Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2014

Application of graphene oxide as a hydrothermal catalyst support for synthesis of TiO_2 whiskers

Electronic Supplementary Information (ESI)

METHODS

Materials. Natural flake graphite (99.95%, 200 mesh) was purchased from Qualikems, India and used as received without further purification. Analytical grade reagents, H_2SO_4 (98%), H_2O_2 (30%), $KMnO_4$, $NaNO_3$, NaOH and TiO_2 were obtained from Merck, India. Ultrapure Milli-Q water (resistivity of 18.5MΩ/cm) was used throughout all the experiments.

Synthesis of graphene oxide. GO was synthesized from natural flake graphite-using a modified Hummers' method and the process was described elsewhere. [1]

Synthesis of GO-TiO_2 composite, GO-sodium titanate whiskers and sodium titanate nanograss. GO-TiO_2 composite was synthesized by using simple sonication technique. 10% (w/w) ratio of GO (1 g/L) was first diluted in acetone and ultra sonicated for 1 h for complete exfoliation. TiO_2 was added and sonicated for another 30 min to achieve uniform distribution. Solution was then dried at 70 ^{0}C in air to obtain GO-TiO_2 composite. GO-Sodium titanate whiskers composite was prepared through an alkaline hydrothermal treatment. Initially, 10% (w/w) ratio of GO (1g/L) was sonicated for 1 h in deionized water to achieve complete exfoliation and uniform dispersion. Then, TiO_2 nanoparticles were added as per weight ratio and aged with vigorous stirring for 1 h to obtain homogeneous suspension at room temperature. NaOH was added to make the resulting suspension 7M concentration. This suspension was transferred to 30 ml poly tetra fluoroethylene lined stainless steel autoclave maintained at 180 ^{0}C under static condition for 48 h and 72 h and then cooled to room temperature naturally. The resulting grey slurry was then washed several times with water to neutralize and fully dried at 80 ^{0}C in oven to get GO-sodium titanate whiskers. Same procedure was repeated without adding GO to get sodium titanate nanograss. Here, it should be noted that parameters like temperature, heating time, % filling of autoclave, amount of TiO_2 taken in autoclave, molarity of NaOH solution, heating and cooling conditions, autoclave, and even oven in which autoclave was kept were same. The synthesis conditions, size distribution and phase composition of the derived compound/composites are summarized in Table 1.

Conversion of synthesized materials in to photoactive TiO_2 (anatase) and TiO_2 (B) form. As synthesized GO-sodium titanate whiskers and sodium titanate nanograss were separately added in autoclave with 1 M HCl solution at 180 ^{0}C for 24 h to convert in to photoactive form. This treatment promotes ion exchange i.e. sodium ion was replaced with hydrogen. Finally, annealing process at 450 ^{0}C for 30 min results in to GO-TiO_2 (B) whiskers and anatase TiO_2 nanograss.

Characterization. The morphologies of synthesized GO, GO-TiO_2 composite, GO-sodium titanate whiskers, sodium titanate nanograss, GO-TiO_2 whiskers and TiO_2 nanograss were characterized by scanning electron microscopy (SEM) images (LEO series VP1430) equipped with energy dispersive X-ray (EDX) facility (Oxford Instruments) and transmission electron microscopy (TEM) images (JEOL JEM-2100) with acceleration voltage of 200 keV. Powered X-ray diffraction (XRD) patterns were obtained on a Philips X'Pert MPD system using Cu-Kα radiation (λ= 1.5406 Å). Fourier transform-infrared (FT-IR) absorption spectra were recorded using a Perkin-Elmer FT-IR spectrometer (Model-FT-1730) equipped with a KBr beam splitter (KBr, FTIR grade) at room temperature.

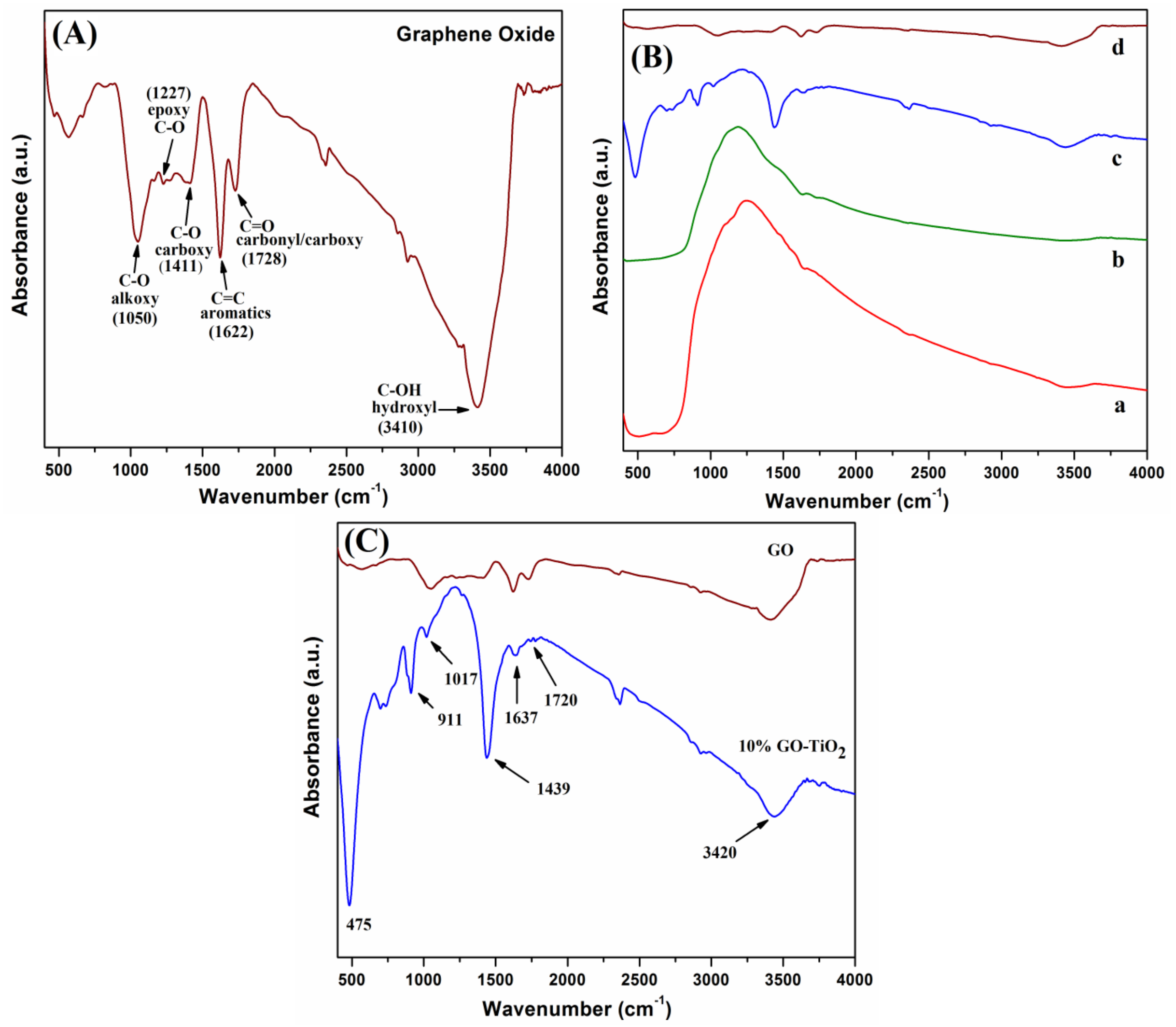


Fig. S1 FTIR patterns: (A) GO, (B) (a) pure TiO$_2$ (b) 10% GO –TiO2 composite (c) 10% GO -sodium titanate whiskers and (d) GO and (C) GO and 10% GO-sodium titanate whiskers

In fig. S1C band at 3420 cm^{-1} relates to C-OH group due to the removal of water, 1720 cm^{-1} corresponds to carboxyl group which is significantly reduced and peak at 1637 cm^{-1} is the signature peak of graphene (C=C aromatic vibrations). Bands at 1439 and 1017 cm^{-1} correspond to C-O-H bending vibrations and C-O starching vibrations. New band at 911 cm^{-1} corresponds to non-bridging Ti-O and presence of Ti-O-Na bond due to the formation of one dimensional structure. This peak was not present in pure TiO$_2$ or GO. Intense peaks at 475-700 cm^{-1} correspond to different types of Ti-O-Ti and Ti-O-C vibrations. These new peaks are due to breaking of Ti-O bonds and formation of titanate layers which contain Na+ and OH- ions.[3]

.

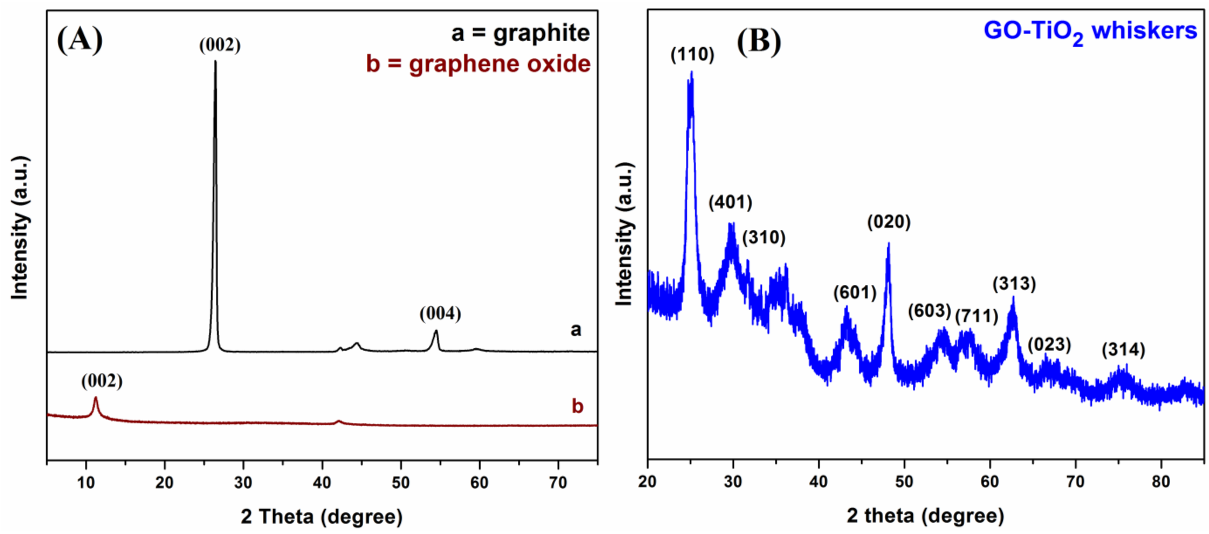
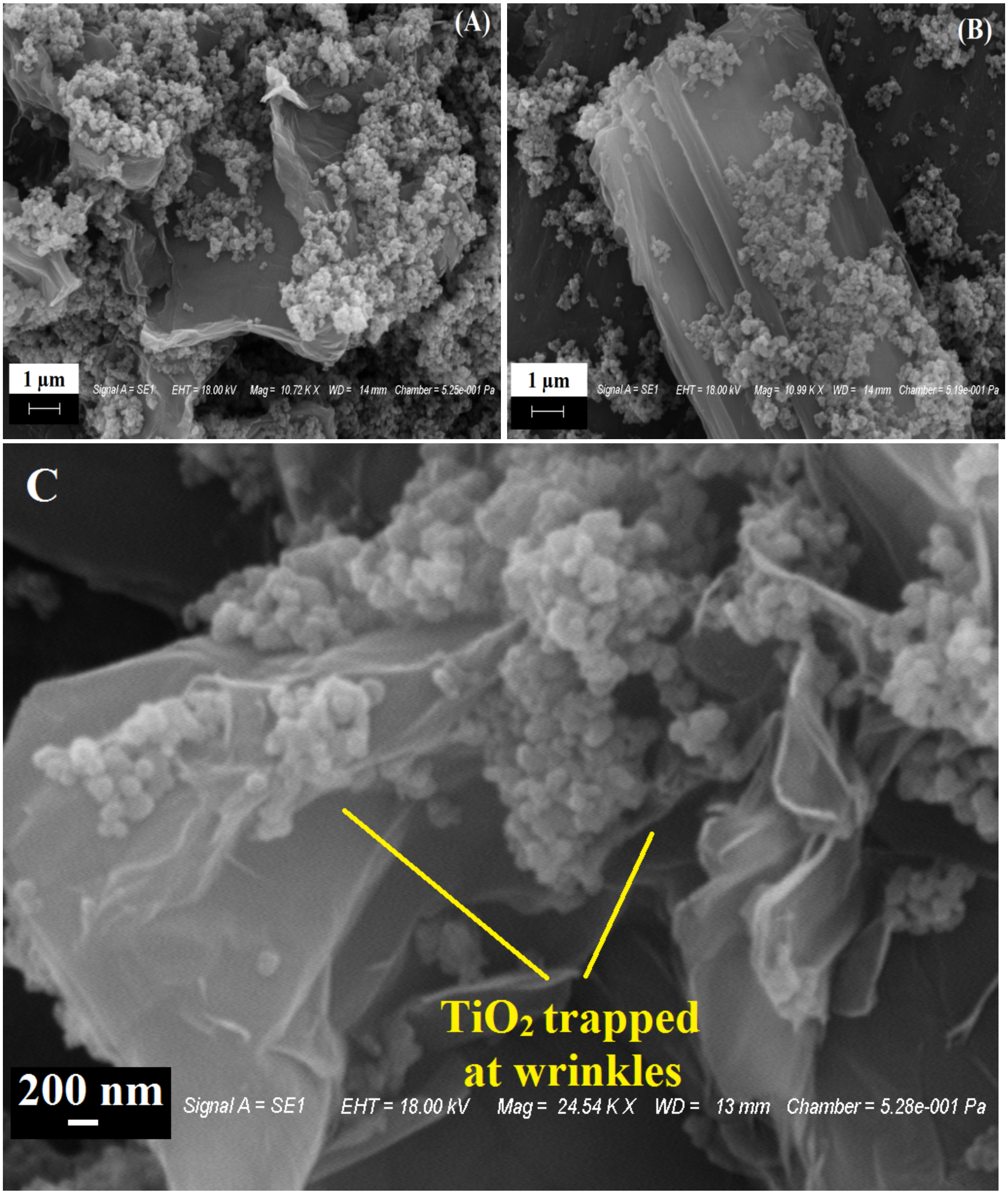


Fig. S2 XRD patterns: (A) graphite (a) and GO (b) (B) GO-TiO_2 whiskers after ion exchange by HCl


(A)
1 µm
Signal A = SE1
EHT = 18.00 kV
Mag = 10.72 K X
WD = 14 mm
Chamber = 5.25e-001 Pa
(B)
1 µm
Signal A = SE1
EHT = 18.00 kV
Mag = 10.99 K X
WD = 14 mm
Chamber = 5.19e-001 Pa
C
TiO₂ trapped at wrinkles
200 nm
Signal A = SE1
EHT = 18.00 kV
Mag = 24.54 K X
WD = 13 mm
Chamber = 5.28e-001 Pa

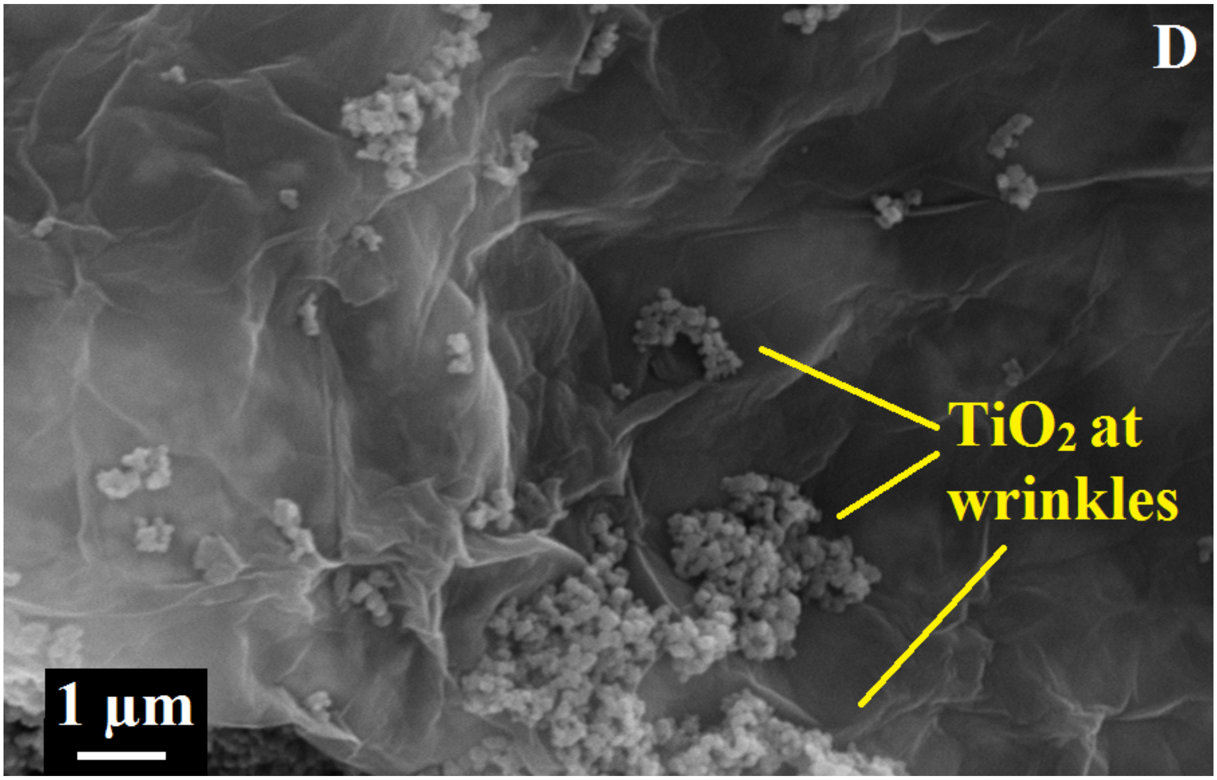


Fig. S3 SEM images of GO-TiO_2 composite with wrinkled morphology and step edges. (A-D)

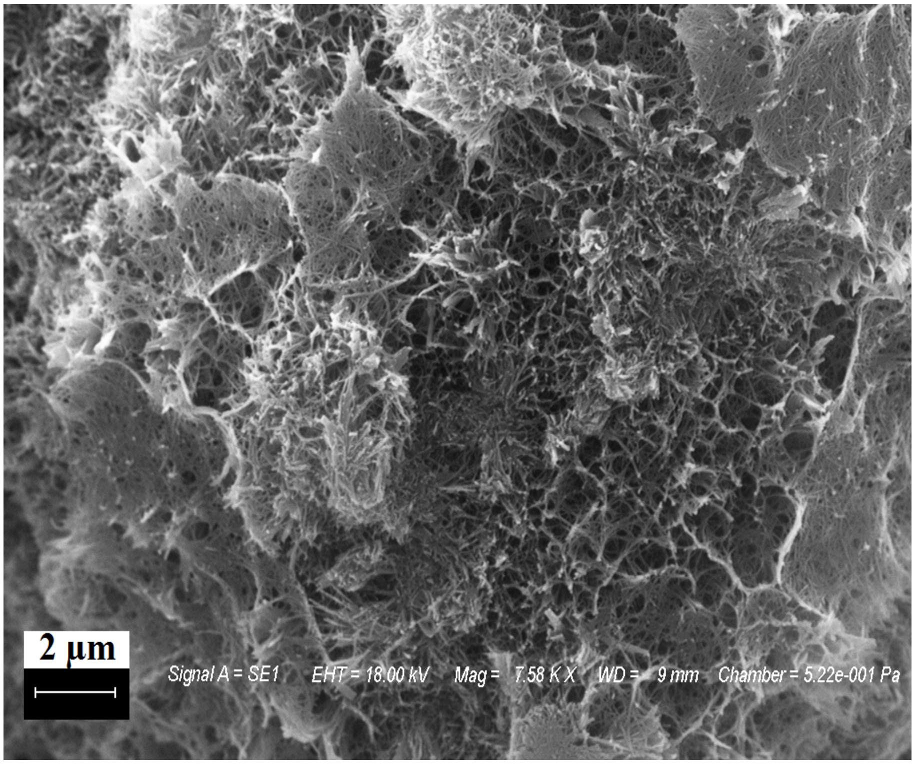


Fig. S4 SEM image of TiO_2 nanograss

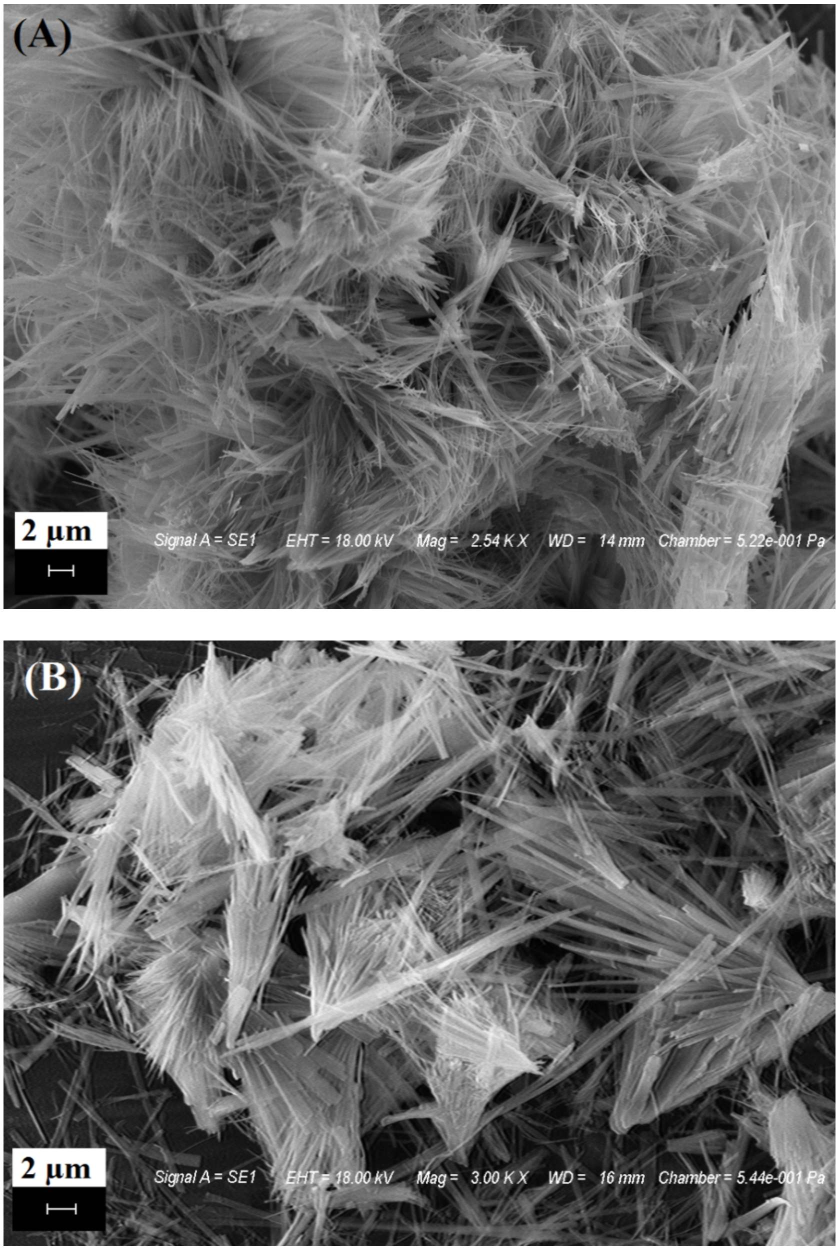


Fig. S5 Comparison of GO-sodium titanate whiskers prepared by varying hydrothermal time. 48 h (A) and 72 h (B)

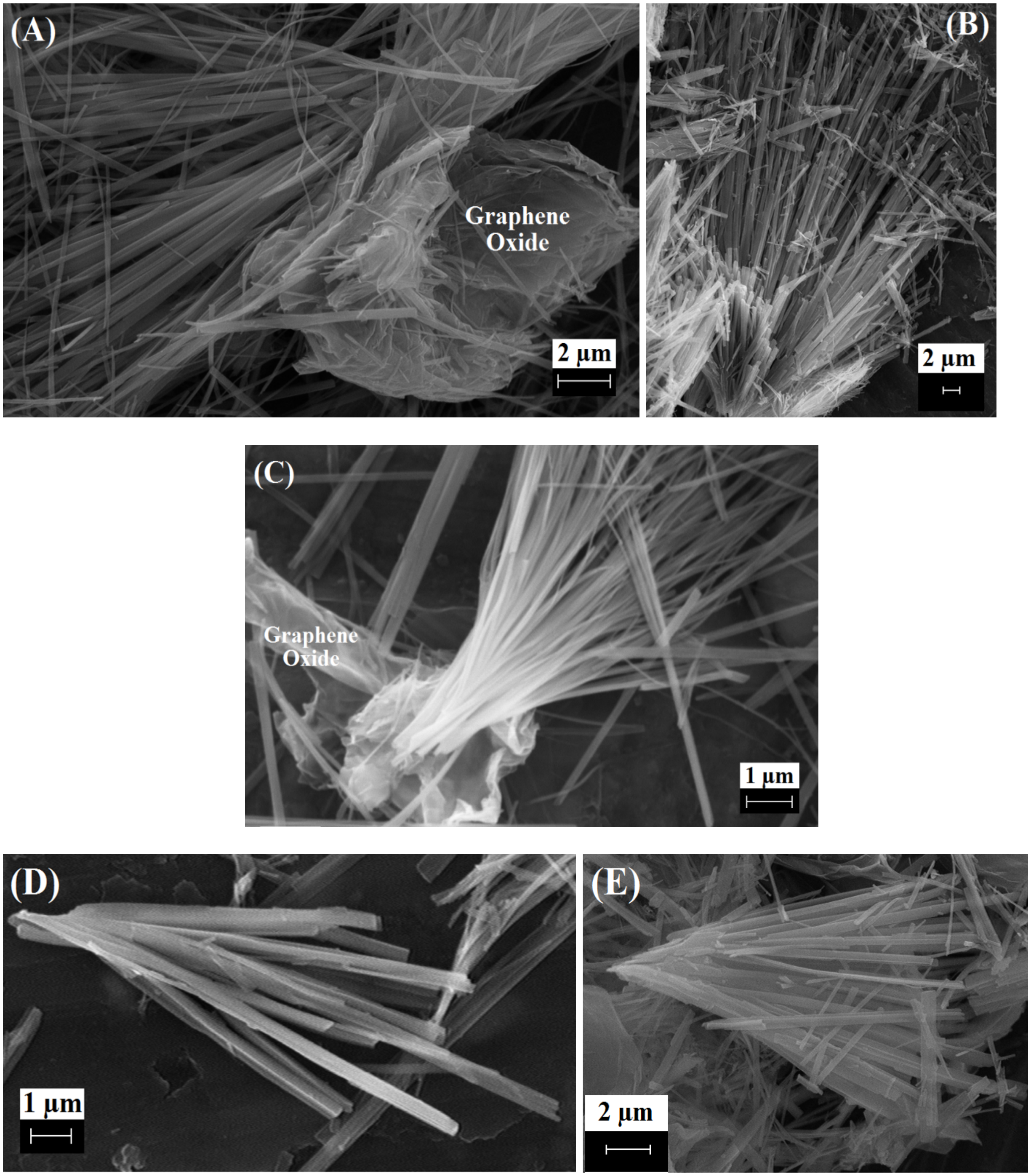


Fig. S6 SEM images of GO-sodium titanate whiskers. (72 hydrothermal time)

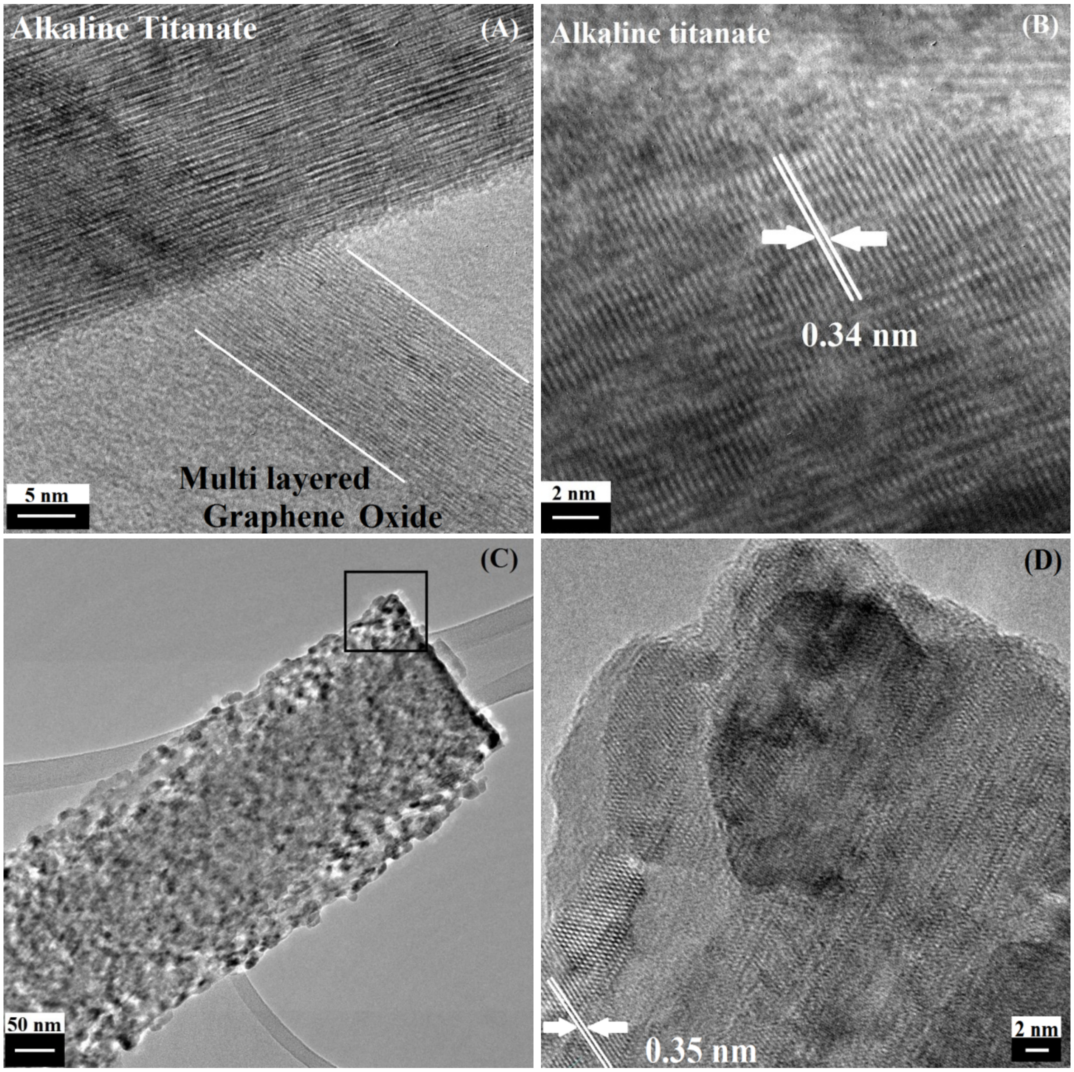


Fig. S7 TEM images: (A) GO-alkaline titanate composite. (B) High resolution image of GO-sodium titanate whisker (C) Alkaline titanate rod from GO-alkaline titanate whiskers and its high resolution image (D).

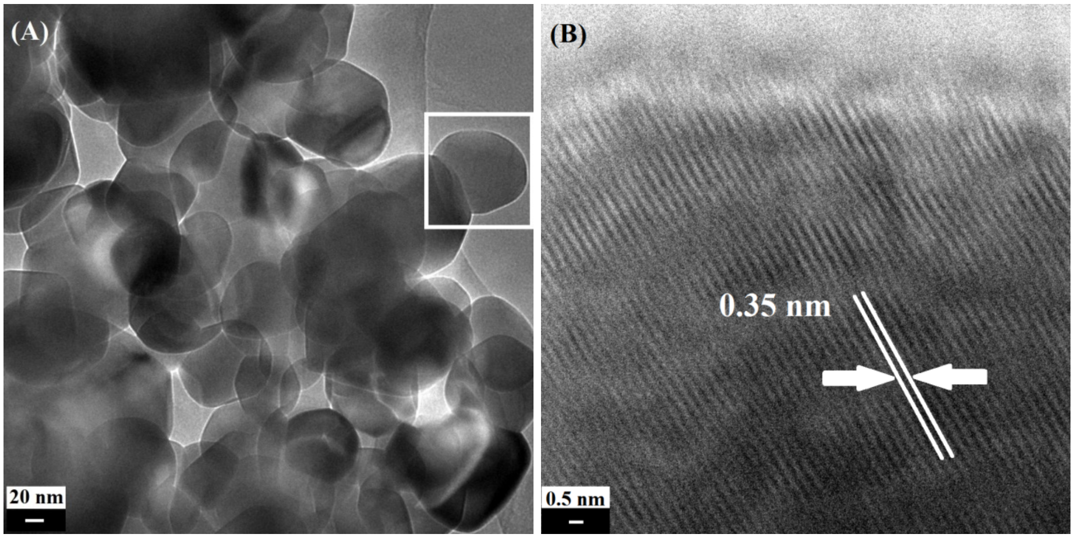


Fig. S8 TEM images: (A) GO-TiO_2 composite (B) High resolution image of a TiO_2 particle (Indicated in square box in S8A)

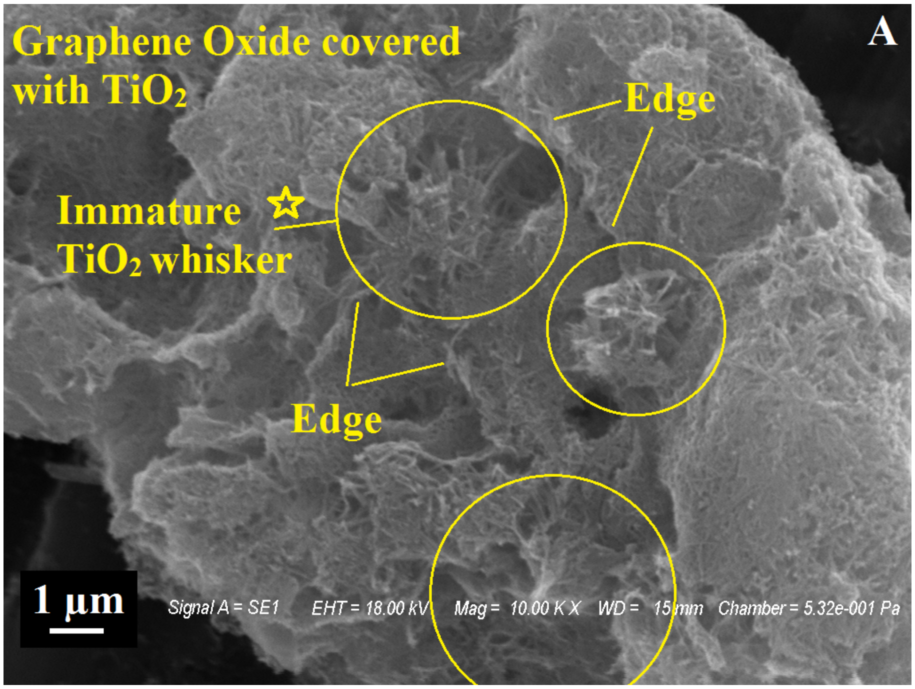
Table 1. Various conditions, size distribution and phase composition of and synthesized compound/composites

Product/ Composite	**Raw Materials**	**Conditions**	**Size of composite from SEM/TEM (approx. size)**	**Phase of TiO_2 in composite**
GO	Graphite	Modified Hummer	200 mesh <74 µm	-
GO-TiO_2 composite	GO, TiO_2 nano particles	Sonication	GO: <74 µm TiO_2 NPs: 80-100 nm	Anatase
GO-sodium titanate whiskers	GO, TiO_2 nano particles	Hydrothermal 7M NaOH 180°C, 48 h	L: 15-20 µm W: 100 nm	$Na_2Ti_nO_{2n+1}$, n=3,4,9
		Hydrothermal 7M NaOH 180 °C, 72 h	L:15-20 µm W:150-200 nm	
Sodium titanate nano grass	TiO_2 nano particles	Hydrothermal 7M NaOH 180°C, 48 h	L: 5-10 µm W: <50 nm	$Na_2Ti_nO_{2n+1}$, n=3,4,9
GO-TiO_2 (B) whiskers	GO-sodium titanate whiskers	Hydrothermal 1M HCl 180°C, 24 h	L: 15-20 µm W: 100 nm	TiO_2 (B)
TiO_2 nano grass	Sodium titanate nano grass	Hydrothermal 1M HCl 180°C, 24 h	L: 2-5 µm W: <50 nm	Anatase

L: length; W: width

TiO_2 whisker formation mechanism

A set of experiments were conducted at lower temperature to get further evidence on TiO_2 whisker formation mechanism. As hydrothermal growth is highly depended on temperature[2], by lowering the temperature, we can obtain earlier stage of nucleation and crystal growth of TiO_2 on GO. Alkaline hydrothermal reaction was carried out at 160 ºC instead of 180 ºC for 48 h and all other parameters like molarity of solution, catalyst loading, and autoclave filling were kept same. SEM characterization of the prepared catalyst shows that TiO_2 whiskers were not fully grown at that temperature. Small immature whiskers can be seen at the edges and/or wrinkles of GO. Figure S9A shows immature growth of TiO_2 whisker on GO and its magnified image (i.e. 200 nm) is shown in Figure S9B. These images demonstrate that TiO_2 whisker is growing from GO edges/wrinkles. Fully grown whiskers were obtained at higher temperature (180 ºC). Therefore, it can be concluded that TiO_2 whiskers grow from the edges and/or wrinkles of GO. Later fully grown TiO_2 whiskers may get separated from GO due to its large size.



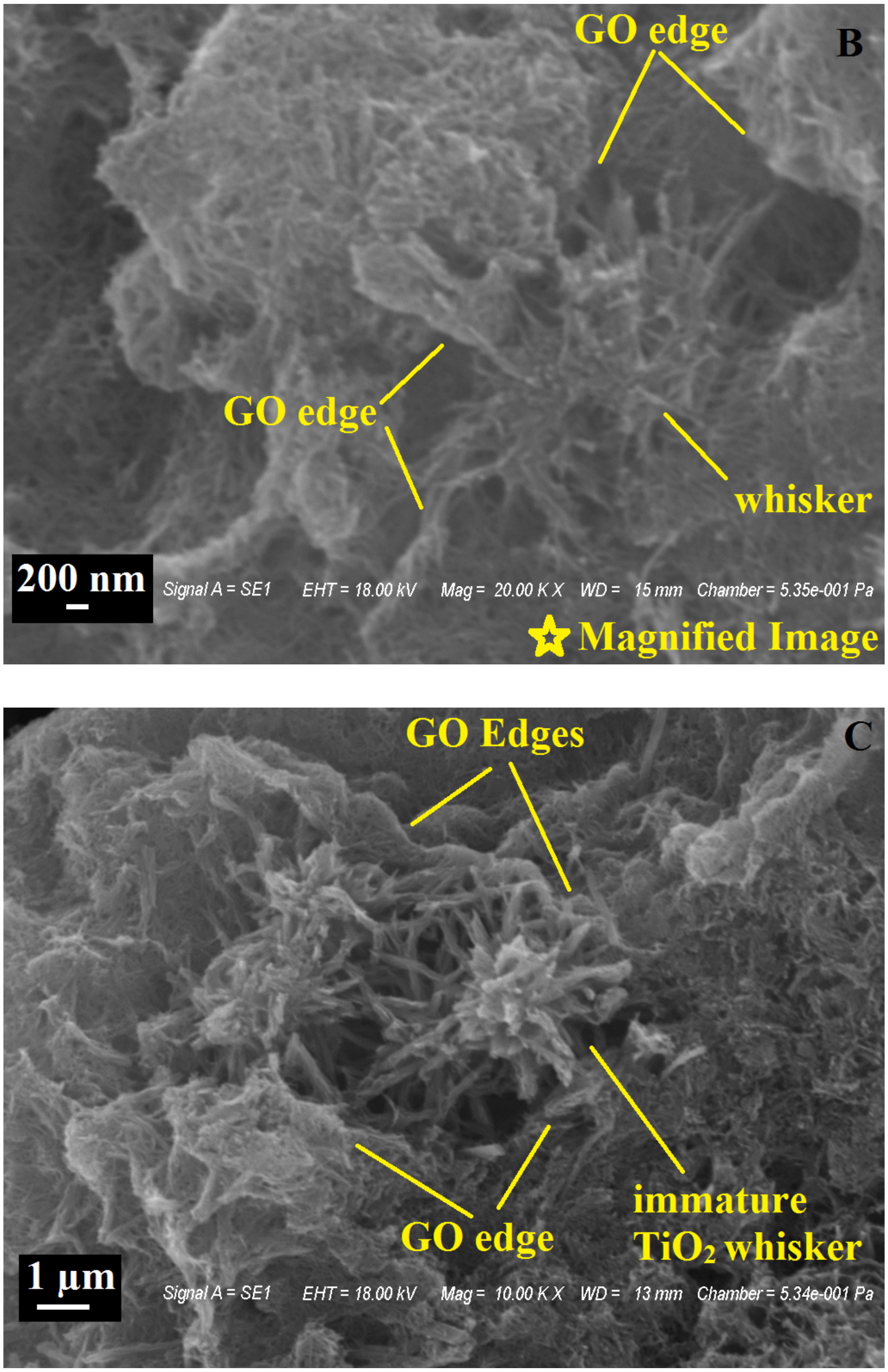


Fig. S9 SEM images of immature TiO_2 whisker from the edge/wrinkle of GO.

Reference

1. Parmar, K. R.; Patel, I.; Basha, S.; Murthy, Z. V. P. J. Mater. Sci. 2014, 49, 6772.
2. Rabenau, A. Angew. Chem. Int. Ed. Engl. 1985, 24, 1026
3. (a) Milanovic, M.; Stijepovic, I.; Nikolic, L. M. Process. Appl. Ceram. 2010, 4, 69; (b) Park, S. J.; Cho, S. M.; Kim, W. J.; Park, J.; Yoo, P. J. ACS Appl. Mater. Interfaces 2011, 3, 360