Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

SUPPORTING INFORMATION:

Characterizations:

Crystallinity and morphology of the synthesized products were examined by x-ray diffractometer, high resolution transmission electron microscope (HRTEM, JEM 2100) and field emission scanning electron microscope (HITACHI S-4800) respectively. Compositional analysis of the samples were investigated by x-ray photoelectron spectroscopy (XPS) using a SPECS HSA-3500 hemispherical analyzer with a monochromatic Mg Kα x-ray source. Room temperature cathodoluminescence (CL) spectra and image were recorded with Gatan Mono CL3 equipment attached with FESEM. Thickness of the graphene layer was estimated through atomic force microscopic measurement (AFM; CPII VEECO). Raman spectroscopic characterization was performed with WITec alpha 300RA Raman Confocal Microscope with 532 nm diode laser. The field emission performance was investigated in a high vacuum system under vacuum~2 × 10^{-6} mbar with a parallel plate configuration where the nanostructure on ITO substrate served as the cathode and a conically shaped stainless steel electrode as the anode having the tip diameter of ~ 1.5 mm. The separation between the cathode and anode was kept fixed at 200 μm.

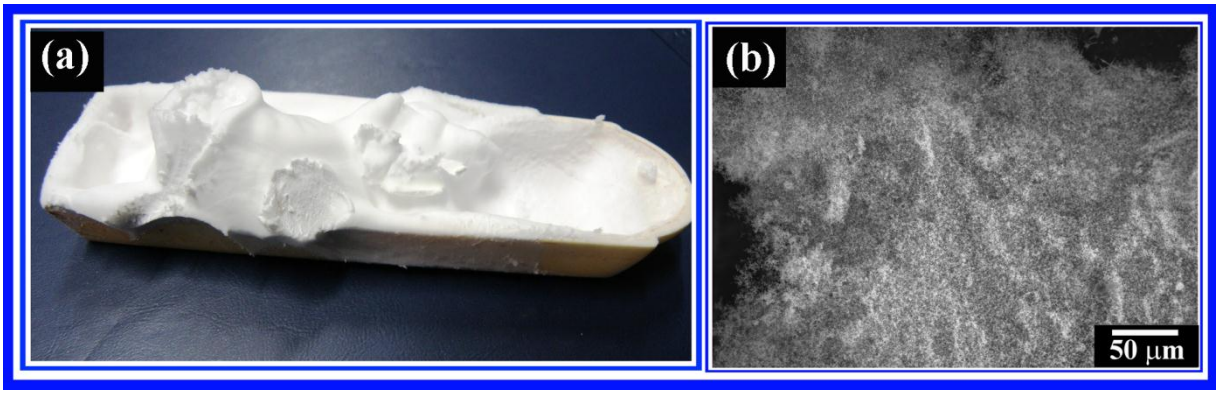


Fig.S1: (a) Digital image and (b) FESEM image showing scalability.

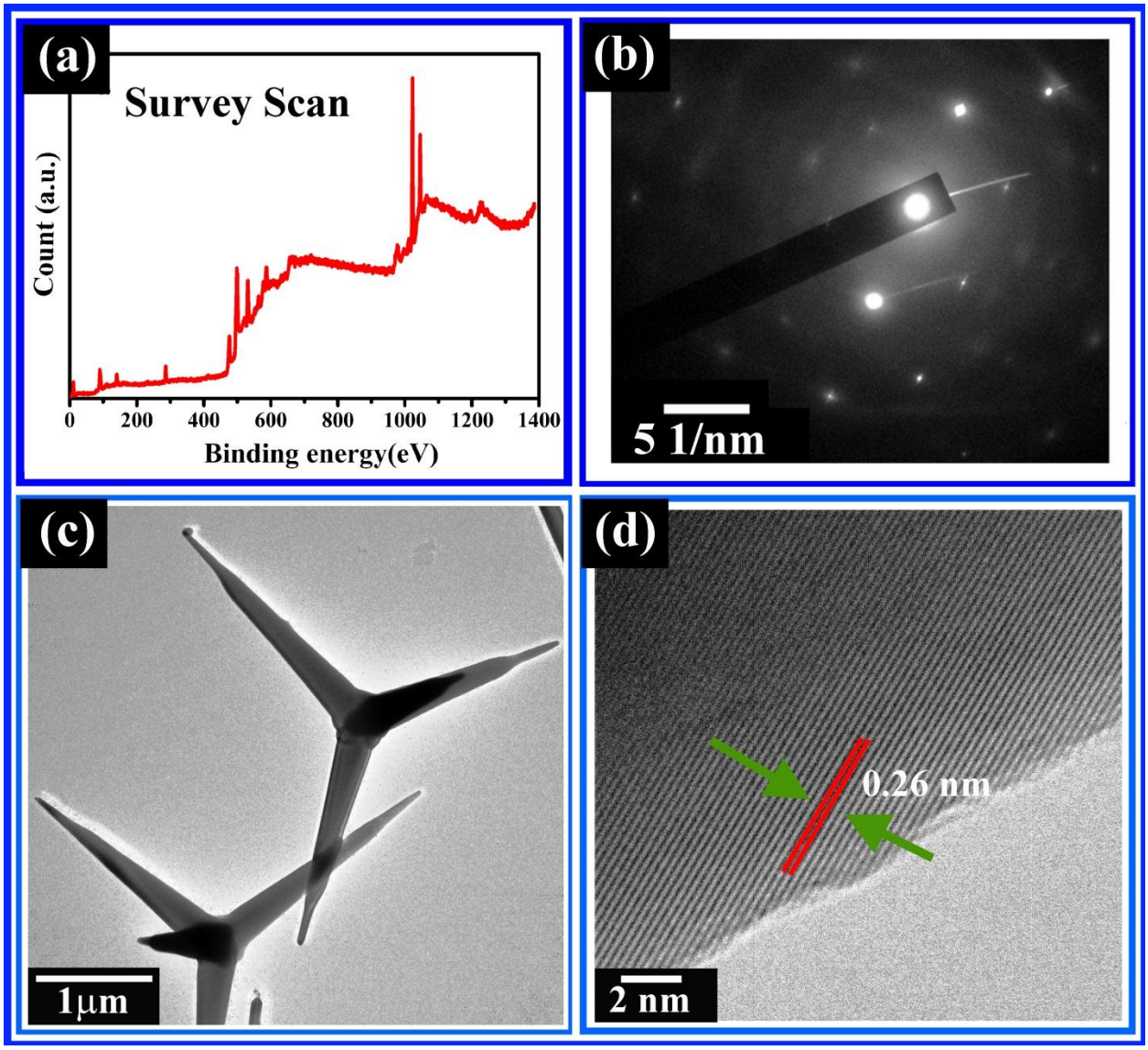


Fig.S2 (a) Survey scan of ZnO (b) SAED pattern corresponding to long prong (c) TEM image and (d) HRTEM image of short prong.

Thermally reduced graphene oxide (TGO) and their characterizations:

Graphite oxide (GO) was prepared via a modified Hummer's method and was dried in vacuum. Thereafter 250 mg of dried GO was placed inside a 1 m long and 30 mm inner diameter, one end sealed quartz tube. Then the sample was flushed with argon for 10 min, and the quartz tube was quickly inserted into a preheated furnace at 1050°C and maintained there for 30s.

FESEM image of the thermally reduced graphene oxide (TGO) in figure S3a demonstrates ultrathin, transparent sheet with crumbling and rippled like features in it.

TEM image in figure S3b reveals large TGO sheets with wrinkle and folded regions. Additionally the transparent sheets comprise of single or very thin layers which are noticeable from the image. The SAED pattern in the inset (figure S3b) with multiple hexagon indicates an overlay of crystalline graphene sheets where the first set of bright spots and second set of faint spots are related to {1100} and {2110} plane respectively. Furthermore the existence of the single layer graphene can be confirmed from the brighter intensity of the first planes compared to the latter as for single layer graphene the intensity ratio must be greater than unity i.e. $I_{\{1100\}}/I_{\{2110\}} > 1$. [Hernandez Y et al 2008 Nature Nanotechnology 3 563]

Additional insights into de-oxygenation of the TGO can be obtained from the XPS investigation. The C1s contribution of TGO was taken into account. The deconvoluted C1S spectra corresponding to TGO consists of one main peak centered at 284.6 eV and other low intensity peaks in the higher binding energy region. The peak at 284.6 eV is associated to the sp^2 aromatic rings. And higher binding energy peaks are related to alkoxy and epoxy group (C–O), COOH etc. (figure.S3c) Higher intensity ratio of the peak related to sp^2 aromatic ring to the other

functional group related peak indicates sufficient amount of reduction of graphene oxide occurred during thermal treatment [Maiti et al. 2011, 22, 505703].

To determine the sheet thickness we also carried out the AFM measurement of graphene sample on freshly cleaved mica substrate. The thickness of the graphene sheet was estimated from the height profile along the line and found to be ~ 1 nm, which is consistent with previous report (figure S3d).

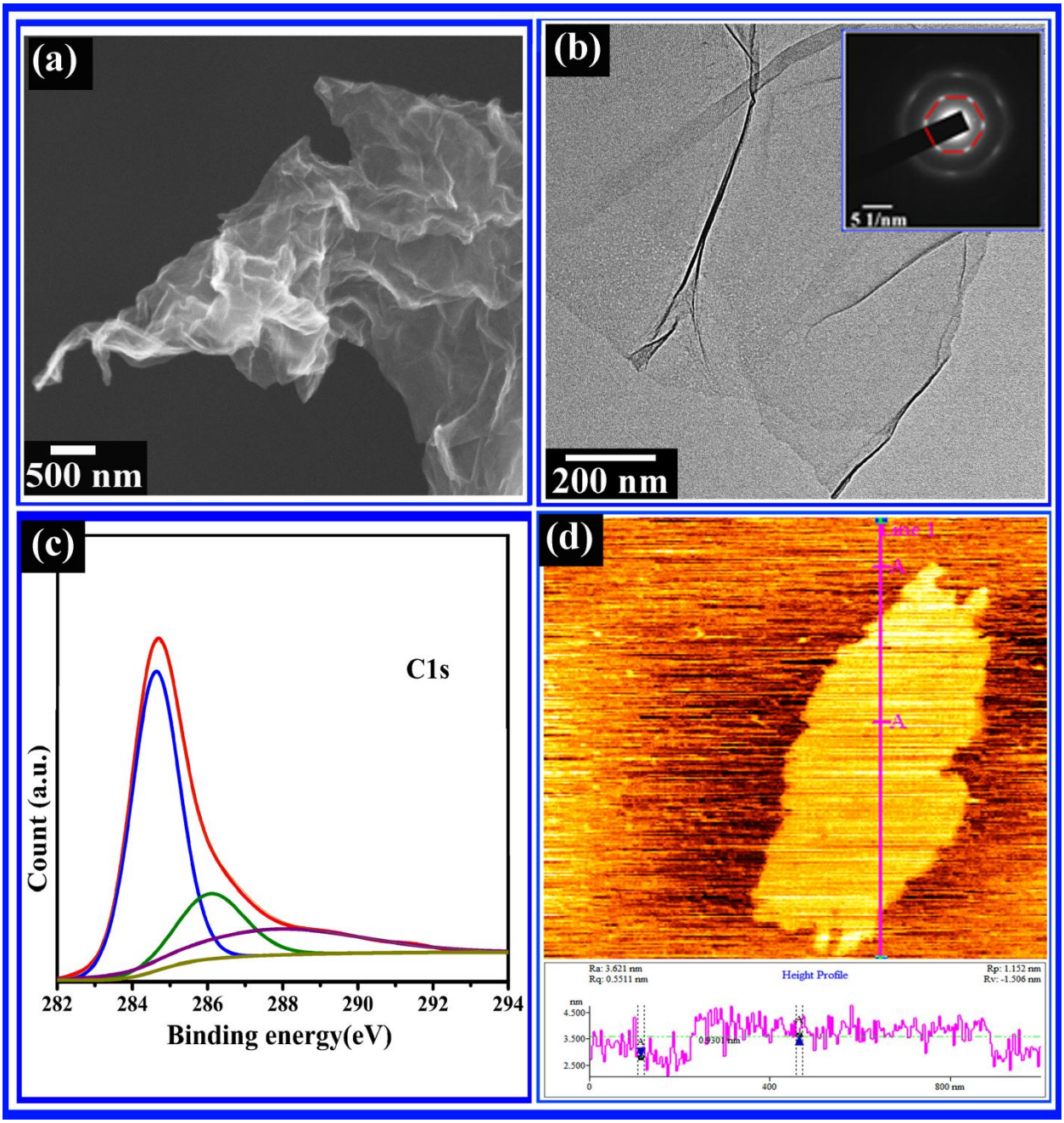
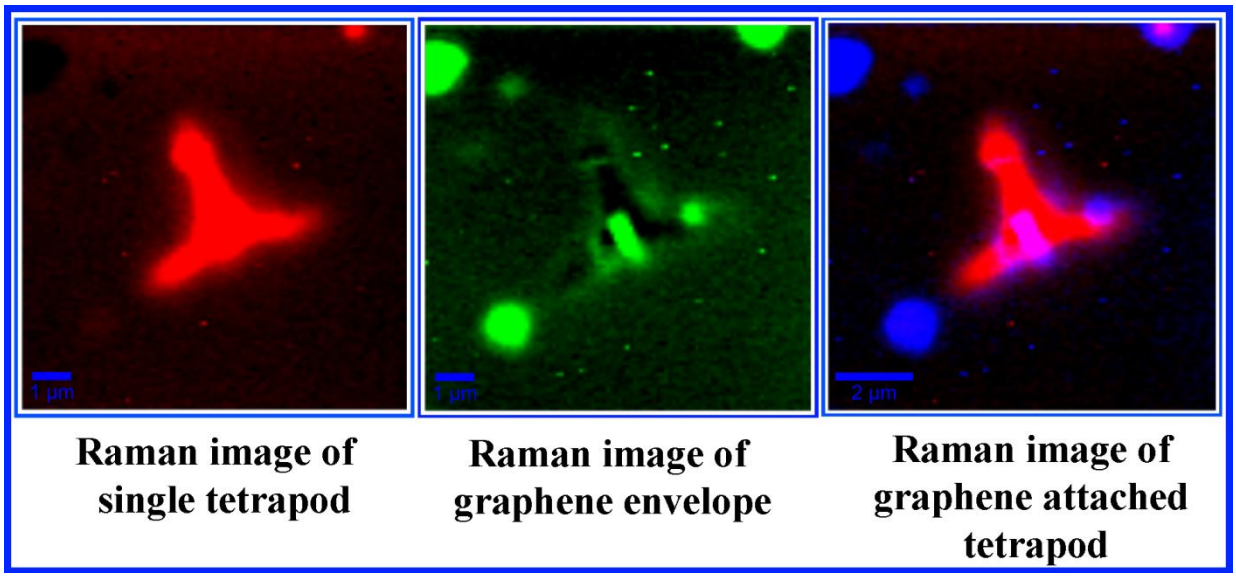


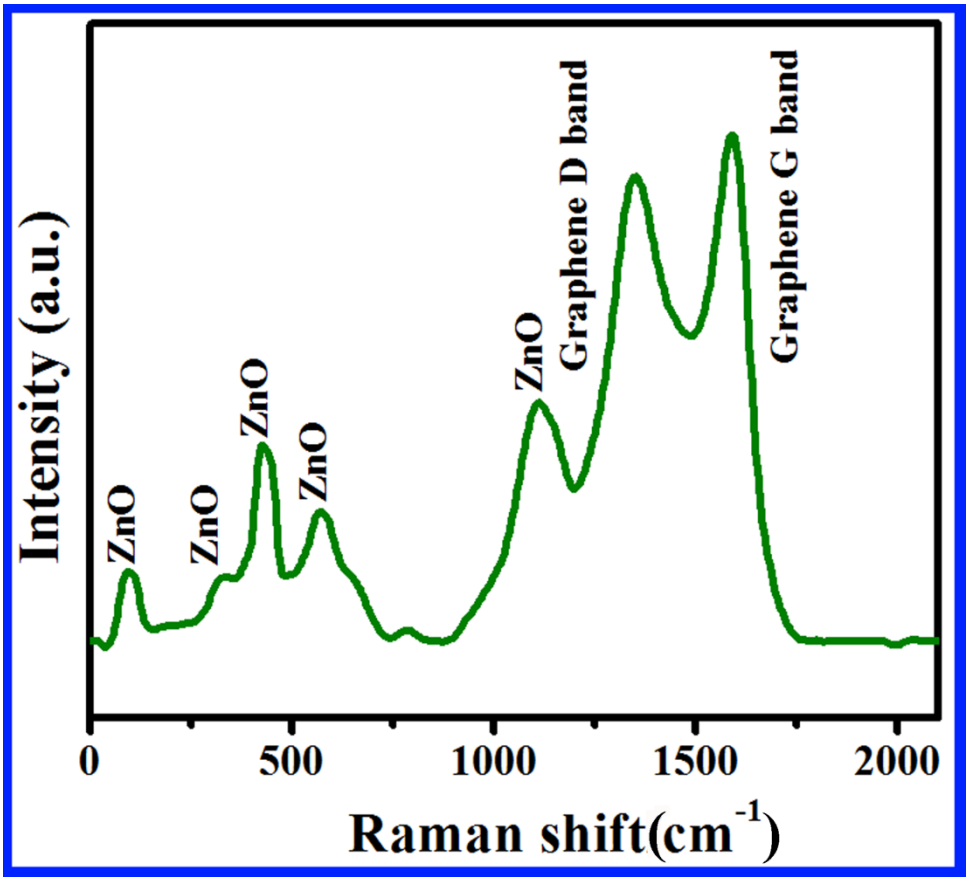
Fig.S3: (a) FESEM image of graphene sheet (b) TEM image showing single layer, inset showing SAED pattern (c) carbon C1S spectra for thermally reduced graphene oxide (d) AFM images showing single layer.

Raman analysis:

Raman image:



Raman spectra:



Details of the Raman peaks:

Peak Centre	Vibrational mode	References
98 cm^{-1}	E_2 Low	Science of Advanced Materials, 2, 572, 2010
331 cm^{-1}	E_{2H}–E_{2L} (multi-phonon)	Journal of Alloys and Compounds, 477, 2009, 635
437 cm^{-1}	E_2	Science of Advanced Materials, 2, 572, 2010
580 cm^{-1}	Superimposition of A_1 (LO) and E_1 (LO)	Journal of Alloys and Compounds, 477, 2009, 635
1105 cm^{-1}	Multiple phonon scattering process	Applied Surface Science, 256, 2010, 6814.
1350 cm^{-1}	D band	Nano Lett., 9, 2009
1582 cm^{-1}	G band	Nanotechnology 22,2011, 505703