# Electronic Supplementary Information

## Light-triggered $C_{60}$ release from graphene/cyclodextrin nanoplatform for the protection of cytotoxicity induced by nitric oxide

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### 1. Experimental section

1.1. Synthesis of bis(4-(dimethoxyl)phenyl)diazomethane

A solution of 4, 4'-dimethoxybenzophenone (1.0 g, 4.13 mmol) in ethanol (15 mL) was treated with hydrazine hydrate (1.0 mL, 41.3 mmol). The resulting mixture was heated to reflux for 72 h. After the reaction, water was added to the solution until precipitate was appeared. Remove some EtOH in vacuum to concentrate the solution. Ice bath to make the product crystallize, filtered to get the product (Figure S1). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 3.80, 6.75, 6.88, 6.98, 7.14, 7.73. $^{13}C$ NMR ($CDCl_3$, 400 MHz, $\delta$): 55.5, 113.5, 125.2, 130.2, 149.3, 159.9. IR: 3395, 2836, 1605, 1507, 1242, 1109, 832 $cm^{-1}$. MS m/z (%): 257.2 (100).

Added 0.25 g (1.0 mmol) 4, 4'-dimethoxybenzophenone -hydrazone, 0.22 g (2.5 mmol) $MnO_2$, 0.144 g $Na_2SO_4$ and 0.1 ml EtOH (KOH saturated solution) into 5 mL dry THF. Stir the mixture in dark for 3 hours. Trace the reaction with MS spectra to check whether or not there was complete consumption of starting materials. Using IR to check whether or not there was a characterized peak for $=N_2$ group (2028 $cm^{-1}$). Filter the mixture through a celite plug, and dry under vacuum to give a purple powder product (Figure S2). $^1H$ NMR ($CDCl_3$, 400 MHz, $\delta$): 3.74, 6.87, 7.09. $^{13}C$ NMR ($CDCl_3$, 400 MHz, $\delta$): 55.3, 114.8, 121.7, 126.6, 132.4, 158.3. IR: 2867, 2028, 1510, 1251, 1180, 1027, 829 $cm^{-1}$. MS m/z (%): 297.1 (100).

1.2. The synthesis of diazonium salts

A stirring solution of the amine (1 eq) in THF/$H_2O$ was cooled to -5 $^oC$ then 3 mol/L hydrochloric acid (2 eq) was added to the mixture. Dissolve $NaNO_2$ (1.1 eq) in 1 mL water, cooled down, and then added into the above mixture. The solution was stirred for up to 30 minutes. H-acid test confirmed presence of the diazonium salt. NaOAc (2 eq) was added to neutralize the solution. The diazonium salts were used immediately.

## 2. The characterization of 4, 4'-dimethoxy benzophenone-hydrazone

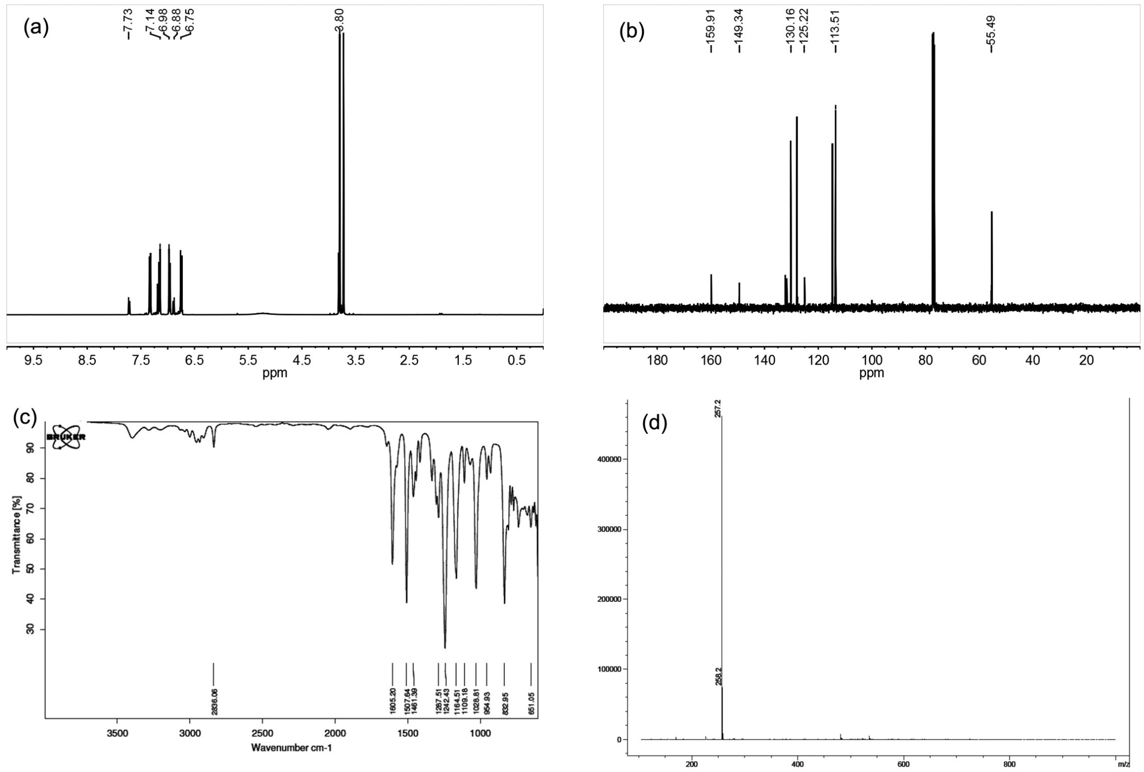

Figure S1 (a) $^{1}$H NMR, (b) $^{13}$C NMR, (c) FTIR, (d) MS spectra of 4, 4'-dimethoxy benzophenone-hydrazone.

## 3. The characterization of bis(4-(dimethoxyl)phenyl)diazomethane

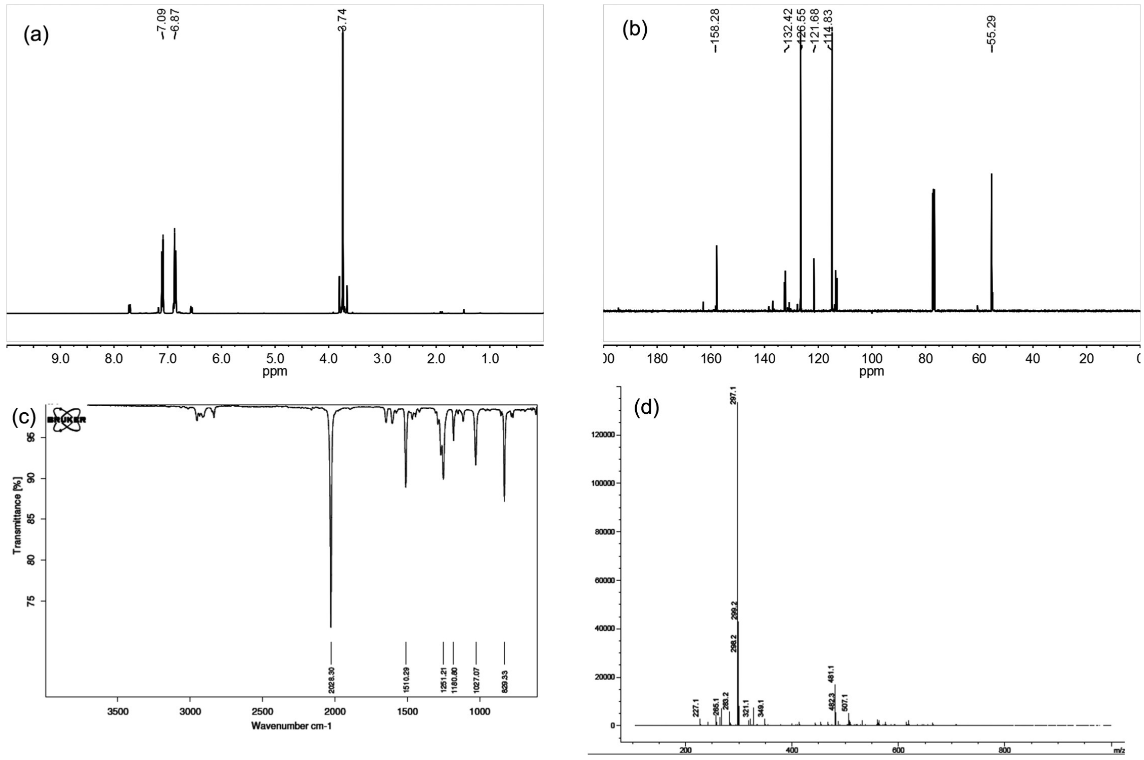

Figure S2 (a) $^{1}$H NMR, (b) $^{13}$C NMR, (c) FTIR, (d) MS spectra of bis(4-(dimethoxyl)phenyl)diazomethane.

## 4. The characterization of $C_{60}[C\{C_6H_4(OMe)_2\}_n]$

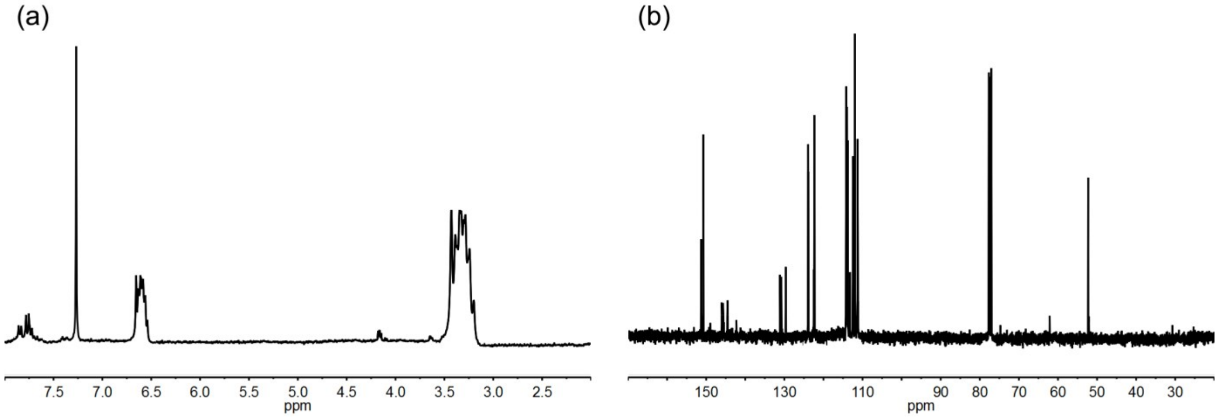

Figure S3 The (a) $^1$H NMR and (b) $^{13}$ C NMR spectra of $C_{60}[C\{C_6H_4(OMe)_2\}_n]$

## 5. The characterization of Azo-$C_{60}$

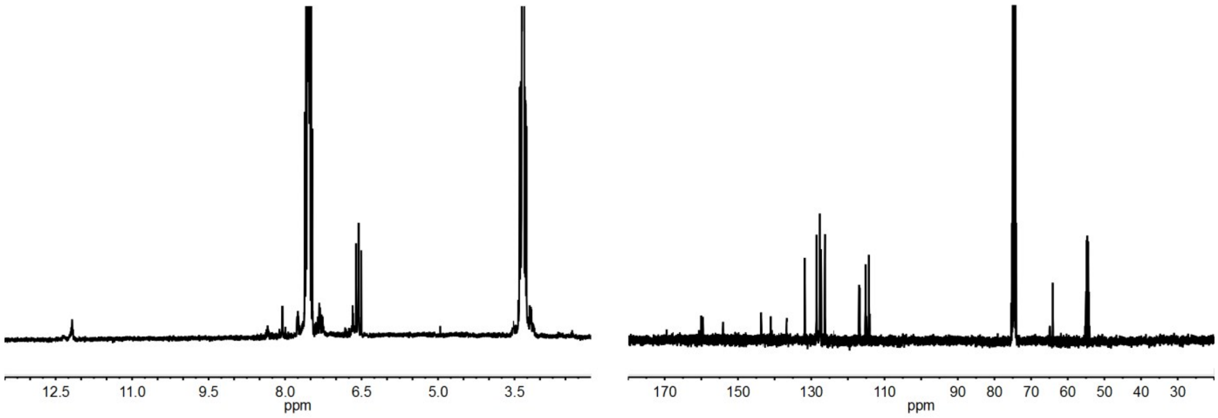

Figure S4 The (a) $^1$H NMR and (b) $^{13}$ C NMR spectra of Azo-$C_{60}$

## 6. The solubility and dispersibility of rGO/β-CD/$C_{60}$

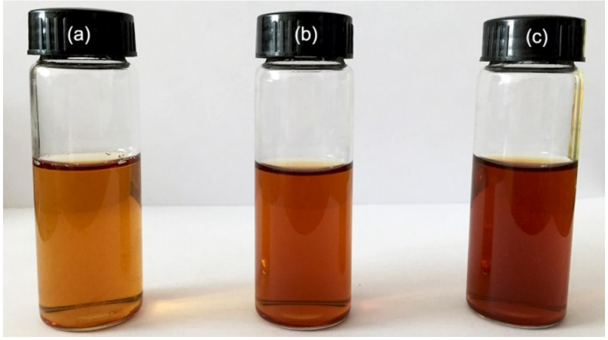

Fig. S5 Photograph of aqueous dispersions (a) GO, (b) rGO/β-CD, and (c) rGO/β-CD/$C_{60}$ (50 μg/mL).

## 7. The morphology of rGO/β-CD/$C_{60}$ in water after UV irradiation

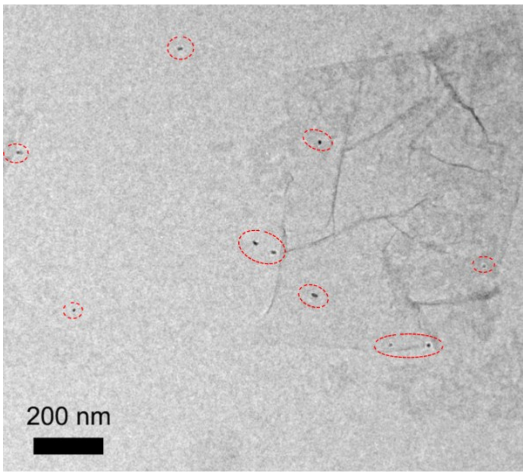

Figure S6 Representative TEM image of rGO/β-CD/$C_{60}$ under 365 nm UV light irradiation for 90 s. The red ellipses indicate the Azo-$C_{60}$ aggregates. The average diameter of the released Azo-$C_{60}$ colloidal aggregation is estimated to be ~10 nm.

## 8. The scavenging effects of rGO/β-CD/$C_{60}$ on nitrite levels in SNP solution

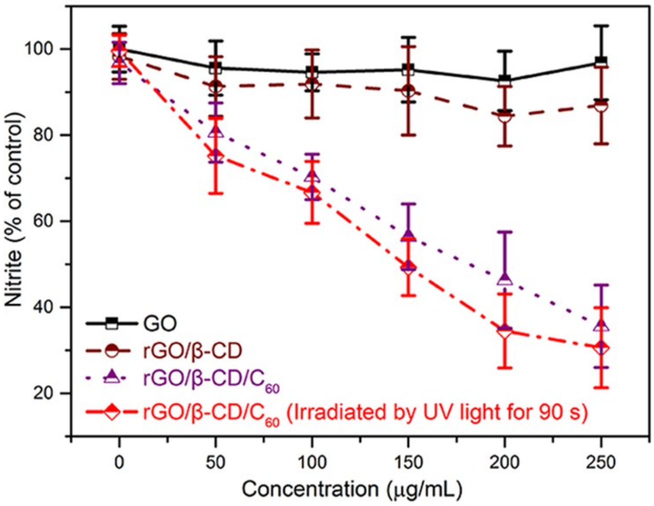

Figure S7 The effects of rGO/β-CD/$C_{60}$ on nitrite levels in SNP solution (1 mM). Data were expressed as mean ± S.D (n = 3).

## 9. The cytotoxicity of rGO/β-CD/$C_{60}$ in dark

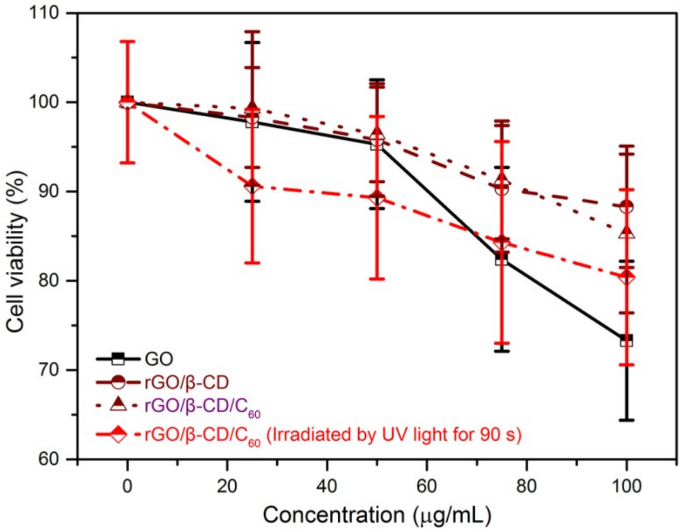

Figure S8 Cytotoxicity caused by nanocarbons in the dark. Cell viability was measured by the conventional MTT reduction assay. Data were presented as mean ± S.D (n = 3).

## 10. The NO scavenging effects of β-CD/$C_{60}$

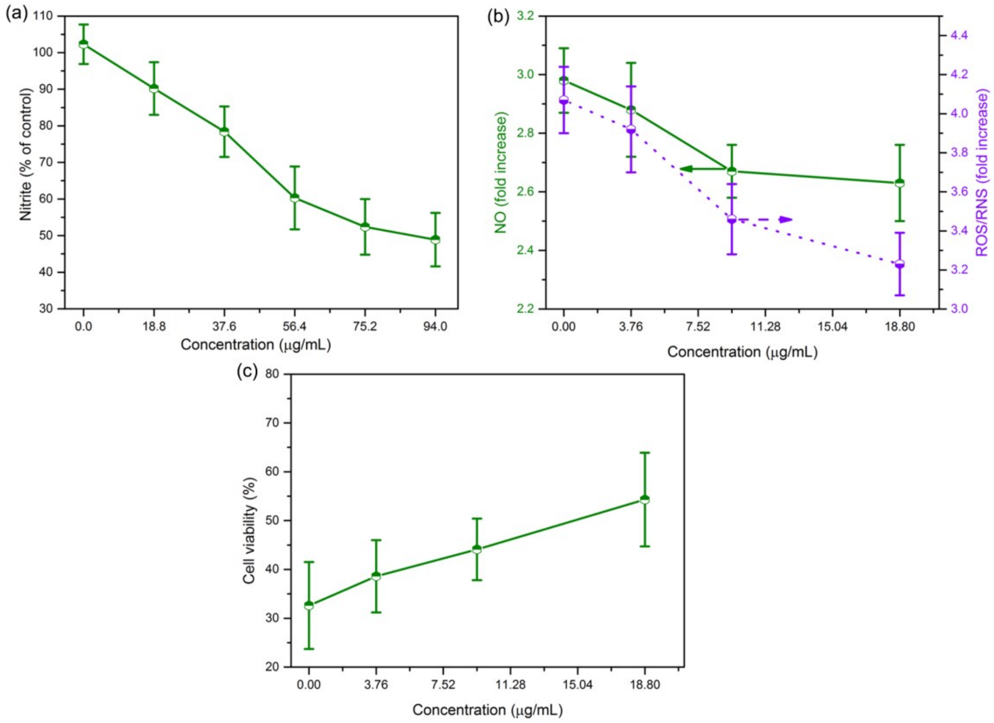

Figure S9 (a) The effects of β-CD/$C_{60}$ on nitrite levels in SNP solution (1 mM). (b) Intracellular ROS/RNS and NO levels detected by flow cytometry. PC12 cells were pretreated with different concentrations of β-CD/$C_{60}$ for 12 h, then 1 mM SNP was added for another 12 h incubation. (c) Cell viability data obtained from the conventional MTT reduction assay of PC12 cells. Data were expressed as mean ± S.D (n = 3).

A mixed solution consisting of Azo-$C_{60}$ (73.35 mg, 50 μmol) in THF (20 mL) and β-CD (56.75 mg, 50 μmol) in water (20 mL) was refluxed for 24 h under vigorous mechanical stirring. The solvent was removed by vacuum distillation to get the product. The pulverized β-CD/$C_{60}$ was dispersed in water by ultrasonication for 5 min. Trace insoluble particles was removed by centrifugal separation. The above solution was used for the following NO scavenging abilities tests.

In the present study, the NO scavenging abilities are mainly attributed to the $C_{60}$ component in the nanohybrid. To make the content of $C_{60}$ molecules is equal in all testing samples, the concentration of β-CD/$C_{60}$ is set to 37.6% of rGO/β-CD/$C_{60}$ (Based on the TGA results, the content of Azo-$C_{60}$ molecules can be calculated to be 21.2 % of rGO/β-CD/$C_{60}$. Meanwhile, it is assumed that the Azo-$C_{60}$ and β-CD are assembled with equal molar ratio. Then, the concentration of β-CD/$C_{60}$ is determined accordingly.).