Electronic supplementary information

Fabrication of graphene/C_{60} nanohybrid via γ-cyclodextrin host-guest chemistry for photodynamic and photothermal therapy

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1. Experimental section

1.1. The synthesis of amino γ-CD derivative

The γ-CD (13.0 g, 10 mmol) was dispersed into 300 mL of deionized water under stirring, and then p-toluenesulfonyl chloride (TsCl, 2.85 g, 15 mmol) was added in the system slowly. After vigorous agitation overnight at ambient temperature, 50 mL of 4.5 g NaOH solution was added dropwise slowly. The resultant solution was filtered to remove unreacted TsCl. NH_4Cl (13.5 g) was then added to the above filtrate solution. After the reaction was completed, the solution was acidized to pH≈8 to terminate the reaction. The obtained solution was kept in a refrigerator overnight to make the product precipitate. The precipitation was collected by suction filtration. Finally, to remove unreacted γ-CD, the white precipitate (Ts-γ-CD) was further purified by recrystallization from deionized water at least three times (yield: 29.7%).

The Ts-γ-CD was dissolved in a substantial excess of ammonia at 75 °C. The reaction was reacted for 4 h, and then cooled to room temperature. Added appropriate amount of acetone into the solution, a mass of white precipitate separated out immediately. After recovered by suction filtration, the white precipitate was dissolved in mixed solution of H_2O/CH_3OH (v/v=3:1) and precipitated by acetone. This operation was repeated for 5 times to remove the unreacted

Ts-γ-CD and ammonia. The white precipitate was recovered by suction filtration and dried in vacuum at 50 °C for 24 h (yield: 56.8%).

2. The characterization of Py-γ-CD

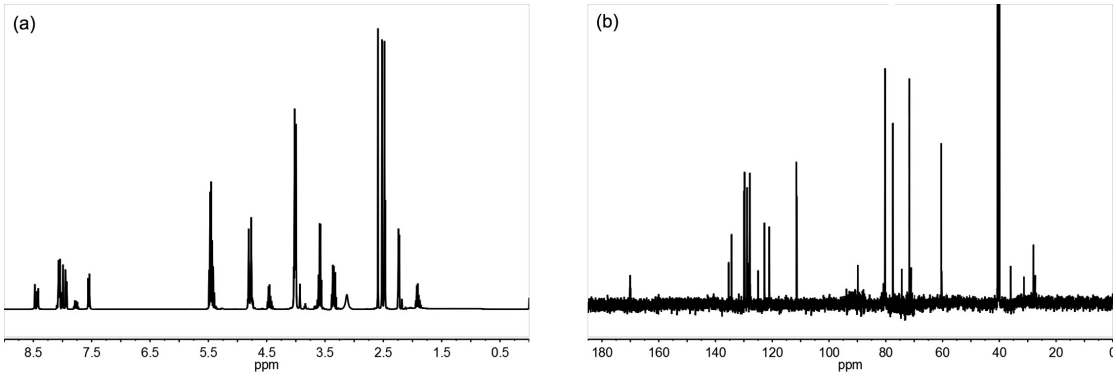

Fig. S1 The (a) ^{1}H NMR and (b) ^{13}C NMR spectra of Py-γ-CD

3. The solubility and dispersibility of GO-FA/Py-γ-CD/C_{60}

Fig. S2 Photograph of aqueous dispersions GO-FA, GO-FA/Py-γ-CD, and GO-FA/Py-γ-CD/C_{60} (from left to right, 30 μg/mL)

4. The cytotoxicity of GO-FA/Py-γ-CD/C_{60} in dark

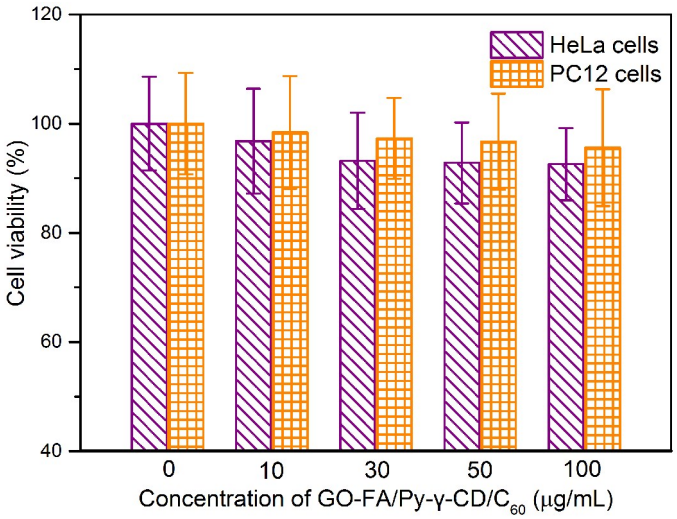

Fig. S3 Cytotoxicity caused by GO-FA/Py-γ-CD/C_{60} in dark. MTT reduction assay was used to evaluate the cell viability of PC12 and HeLa cell. Data were expressed as mean ± S.D (n = 3).

5. Concentration-dependent cell viability incubated with GO-FA/Py-γ-CD/C_{60}

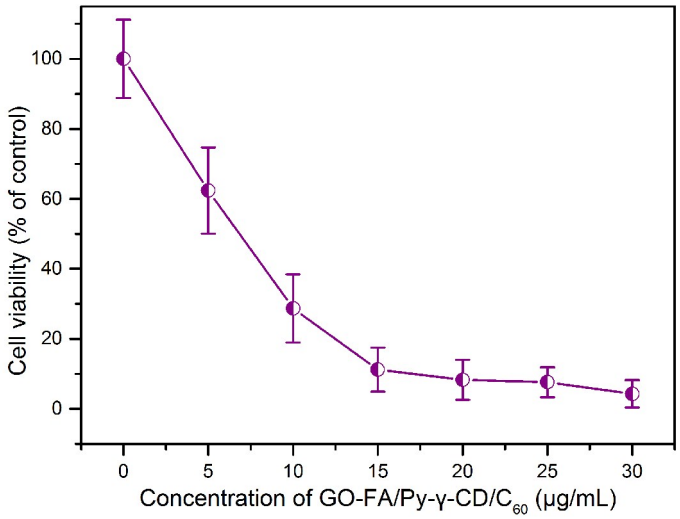

Fig. S4 Relationship between the cell viability and the concentration of GO-FA/Py-γ-CD/C_{60}. HeLa cells were preincubated with the nanohybrid for 12 h before irradiation (Xe lamp, 2 W/cm^2, 10 min). MTT reduction assay was used to evaluate the cell viability of PC12 and HeLa cell. Data were expressed as mean ± S.D (n = 3).

6. Concentration-dependent intracellular ROS accumulation incubated with GO-FA/Py-γ-CD/C_{60}

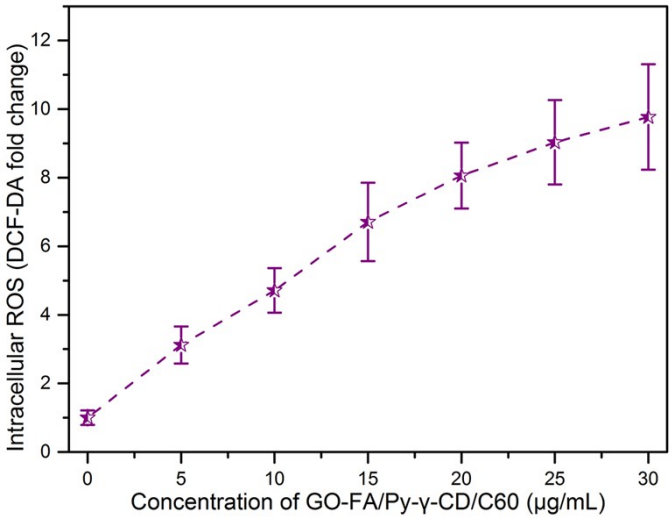

Fig. S5 Relationship between the intracellular ROS generation of HeLa cells and the concentration of GO-FA/Py-γ-CD/C_{60}. HeLa cells were preincubated with the nanohybrid for 12 h before irradiation (Xe lamp, 2 W/cm^2, 10 min). Data were expressed as mean ± S.D (n = 3).

7. Determination of apoptosis

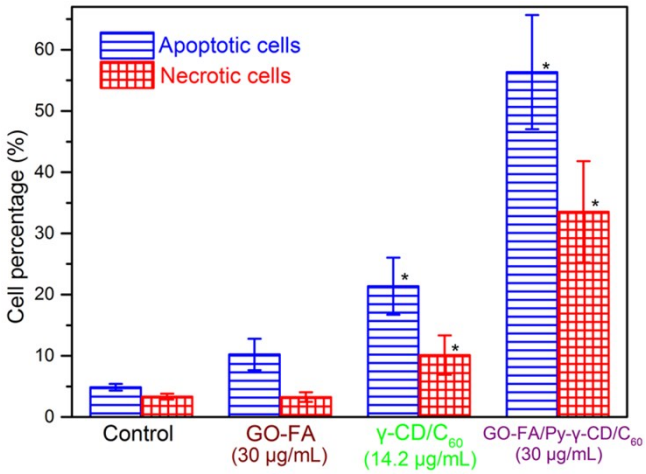

Fig. S6 GO-FA/Py-γ-CD/C_{60} induced apoptosis in HeLa cells in the presence of irradiation. HeLa cells were incubated with nanocarbons for 12 h prior to Xe lamp irradiation for 4 min. DNA fragmentation was determined by flow cytometry. Data were expressed as mean ± S.D (n = 3). *p < 0.05 vs blank group.