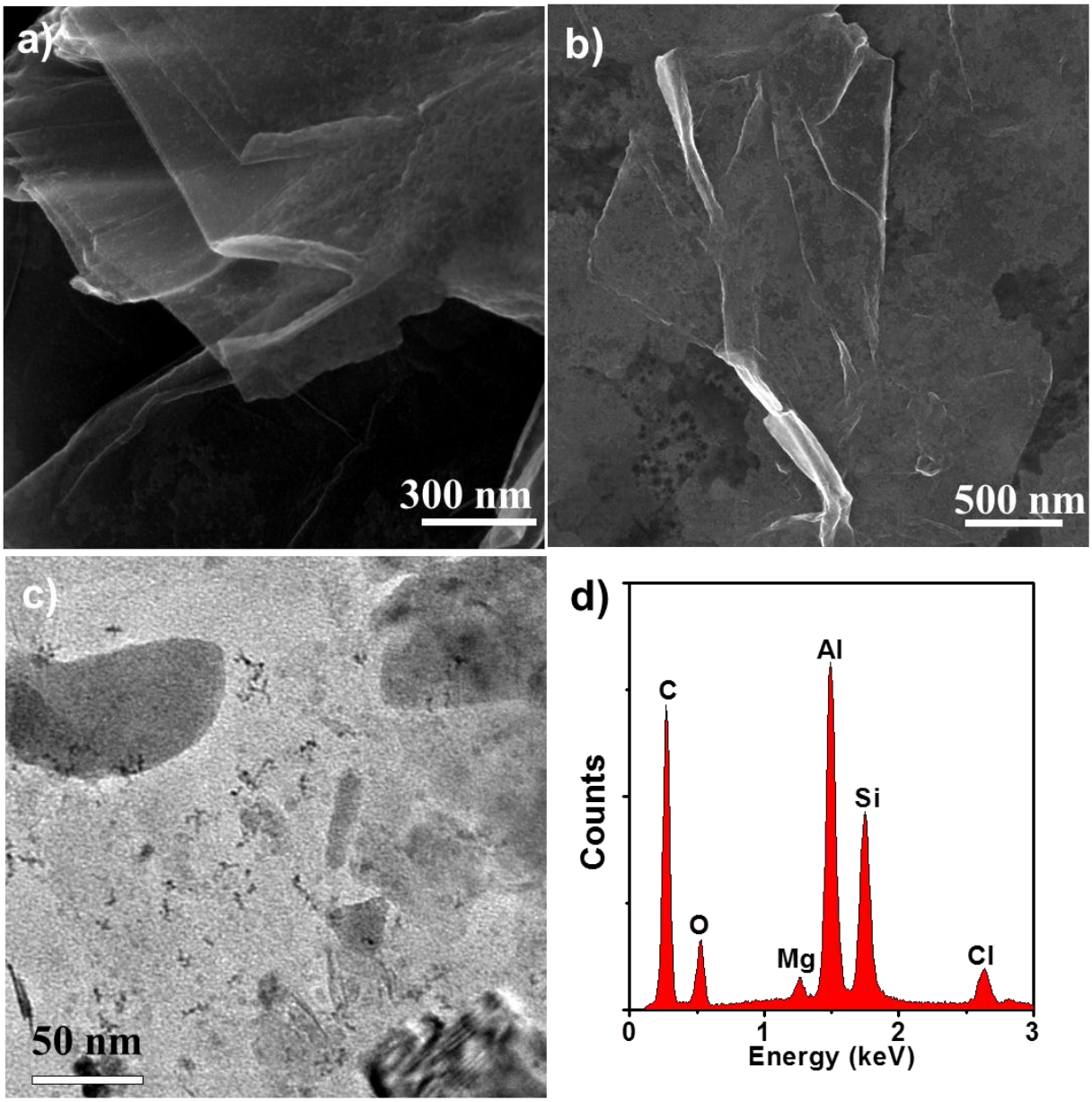

Figure S2. a), b) FESEM images of the hybrids showing clay nanoparticles deposited on RGO. Distribution of clay nanoparticles is not very uniform. c) TEM image shows the presence of clay nanoparticles of size 5- 50 nm on RGO sheet. d) EDAX analysis of the composite showing presence of Mg, Cl and Si along with carbon, which confirms presence of clay in the hybrid.

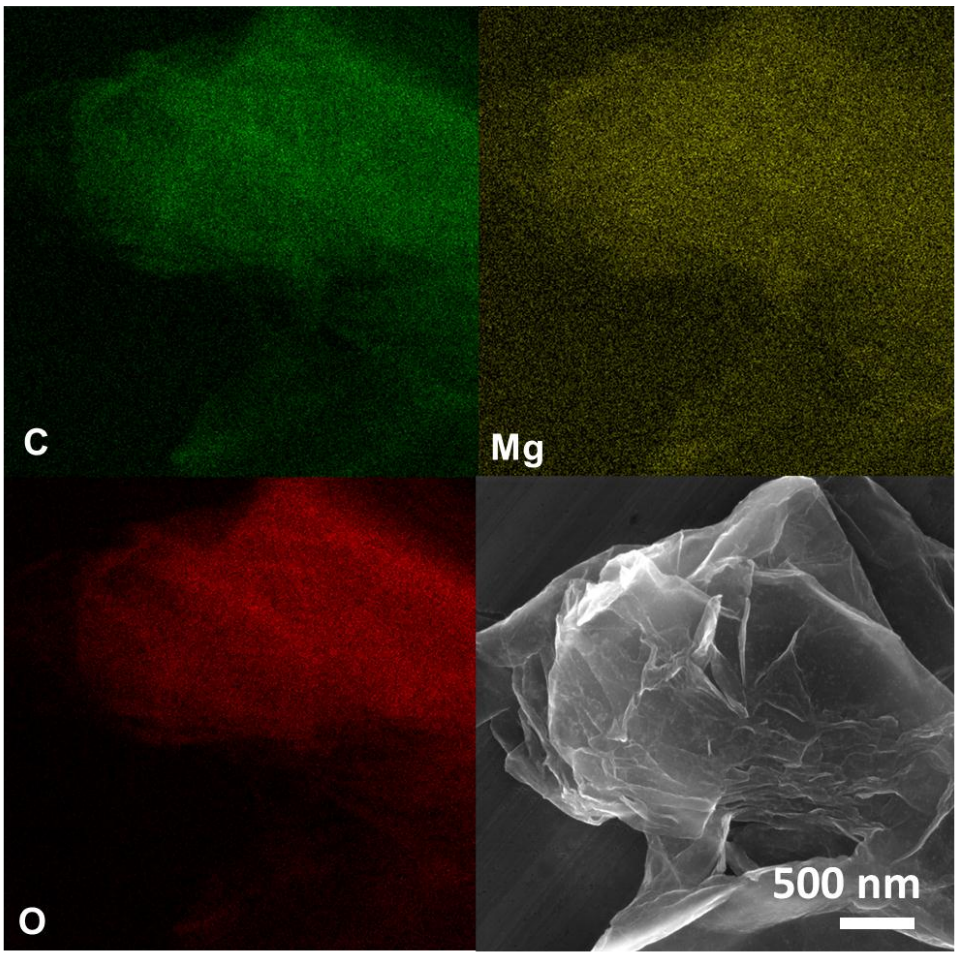

Figure S3. Elemental mapping of the composite AC-RGO-35 showing distribution of aminoclay (Mg,O) on RGO (C,O).

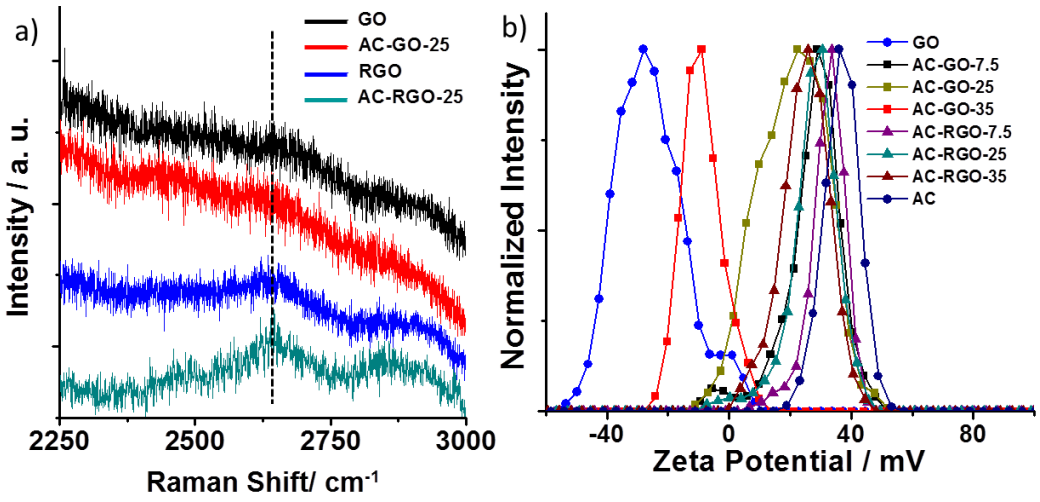

Figure S4. a) Raman spectra of GO, RGO, AC-GO-25 and AC-RGO-25. The presence of 2D (marked, 2650 cm^{-1}) and D+G bands (2905 cm^{-1}) in AC-RGO-25 and RGO is evident. b) Zeta potential distribution of AC-GO and AC-RGO hybrids with aminoclay and GO.

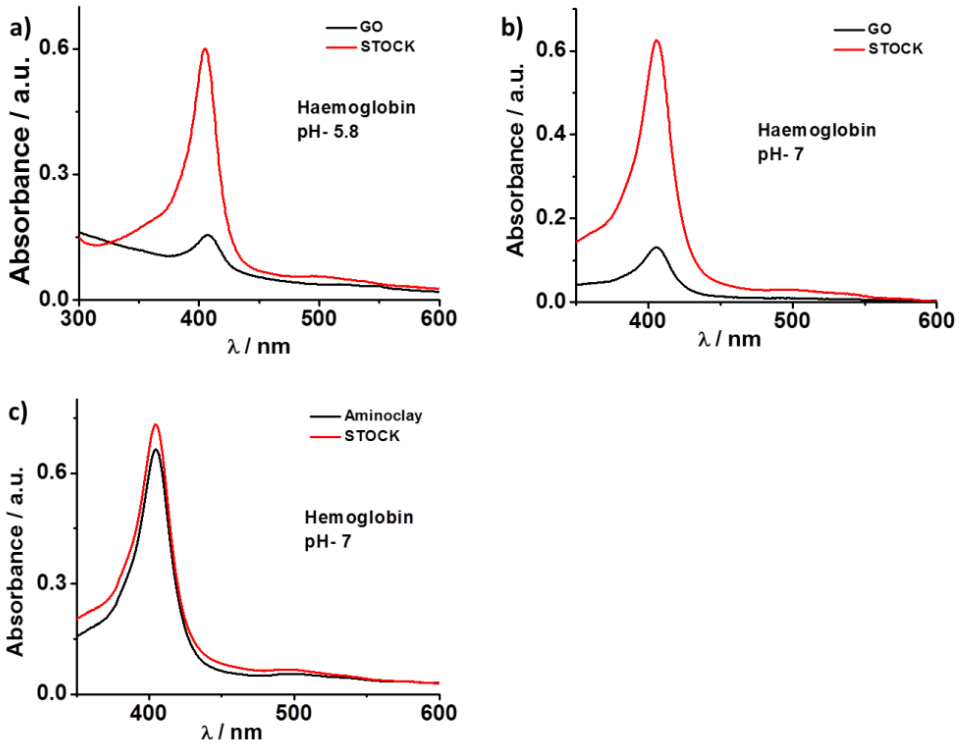

Figure S5. Adsorption profiles of a) Haemoglobin on GO at pH 5.8, where Haemoglobin is positively charged, b) Haemoglobin on GO at pH 7 , where the protein is almost neutral, c) Adsorption of Haemoglobin on AC at pH 7.

4. References

1. W. S. Hummers Jr and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-2678.

2. K. K. R. Datta, D. Jagadeesan, C. Kulkarni, A. Kamath, R. Datta and M. Eswaramoorthy, *Angew. Chem.*, 2011, **123**, 4015-4019.