Supporting information

Facile and Controllable Synthesis of Hydroxyapatite/Graphene Hybrid Materials with Enhanced Sensing Performance towards Ammonia

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Raman spectroscopy analysis

Fig. S1 shows the Raman spectra of GO, fGR, cHA/GR and bHA/GR. The D-band at ~1356cm^{-1}(D band) is an indication of the disordered aromatic structure or the edge effect of graphite oxide, and the G-band at 1594 cm^{-1} appears due to the in-plane vibration of the sp^2 carbon atoms. After the treatment with dopamine, both the D band and the G band of fGR shift to 1347cm^{-1} and 1589cm^{-1}, separately. It suggests the reduction of oxygen containing groups and the reduction of GO to fGR. After the mineralization of HA, the G bands of cHA/GR and bHA/GR are broadened, and shift to 1596cm^{-1} and 1597cm^{-1}, respectively. The spectral shifts could be ascribed to the physical or chemical interactions between GR and HA. The ratio of the intensities of the two bands (ID/IG) can be used to determine the stacking behavior of graphene. The ID/IG ratios of GO, fGR, cHA/GR and bHA/GR are 1.10, 1.13, 1.3 and 1.4, respectively, implying the presence of polydopamine and HA between the GR sheets. Typically, Raman peaks at 961 cm^{-1} is attributed to the symmetric stretching mode ν_1 (PO_4^{3-}). Both XRD patterns and Raman spectrum demonstrate that the mineral assembled on GR belongs to pure HA phase.

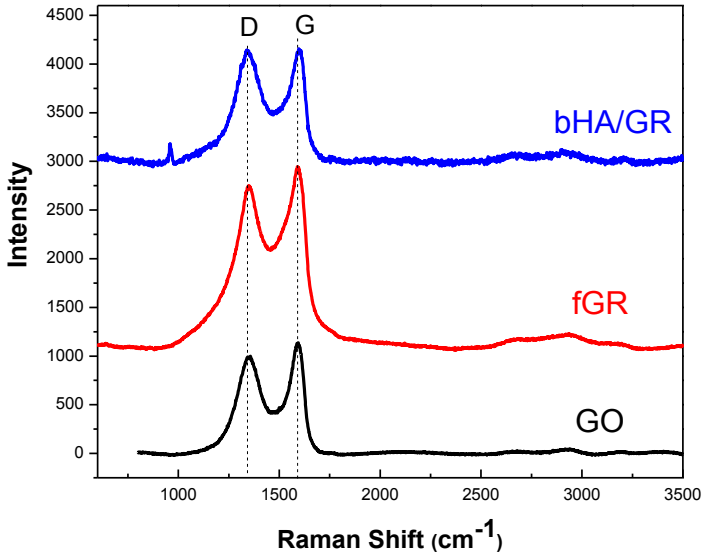

Fig. S1 Raman spectra of GO, fGR, cHA/GR and bHA/GR

Fourier transform infrared spectroscopy (FTIR) analysis

As is shown in the FTIR spectroscopy (Fig. S2), the absorbance bands at 3398, 1730, 1631, 1454 and 1051cm^{-1} are assigned to the stretching of hydroxyl group (-OH), stretching vibration of carboxyl groups (-COOH) on the edges of the basal planes or conjugated carbonyl groups (-C=O), the stretching vibration of C=C, the stretching vibration of C-OH, the stretching vibration of C-O and the characteristic adsorption peak of epoxy groups, respectively. The disappearance of the C=O peak at 1713 cm^{-1} compared to GO provides a solid indication of the reduction of GO. After

the mineralization, characteristic absorption peaks of PO_4^{3-} of HA appear in the spectra, specifically, and the band at 964 cm^{-1} corresponds to the symmetric stretching mode v_1 (PO_4^{3-}), 1038 cm^{-1} to the vibration mode v_3 (PO_4^{3-}), 603 and 567 cm^{-1} to the bending modes of v_4 (PO_4^{3-}).

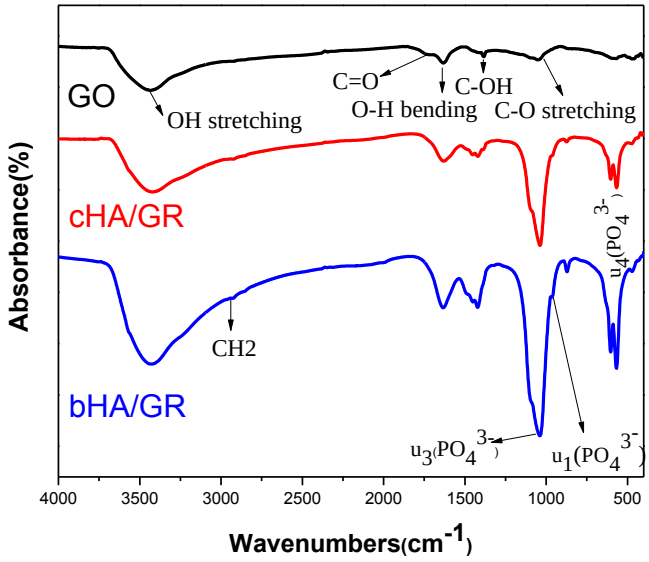

Fig. S2 FTIR spectra of GO, fGR, cHA/GR and bHA/GR

X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis is also employed to calculate the composition quantitatively. After the mineralization by two methods, Ca (2p) peaks and P (2p) peaks corresponding to Ca^{2+} and PO_4^{3-} in HA appear. Interestingly, the Ca/P ratios of HA formed in the composites of cHA/GR and bHA/GR are about 1.46 and 1.59, respectively, slightly lower than the stoichiometric ratio of Ca/P in HA ($\approx$1.67)，but are much closer to that of biological apatite found in humans(Fig. S3a, b). In this regard, the HA deposited on the fGR are calcium-deficient, and the dopamine-assisted mineralization process may have some similarities to the bioinspired mineralization in vivo. Meanwhile, the reduction of graphene oxide is also demonstrated by XPS. The XPS quantitative analysis of fGR indicate C (1s), N (1s), and O (1s) peaks, and the relative content of oxygen atom declines obviously compared with that of GO (Fig. S3c, d), which indicates the simultaneous surface functionalization by dopamine and the reduction of GO to fGR. Moreover, the C1s band obtained from GO can be fitted into four components. The main peak at 284.7 eV is due to graphitic sp^2 carbon atoms, and peaks at 286.8, 287.2 and 288.6 eV can be ascribed to the C-O, C=O and O-C=O, respectively. Compared to GO (Fig. S3e), the oxygenate species are substantially removed, and a peak at 285.1 eV corresponding to C-N group appears (Fig 3f). It suggests both the functionalization and the reduction of GO by dopamine.

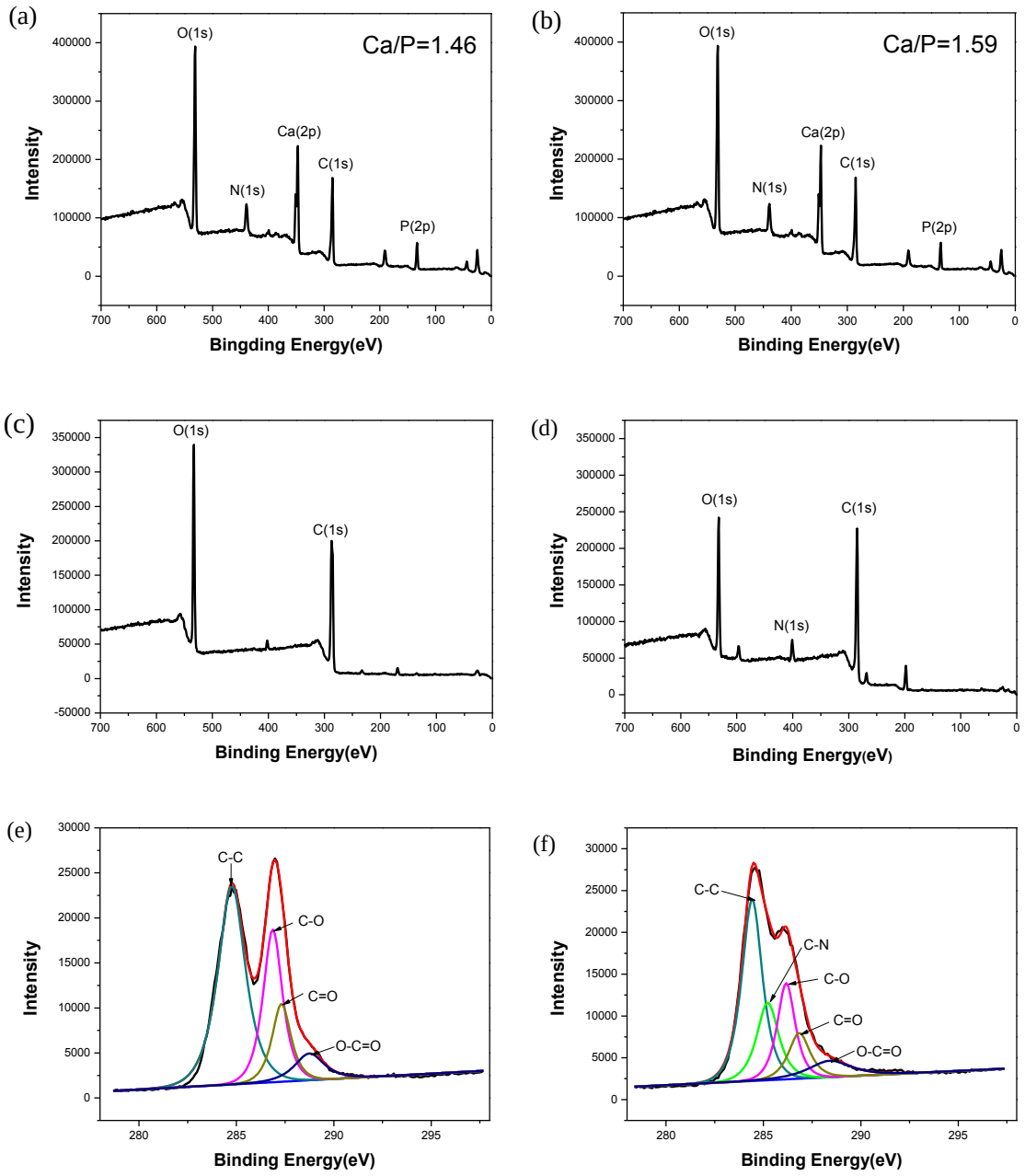

Fig. S3 The survey XPS of the cHA/GR (a), bHA/GR (b), GO (c) and fGR (d); High resolution XPS analyses of C1s of GO (e) and dopamine-functionalized fGR (f),