

## Supporting Information

### Experimental Section

*GO-HAP Composites:* GO was prepared from natural graphite by a modified Hummers and Offema method.<sup>[25]</sup> The GO-HAP composites were synthesized via a facile one-step method. 0.0370g CaCl<sub>2</sub> and 10mg GO were dispersed by 170ml ethylene glycol and 30ml water in a flask (250ml). After ultrasonic treatment (40kHz, 180W, 25°C) for 30min, 0.335ml 0.6M Na<sub>2</sub>HPO<sub>4</sub> and 0.155ml 1M NaOH were added. Then, the mixture was transfer to an oil bath (85±1°C) and reacted for 12h. The product was centrifuged at 8000rpm for 3min and washed by water and ethanol for three times.

*GO-HAP Paper:* The free-standing paper was fabricated by a vacuum filtration of the GO-HAP aqueous solution (20ml, 3mg/ml) through a cellulose acetate membrane filter (47mm in diameter, 0.8µm in pore size). The papers were air dried for 24h, and then dried at 45°C for 6h, before being peeled from the filter membrane.

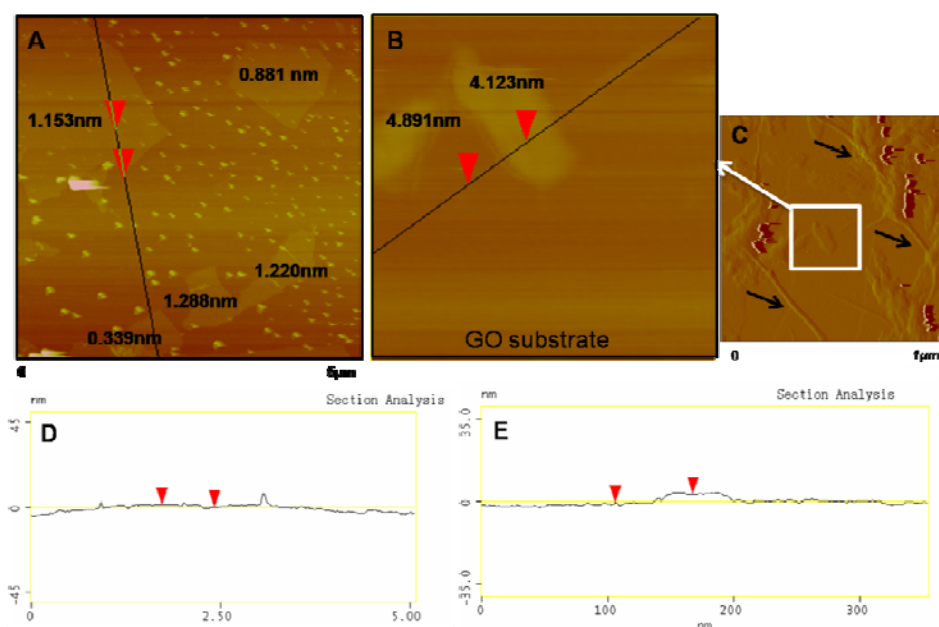
*Characterizations:* TEM observations were performed by a transmission electron microscope (Philips CM200UT, Netherlands) at an accelerating voltage of 160kV. Field-emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan) was employed to investigate the morphology of the samples at an accelerating voltage of 5kV. All samples were sputtered with gold before observation. X-ray diffraction patterns (XRD) were obtained by using an X-ray diffractometers (PANalytical X'Pert PRO, Netherlands) with Cu-Kα radiation and a scanning step of 0.02°. Thermal gravimetric analysis (TGA) was carried out by a TA Instrument SDT Q600 at a temperature range of 30-800°C with a heating rate of 10°C min<sup>-1</sup> under air atmosphere. The XPS measurements of GO and GO-HAP were performed by an X-ray photoelectron spectrometer (VG Scientific ESCALAB MKII, England), using Al-Kα

radiation as the excitation source. Raman spectroscopy measurements were taken by using a LabRamHRUV spectrometer (JOBIN-YVON, France) with excitation wavelength at 514nm. The AFM measurements were performed in tapping-mode using Veeco multimode scanning probe microscope with Nano IVa controller. The measurements were performed using an E head and a silica tip (Veeco) on a cantilever with a spring constant of  $40\text{N m}^{-1}$  in tapping mode with filters off, with a scanning rate of 1Hz. Samples for AFM characterization were prepared by spin-coating diluted dispersion ( $\sim 0.1\text{ mg/ml}$ ) on fresh mica flakes for three times (3000rpm, 40s). Static mechanical uniaxial in-plane tensile tests were carried out with a dynamic mechanical analyzer (Q800, TA Instruments, USA). The samples were mounted using film tension clamps with a clamp compliance of ca.  $0.5\mu\text{m N}^{-1}$ . The width of sample was measured using standard calipers. The thickness of sample was obtained from SEM images of the fracture surface, and the length between the clamps was measured by DMA instrument. Normal tensile tests were initially conducted for 30min at  $35^{\circ}\text{C}$  in controlled-force mode with a preload of 0.01N. After that, tensile force was loaded with a force ramp rate of  $0.05\text{N min}^{-1}$ .

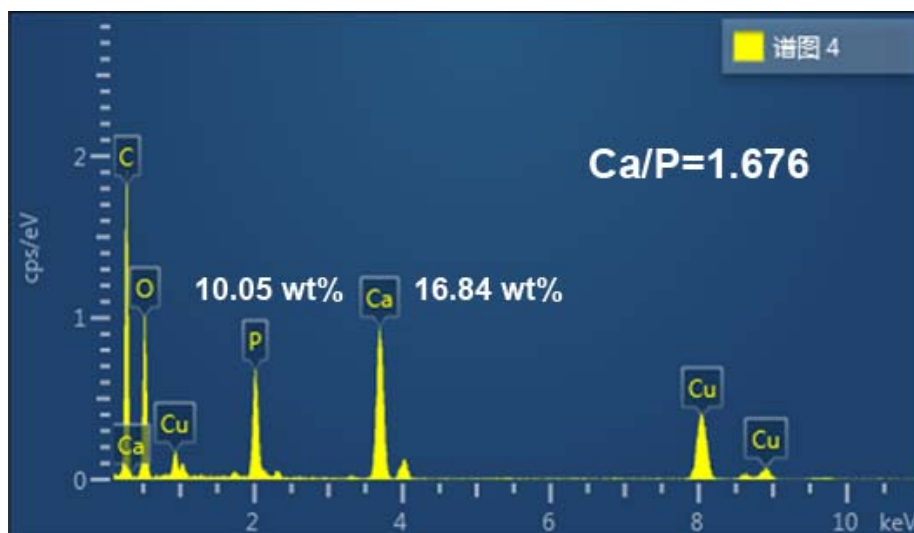
*Cell Culture and Cytotoxicity Assay:* Human osteosarcoma cells (MG-63) were cultured in a DMEM medium supplemented with 10% heat-inactivated fetal bovine serum (FBS),  $100\text{U ml}^{-1}$  penicillin and  $100\mu\text{g ml}^{-1}$  streptomycin at  $37^{\circ}\text{C}$  in a humidified incubator with  $5\%\text{CO}_2$ . The in vitro cytotoxicity was measured via an MTT assay. Typically,  $100\mu\text{l}$  of cells were seeded into a 96-well culture plate at a density of  $10^5\text{ cells ml}^{-1}$ . After incubation for 24h, the medium was replaced with  $100\mu\text{l}$  of fresh media containing free GO, GO-HAP, and HAP at different concentrations. After 24h exposure, the cells were washed with PBS for three times and incubated with  $100\mu\text{l}$  MTT ( $0.5\text{mg ml}^{-1}$  in PBS) for 4h. Finally, the MTT solution was removed and the formazan crystals produced by live cells were dissolved in DMSO ( $150\mu\text{l}$  per well). The plate was gently shaken for 5min. The absorbance was recorded by a microplate reader (Bio Tek, USA) at 570nm, with 655nm as the background absorbance. The

cell viability (%) was calculated from  $(A_{\text{test-570}} - A_{\text{test-655}}) / (A_{\text{control-570}} - A_{\text{control-655}}) \times 100\%$ , in which  $A_{\text{test-wavelength}}$  and  $A_{\text{control-wavelength}}$  were absorbance values of the wells with composites and control wells respectively. Each sample was conducted with six wells in parallel.

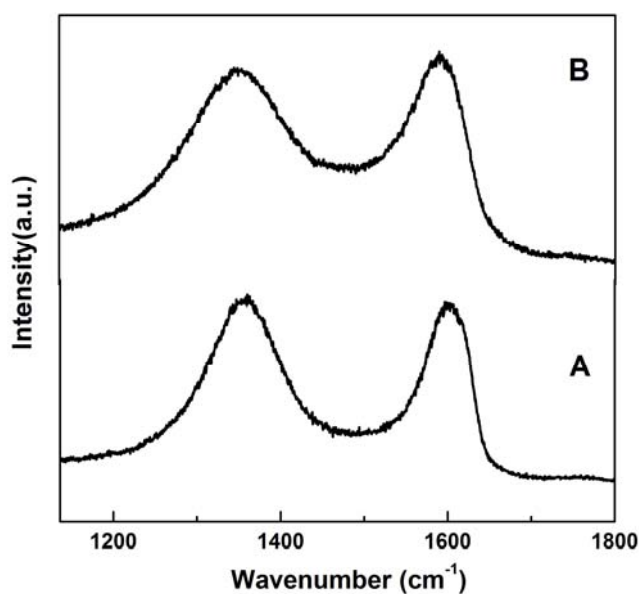
*Cell Staining and Fluorescence Investigation:* For the preparation of different substrates coated with films of GO, GO-HAP and conventional HAP (purchased from Aladdin), glass substrates (15mm in diameter) were washed by deionized water and ethanol. Films were obtained by slowly coating dried glass with 30 $\mu$ l different sample solutions (5mg/ml) for five times. Prior to the in vitro assays, all the films were sterilized overnight under ultraviolet germicidal lamps. To investigate cell morphology, 0.5ml of cells were seeded on each films in a 24-well culture plate at a density of 10<sup>4</sup> cells ml<sup>-1</sup>. After incubation for 48h, the cells were fixed with 4% paraformaldehyde at 4°C for 30min, and then stained with acridine orange at 37°C for 2h. Before fluorescent analysis (TE2000-5, Nikon), all wells were washed with PBS for three times to remove free dyes.



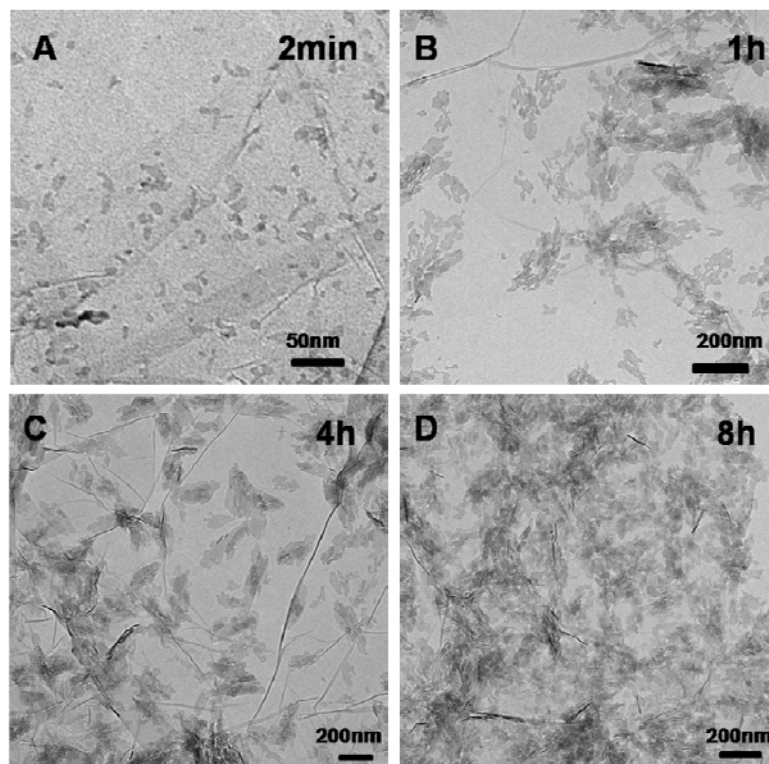
**Figure S1.** AFM height image and its section line analysis of GO(A,D) and GO-HAP(B,C,E) composites. B is the magnified image of the white rectangle in C, and the black arrows in C indicates the wrinkle of GO. To precisely measure the thickness of a single HAP nanoplate, we chose samples reacted for 1h, when the GO sheets were partly covered with HAP, eliminating the interference from adjacent plates in the measurement.



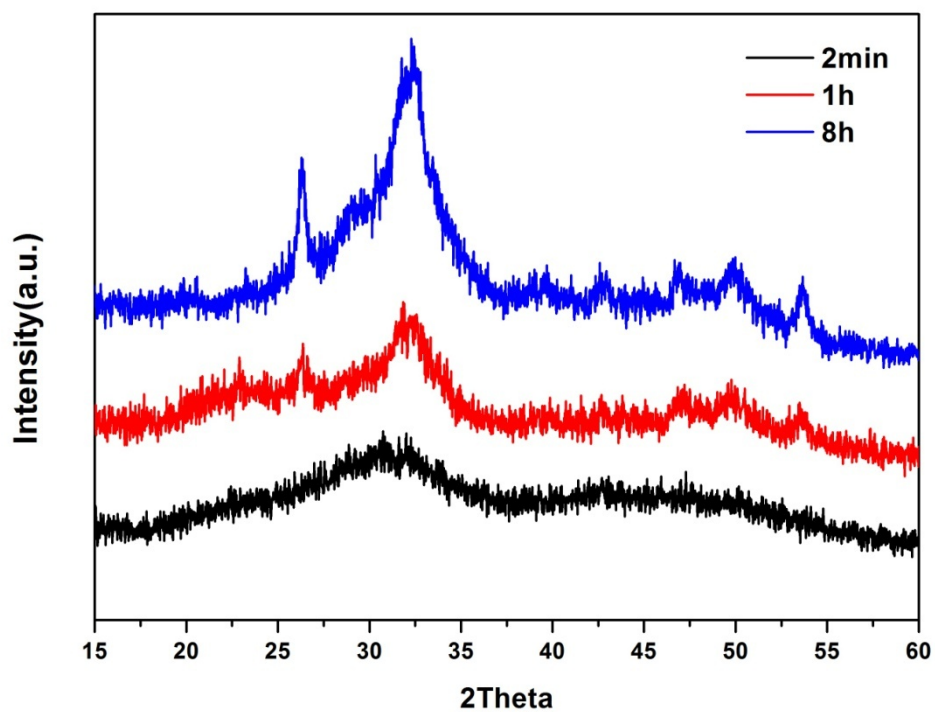
**Figure S2.** Energy dispersive spectroscopy analysis (EDS) of GO-HAP. It demonstrated that the newly formed nanoplates contained large amounts of Ca and P elements. The Ca/P ratios were calculated as 1.676, very close to the stoichiometric ratio of Ca/P in HAP.



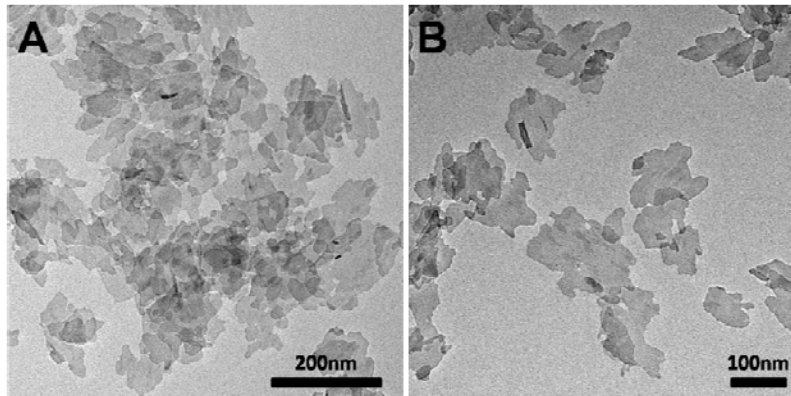
**Figure S3.** Raman spectra of GO(A) and GO-HAP(B). The D band( $1340\text{cm}^{-1}$ ) was associated with the presence of disorder in the aromatic structure or the edge effect of graphene, and the G band( $1595\text{cm}^{-1}$ ) was due to the in-plane vibration of the  $\text{sp}^2$  carbon atoms. The intensity ratio of D and G bands ( $I_D/I_G$ ) for GO(1.02) and GO-HAP(1.04) were rather close, implying the disordered structure of the GO sheets.<sup>[28]</sup>



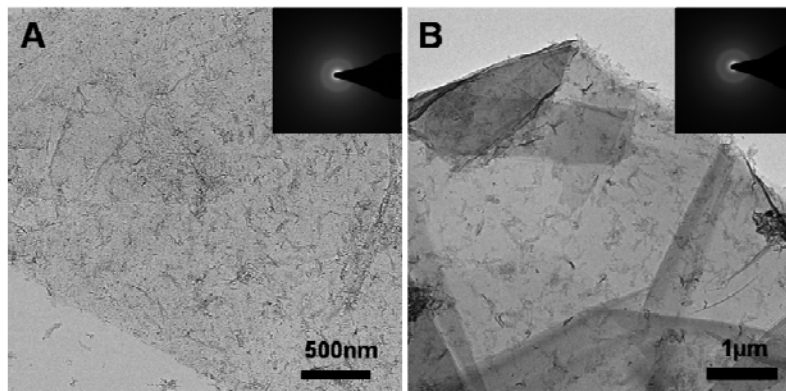
**Figure S4.** TEM images of samples with different reaction time, (A) 2min, (B) 1h, (C) 4h, (D) 8h.



**Figure S5.** XRD patterns of samples with different reaction time.

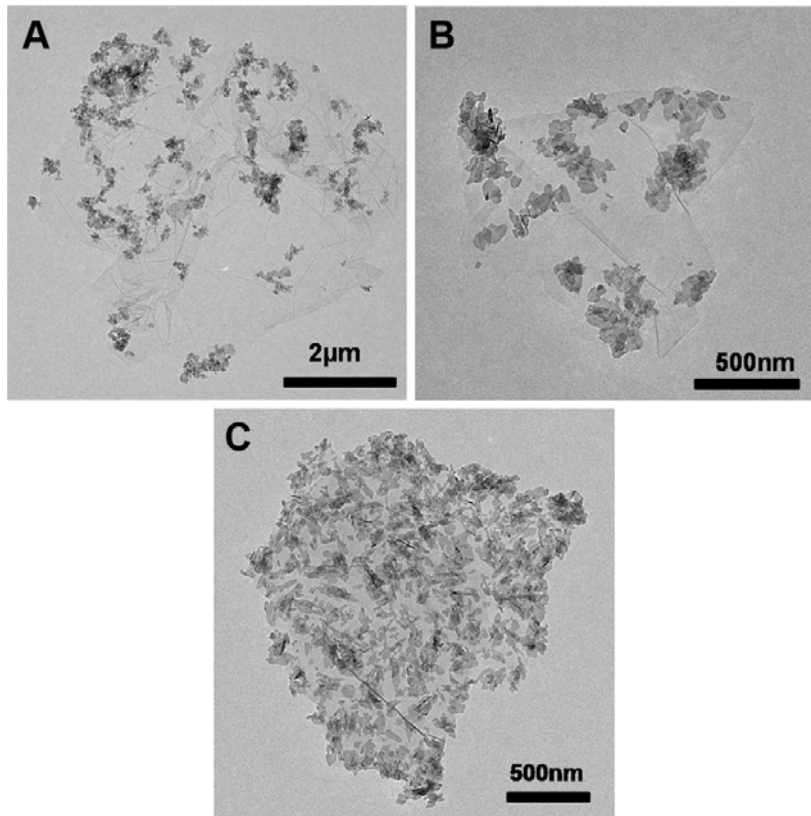


**Figure S6.** TEM images of HAP crystals (A) without GO in the same system. (B) was the magnified image. The crystal morphology was similar nanoplates as in Figure 1.

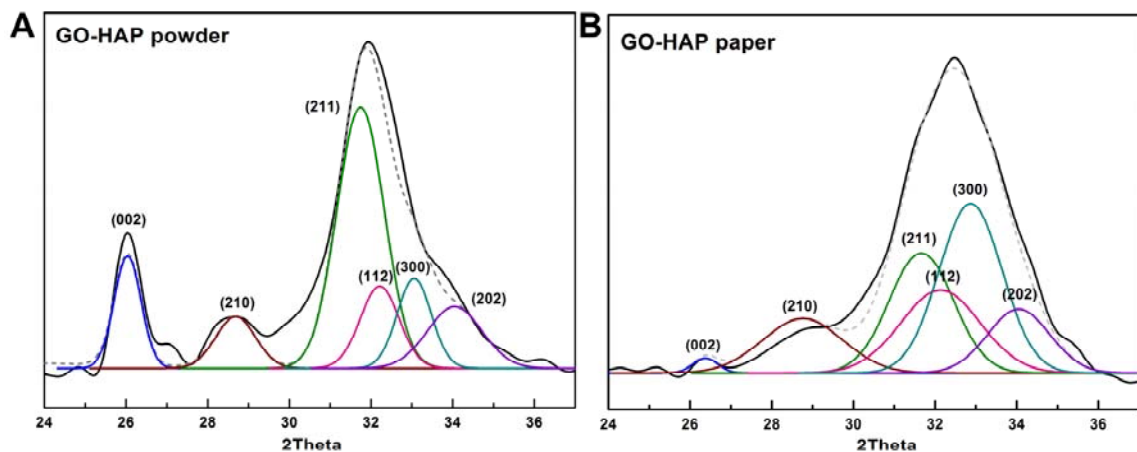


**Figure S7.** TEM images of samples in the case of less water content: (A) 0ml; (B) 3ml. Inset were SAED of the sample.





**Figure S8.** GO and HAP nanoplates (synthesized without GO) were mixed and kept at 85°C for 12h. TEM images show the as-received samples before(A) and after(B) an ultrasonication treatment (40 kHz, 180W, 25°C, 2h). (C) GO-HAP composites after the same ultrasonication treatment. The GO-HAP sheets underwent no obvious change, and no individual scattered HAP nanoplates were found.



**Figure S9.** The peak (211), (112) and (300) in XRD patterns were separated by software (PeakFit v4.12). The obvious reducing of (002) and enhancement of (300) in GO-HAP paper could be quantized by the peak area ratio of (300) to (002) planes.