Supporting Information

A simple and controllable graphene-templated approach to synthesise 2D silica-based nanomaterials using water-in-oil microemulsions

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Experimental Section

Materials

All chemical reagents were of analytical grade available from Shanghai Reagents Co. (China) and used as-received without further purification.

Preparation of graphene oxide (GO)

Graphene oxide (GO) was synthesized according to a previously published report.[S1]

Preparation of silica-coated graphene oxide (SiO_2/GO)

Typically, GO suspension (1 mg/mL, 300 mL) and BnOH (150 mL) were placed in a one-neck bottom flask. The mixture was treated in an ultrasonic bath (40 kHz) for 4 h. Water was removed from the obtained emulsion via rotary evaporation at 60 °C. The above procedure was repeated once to obtain a homogeneous dispersion and the weight ratio of BnOH to H_2O in the resulting suspension was 9 (determined by ^{1}H-NMR). Then, the dispersion was transferred to a two-neck bottom flask and 1.96 g ammonia was added. After mechanical stirring for 0.5 h at 40 °C, tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS) was slowly added into the above mixture. After reaction for 24 h, the obtained products were micro-filtered three times with an excessive amount of ethanol and dried at 60 °C *in vacuo* overnight.

Preparation of silica-coated thermal reduced graphene oxide (SiO_2/TRGO) and silica nanoflakes (SiO_2/NF)

The thermal reduction of SiO_2/GO was processed under a 5 wt.% H_2/Ar flow of 60 mL/min. First, the SiO_2/GO powder was heated from room temperature to 280 °C at the rate of 2 °C/min, and kept at 280 °C for 1 h. Second, the temperature was increased from 280 to 700 °C at the rate of 2 °C/min, and then the specific temperature was kept for 3 h. Finally, after being cooled to room temperature under 5 wt.%

H_2/Ar flow, the sample was washed with ethanol three times and dried at 60 °C *in vacuo* overnight. Silica nanoflakes (SiO_2/NF) were prepared by the same thermal treatment procedure except under air flow.

Characterization

The thermal degradation behavior of the samples was measured using a Pyris1 thermogravimetric analyzer (TGA) from room temperature to 800 °C at a heating rate of 20 °C/min under an air atmosphere. Raman spectra were recorded from 800 to 3000 cm^{-1} on a LabRAM HR800 Raman microprobe using a 532 nm Nd-YAG laser. Powder X-ray diffraction (XRD) analyses were performed on a PANalytical X'Pert PRO diffractometer with Cu-Kα radiation. The diffraction data were recorded for 2θ angles between 5° and 90°. The morphology of samples were observed using a Tacnai G^2 20 transmission electron microscope (TEM) operated at 200 kV. Scanning electron microscopy (SEM) images were taken with a Sirion 200 microscope using an accelerating voltage of 5-15 kV and a Nova NanoSEM450 with an accelerating voltage of 10 kV. XPS measurements were obtained [AXIS-ULTRA DLD-600W (Shimadzu-Kratos)] using a monochromatized Al Kα anode. Fourier transform infrared spectroscopy in combination with the attenuated total reflectance technique (FTIR-ATR) spectra were measured on a Bruker Equinox 55 Fourier transform infrared spectrometer.

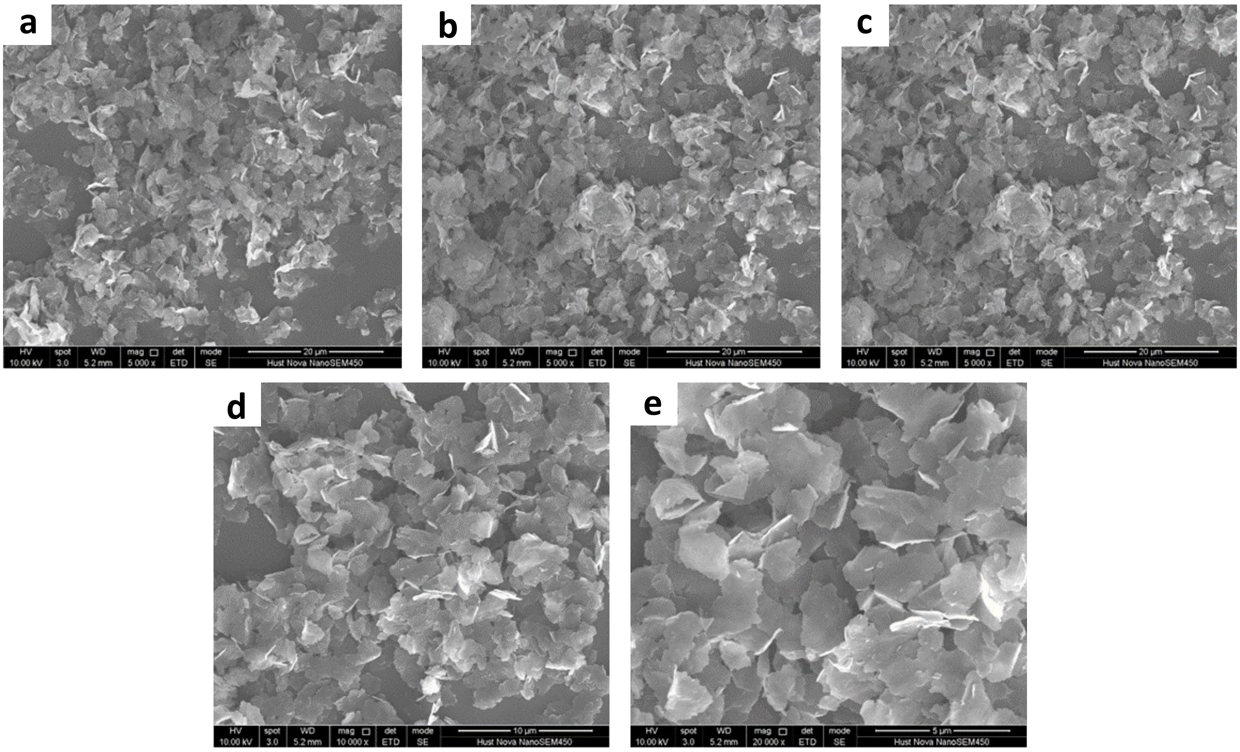

Fig. S1 SEM images of SiO_2(TEOS)/GO from different observed areas with different magnification [Scale bars: (a-c) – 20 µm; (d) - 10 µm; and (e) – 5 µm]

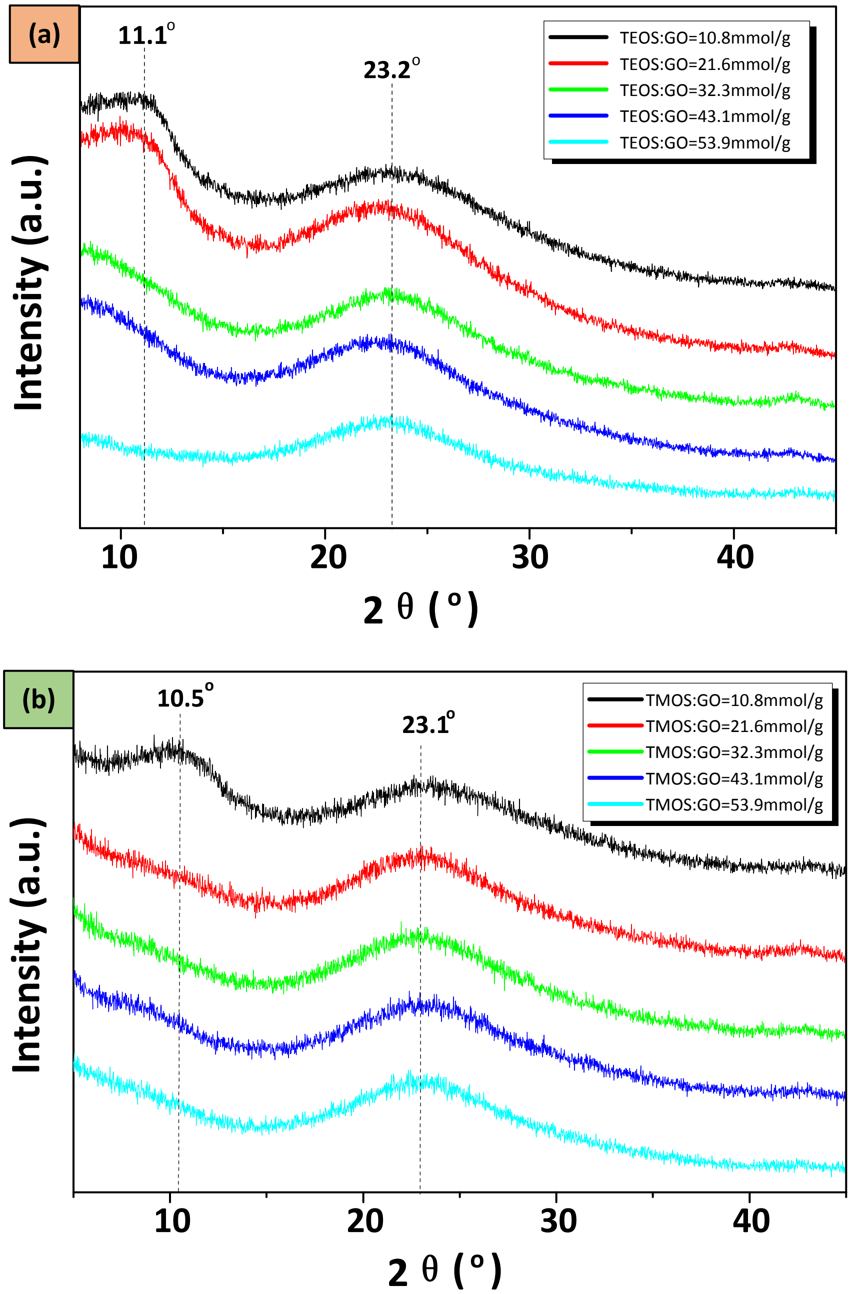

Fig. S2 (a) XRD pattern of SiO_2(TEOS)/GO with increasing TEOS amount; and (b) SiO_2(TMOS)/GO with increasing TMOS amount.

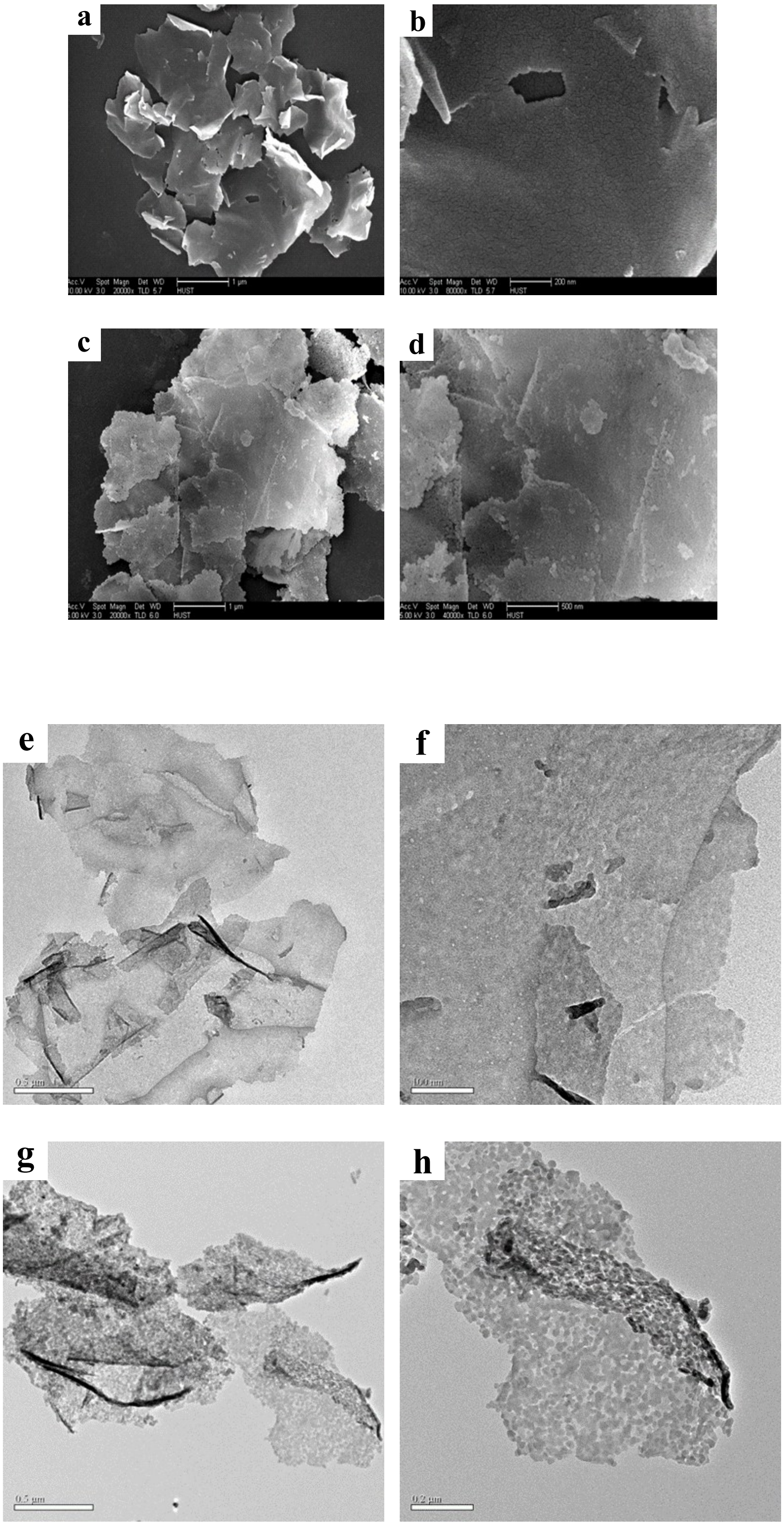

Fig. S3 Morphology of SiO_2/NF from SiO_2(TMOS)/GO [SEM (a, b) and TEM (e, f) images] and SiO_2(TEOS)/GO [SEM (c, d) and TEM (g, h) images].

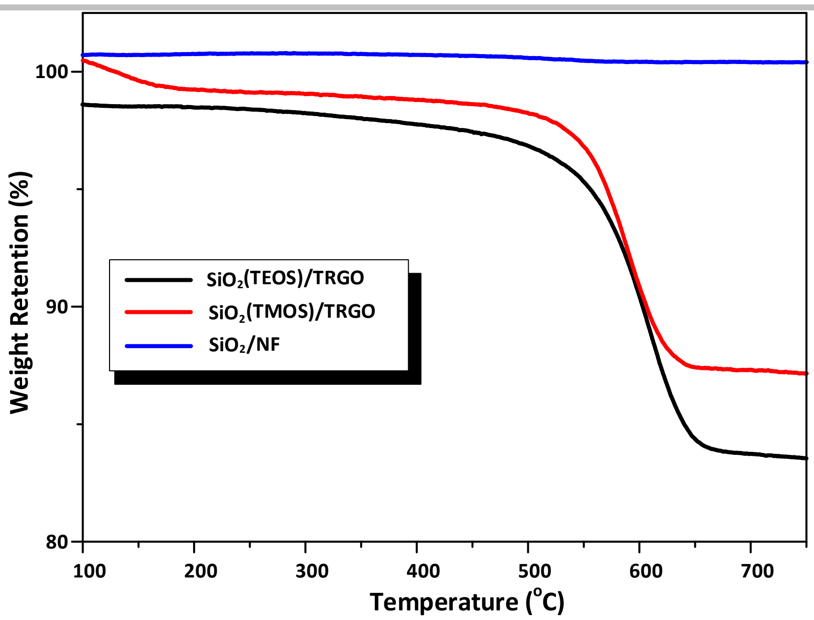

Fig. S4 TGA curves of SiO_2(TEOS)/TRGO, SiO_2(TMOS)/TRGO and SiO_2/NF.

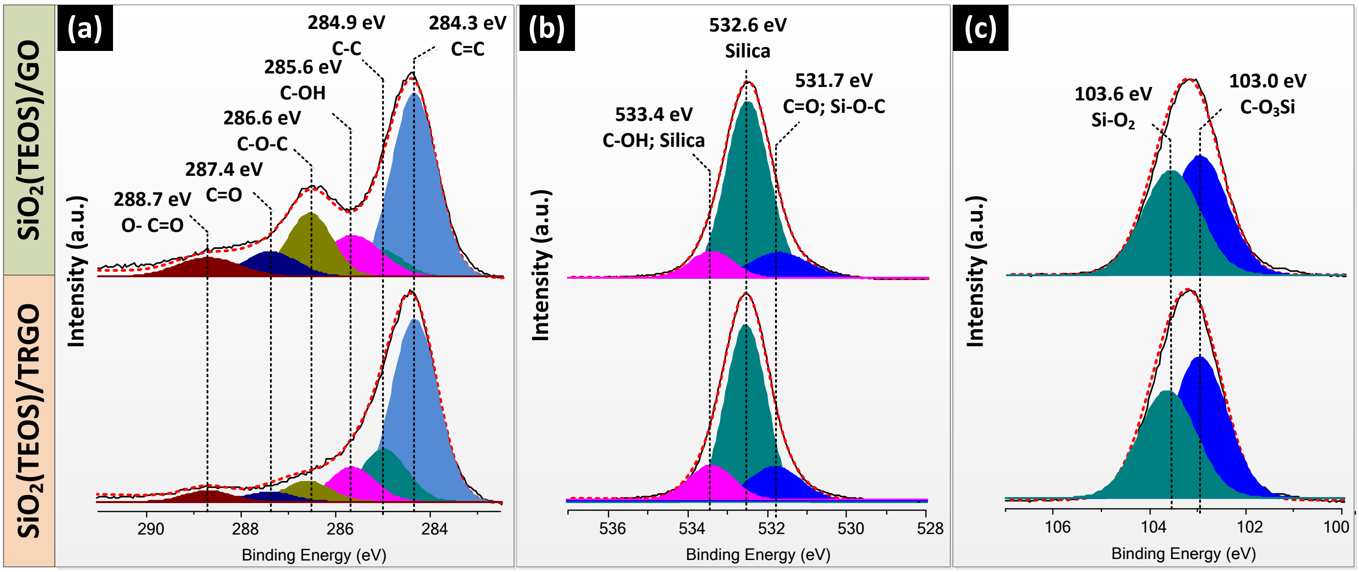

Fig. S5 (a) Carbon 1s XPS profile, (b) O 1s, and (c) Si 2p of SiO_2(TEOS)/GO and SiO_2(TEOS)/TRGO.

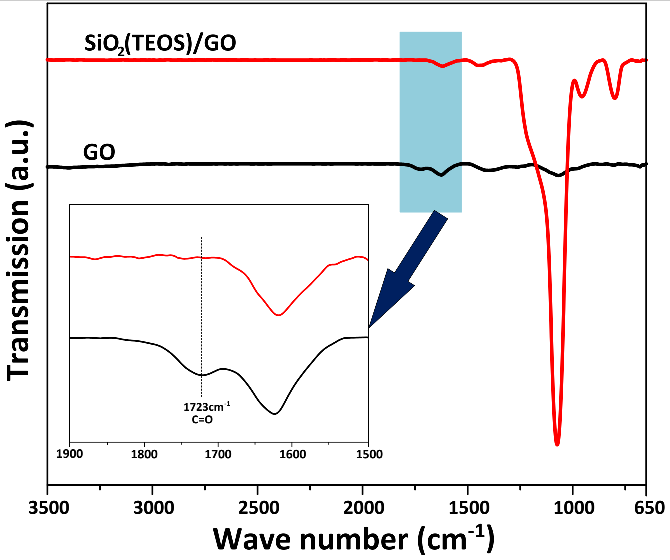

Fig. S6 FTIR-ATR spectra of GO and SiO_2(TEOS)/GO.

The FTIR-ATR spectra of GO and SiO_2(TEOS)/GO were shown in Fig. S6. The typical FTIR-ATR spectrum of GO is consistent with the previous report.[S1] Limited by the sensitivity of FTIR-ATR at high wave numbers, the peak of the hydroxyl group at 3500 cm^{-1} is insignificant. But bands centered at 1399 cm^{-1} could prove the existence of the -OH bond of GO. The 1723 cm^{-1} band was attributed to the stretching vibration of carbonyl or carboxyl groups. After reaction with TEOS, the strong peak at 1073 cm^{-1} is attributed to asymmetric stretching of the Si-O-Si and Si-O-C bonds, while the carboxyl group peak at 1723 cm^{-1} is significantly decreased (see inset of Fig. S6), which indicates the carboxyl group has been converted to Si-O-C bonds.[S2, S3] This evidence confirms the covalent bonding between silica and GO at the surface of GO.

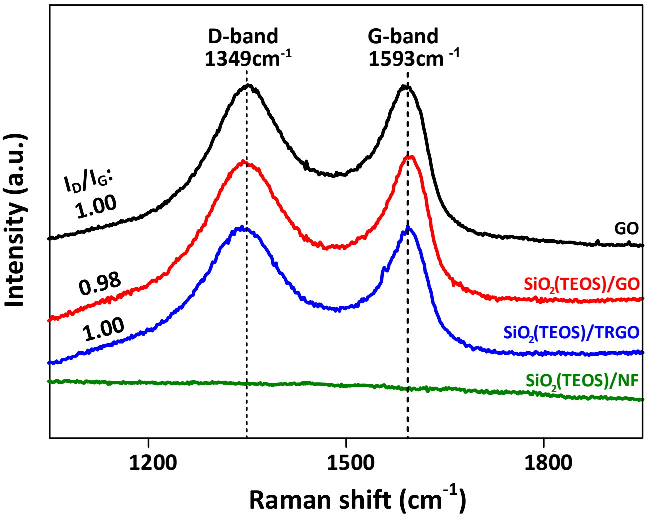

Fig. S7 Raman spectra of GO, SiO_2(TEOS)/GO, SiO_2(TEOS)/TRGO and SiO_2/NF.

Mechanism of growing silica film on GO surface in EtOH/water co-solvent and water/BnOH biphase systems

For water/BnOH biphase system, silica covered GO sheets were prepared by an oil-water biphasic reaction system. Since ammonia hydroxide (catalyst) and BnOH are immiscible, the hydrolysis process cannot proceed in the oil phase. The silica precursor, TEOS or TMOS, undergoes hydrolysis with water and becomes silicic acid which, condensed with the protic functional groups (e.g., -OH, -COOH) on the surface of GO, yields GO-supported hetero-nucleated silica. Subsequently, more and more parasitical silica particles grow laterally on the GO surface. Finally, silica particles cover evenly and densely the surface of GO sheets, thereby leading to the formation of a large uniform silica film on the GO surface. As GO is instantly coated with small silica (SiO_2) particles owing to the confined surface condensation reaction, therefore, free silica particles are not produced during the sol-gel reaction.

For EtOH/water co-solvent system, however, because condensation of silicic acid with hetero-nucleated silica of GO forms silica layers on the GO surface and, simultaneously, with homo-nucleated silica forms free silica particles. These free silica particles together with those silica particles on GO can also condense to form silica. Hence, sphere-like morphology is observed when silica-covered graphene is prepared in EtOH/water co-solvent system.[S3]

References:

[S1] J. Chen, B. Yao, C. Li and G. Shi. *Carbon*, 2013, **64**, 225-229.

[S2] K. G. Lee, R. Wi, M. Imran, T. J. Park, J. Lee, S. Y. Lee and D. H. Kim. *ACS Nano*, 2010, **4**, 3933-3942

[S3] W. L. Zhang and H. J. Choi. *Langmuir*, 2012, **28**, 7055-7062.