

Preparation of graphene oxide by solvent-free mechanochemical oxidation of graphite

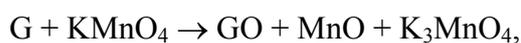
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Supporting Information

S1. Experimental details.

Synthesis of dispersions s1 and s2: Dry mixture of graphite microflakes (#043480, Alfa Aesar) and an oxidant (Ox) KMnO_4 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Aldrich), in molar ratio 1:3 or 1:2 correspondingly, was mechanochemically treated in an agate grinding bowl using planetary ball mill Pulverisette 6 (Fritsch) for 3 hour at a rotation rate of 500 rpm. The weight ratio of reactants to milling media was about 1:20. In the case of potassium permanganate, the product was thoroughly washed with water and 10% hydrochloric acid to remove the residues of the oxidant and manganese oxide formed as a result of reduction of KMnO_4 , and in the case of ammonium persulphate it was washed only with water due to the aqueous solubility of the oxidant and the products of its reduction – NH_4HSO_4 and $(\text{NH}_4)_3\text{HSO}_4\text{SO}_4$. (The presence of the stated reduction products after the end of the mechanochemical synthesis was confirmed by the data of X-ray powder diffraction shown in Fig. S1.) To prepare graphene oxide dispersions (hereinafter **s1** and **s2** for the specified oxidants), a definite amount of the synthesized graphite oxide was ultrasonically (20 W) treated in distilled water (20 mL) for 1 hour using Sonopuls HD 2070 (Bandelin). Dispersions were purified by centrifugation at 4000 rpm for 4 hours, and the upper half of their volume was selected for further studies. The absence of any inorganic substrate in the final dispersions was confirmed by XRD measurements of the films obtained from **s1** and **s2** samples (Fig. S3).

Complete redox equations which correspond to the revealed products of reduction of the used solid oxidants could be written as follows:



where G – the parent graphite, GO – the oxidized graphite.

The yield of the described process in terms of the purified graphene oxides relative to the initial quantity of graphite is about 25%. It could be increased doubled or even tripled by successive ultrasonication of the precipitate formed after the procedure.

It should be also mentioned that analogous ultrasonic disintegration of the parent graphite in water results in a dispersion that is completely unstable during centrifugation.

Characterization: Powder X-ray diffraction patterns were measured with a D8 ADVANCE (Bruker) diffractometer using filtered Cu K α radiation in the range $2\theta=1-80^\circ$ with an increment of 0.05° .

TEM images were obtained on a TEM125K (SEMI) microscope working at 100 kV. Amorphous carbon film which covered the copper grid was used as a carrier for samples. SAED (selected area electron diffraction) patterns were also measured on this facility.

FTIR spectra in KBr tablets were registered by SPECTRUM ONE (PerkinElmer) with a resolution of 2 cm^{-1} .

UV-Vis spectra were measured on double beam spectrophotometer 4802 (UNICO) with a resolution of 2 nm.

AFM micrographs were obtained using NanoScope IIIa Dimension 3000TM (Digital Instruments) in a tapping mode. The samples were prepared from diluted dispersions **s1** and **s2** deposited on freshly cleaved mica. The cross-section profiles were obtained using WSxM 4.0 Software [I. Horcas et al. Rev. Sci. Instrum. 78, 013705(2007)].

Raman spectra were obtained in reflection geometry using T-64000 (Horiba Jobin-Yvon) equipped with cooled CCD detector, using Ar-Kr ion laser (Spectra-Physics 2018 RM) excitation of 514 nm. The light was focused on a sample by Olympus MPlan N 50x/0.75 objective, the power of the incident radiation being 2 mW.

S2. XRD patterns of the parent graphite and products of the mechanochemical treatment of the graphite/oxidant mixtures.

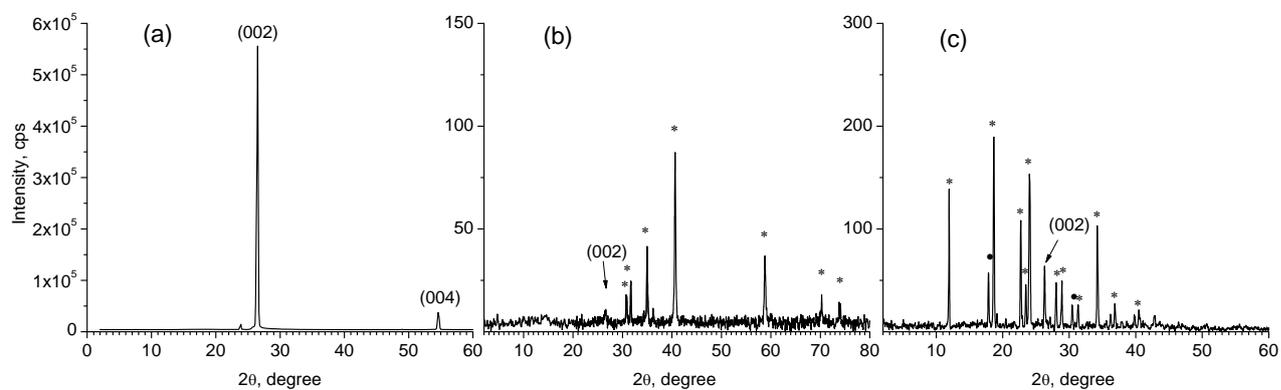


Fig. S1. XRD patterns of the parent graphite and the products of the mechanochemical treatment of the graphite with KMnO_4 (reflexes marked with asterisk correspond to crystals of MnO , #750626 from PDF-2) (b) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (reflexes marked with asterisk and dot correspond to crystals of NH_4HSO_4 и $(\text{NH}_4)_3\text{HSO}_4\text{SO}_4$, #250034 and #421426 from PDF-2) (c).

S3. TEM graphs of s1 and s2 samples.

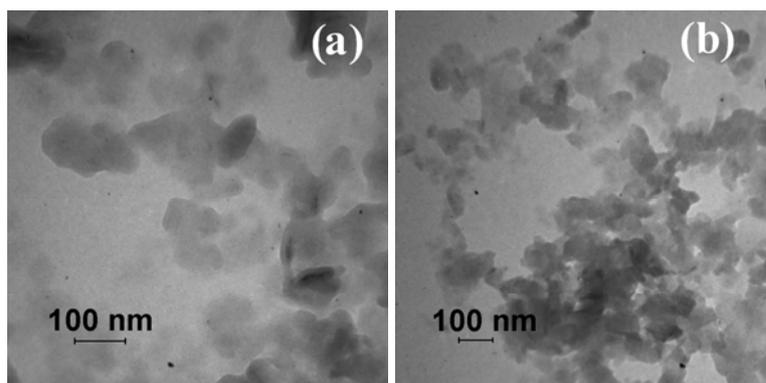


Fig. S2. TEM graphs of **s1** (a) and **s2** (b) samples.

S4. XRD patterns of the films of s1 and s2 samples.

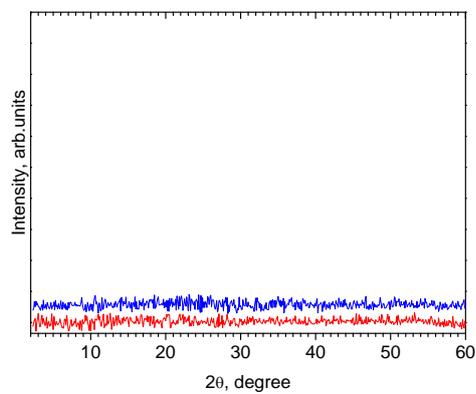


Fig. S3. XRD patterns of the solid films obtained using **s1** (red) and **s2** (blue) samples.
(The upper graph is shifted for convenience.)

S5. AFM graph of s1 sample.

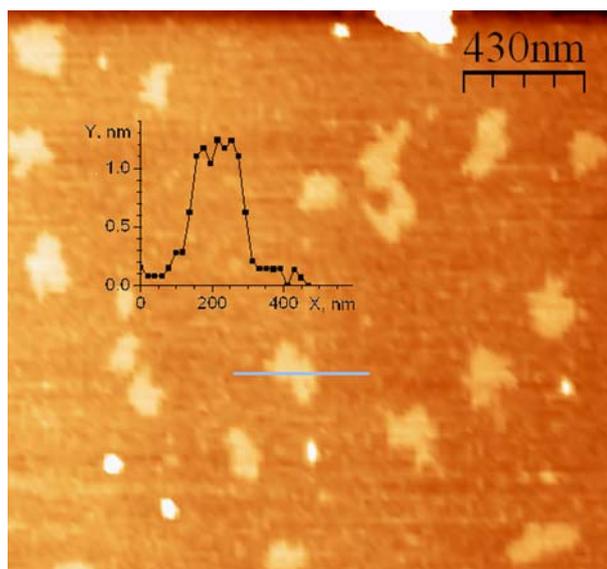


Fig. S4. AFM image of **s1** sample.

S6. Numerical modeling of Raman spectra.

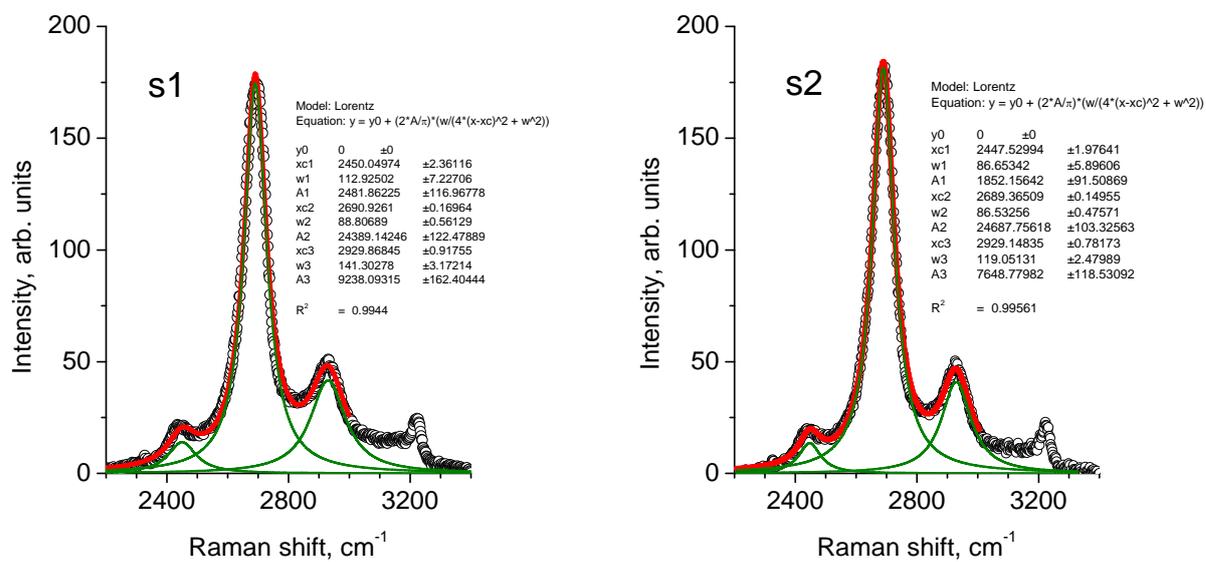


Fig. S5. Fitting of Raman spectra of s1 and s2 samples using Lorentz lines.