Analysis of poly(ADP-ribose) polymerase by enzyme-initiated auto-PARylation controlled aggregation of hemin-graphene nanocomposites

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Preparation of H-GNs

Graphene oxide (GO) was synthesized from natural graphite by Hummers' method with minormodification.²³H-GNs then were prepared by using hydrazine as a reductant. In a typical process, hemin (20 mL, 0.5 mg/mL) was first dissolved in 0.1M NaOH solution, followed by addition of 20 mL as-prepared graphene oxide dispersion. After vigorously shaking for several minutes, 200 μ L ammonia solution and 30 μ Lhydrazine in sequence were added to the solution. The mixture was stirred for 1 h and then was heated to 60°C for 24 h. Then, the dispersion rinsed with ultrapure water was centrifuged at 13000 rpm for 30 mins for several times to obtain H-GNs. The resulting H-GNs could be easily redispersed in water by ultrasonication.

Characterization of H-GNs

To confirm successful composition of hemin on the graphene sheets, hemingraphene nanosheets were characterized by UV-vis spectra (Figure S1A).GO exhibited amaximum absorption peak at 230 nm due to the π - π *transition of aromatic C=C bonds and a shoulder peak at 290-300 nm attributing to the n- π *transition of the C=O bond.²⁴ The absorption spectrum of free hemin showed a strong peak at 385 nm due to the Soret band, and a group of weak peaks between 500 nm and 700 nm attributed to the Q-bands.²⁵After reaction between graphene with hemin, the maximum absorption at 230 nm was shifted to 265 nm in H-GNs, indicating the formation of rGO and the restroration of sp²structure in rGO. For the H-GNs, an absorption characteristic located at about at 418 nm was observed, which should be the Soret band of hemin with a large bathochromic shift. This result revealed the existence of the π - π interactions between rGO and hemin and confirmed that hemin molecules are attached to graphene.



Fig. S1 UV-vis spectra of GO suspension (red), hemin (blue), and H-GNs suspension (black).