Supporting Information for

Plasmon-assisted and visible-light induced graphene oxide reduction and efficient fluorescence quenching

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This pdf file includes:

Materials, methods, and data.

Figs. S1–S9

I. General

The gold nanoparticles (30 nm) were purchased from Ted Pella, Inc. (Redding, CA, USA). All other chemical reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received without further purification. NANOpure H2O (>18.0 MΩ), purified using a Milli-Q water purification system, was used for all of the experiments. The Cy3-modified DNA was purchased from IDT (Iowa, USA) and used without further purification step. The formvar/carbon-coated copper grid (Ted Pella, Inc.) and transmission electron microscopy (H-7650, Hitachi, Japan) and FE-SEM (Hitachi SU-70, Tokyo, Japan) were used for the nanoparticle and graphene analysis. UV-Vis spectrophotometer (S-3100, SINCO, South Korea) was used to obtain UV-Vis spectra. Particle size distribution of micro-size GO and nano-size GO were obtained with particle size analyzer (90-Plus, Brookhaven Instruments Corporation, USA). Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FTIR-4200 spectrophotometer (Maryland, USA). The surface morphology of nano-size GO and micro-size GO were analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi SU-70, Tokyo, Japan). The structural analyses were performed by X-ray diffraction (Rigaku D/MAX 2500 Tokyo, Japan and Raman spectroscopy (Renishaw, Raman micro system 2000, Derbyshire, England) using 633 nm wavelength laser. Fluorescence analysis were performed using JASCO Fluorescence Spectrometers (Maryland, USA). AXIS–NOVA (KRATOS Inc.) was used for XPS analysis.

II. Methods for the preparation of AuNS and AuNR

Gold nanostar (AuNS): Aqueous stock solution of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) with concentration of 100 mM was prepared, and pH was adjusted to 7.4 at 25 ^{o}C by adding 1.0 M NaOH solution. In a typical experiment, 20 mL of HEPES 180 mM was mixed with 30 mL of deionized water and 20 mL of 100 mM phosphate buffer, followed by the addition of 50 uL of 20 mM $HAuCl_4$ solution. Without shaking, the color of solution changed greenish blue within 10 min at 28.5 ^{o}C.[1]

Gold nanorod (AuNR): The gold nanorods were prepared using seed mediated growth solution method, the seed solution was prepared by the addition of a freshly prepared, 0.6 mL ice-cold solution of $NaBH_4$ solution (0.01 M) into an aqueous mixture solution composed of 0.25 mL of $HAuCl_4$ (0.01 M) and 9.75 mL of cetyltrimethylammonium bromide (CTAB, 0.1

M). The resulting mixture was vigorously stirred for 2 minutes and then kept at 28 ^{o}C for 3 h. The growth solution was prepared by mixing 475 mL of CTAB (0.1 M), 3 mL of $AgNO_3$ (0.01 M), 20 mL of $HAuCl_4$ (0.01 M). Then freshly prepared 3.2 mL of ascorbic acid (0.01 M) was added to the mixture followed by the addition of 0.8 mL of an aqueous HCl (1.0 M) solution. In the final step 3.2 mL of seed solution was added to the growth solution at 28 ^{o}C and reaction mixture was subjected to gentle inversion for few seconds. Finally, the resulting mixture was kept undisturbed for at least 6 h. The color of the solution gradually changed into strong purple within 10 - 20 minutes. The temperature of the growth medium was kept constant at 28 ^{o}C after seed addition step.[2]

III. Fluorescence quenching and recovery

Quenching experiment

To check the fluorescence quenching efficiency of GO and r-GO, 20 µl of 10^{-6} M ssDNA-Cy3 (5'-ATC CTT ATC AAT ATT TAA CAA TAA TCC CTC-Cy3-3') is mixed with 25 µl of GO and each r-GO prepared by different route. Then, 1,955 µl of 0.3 M PBS (10 mM phosphate buffer, 2 M NaCl) is added. The fluorescence intensity of these samples is analyzed through spectro fluorometer (Jasco FP-6500, Tokyo, Japan).

Target Detection

For fluorescence recovery experiment, 200 µl of target (5'-GAGGGATTATTGTTAAATATT GATAAGGAT- 3') is added in the solution of 20 µl of 10^{-6} M ssDNA-Cy3, 25µl of different r-GO and 1,755µl of 0.3 M PBS. Three different concentrations i.e. 10^{-6} M, 10^{-7} M, 10^{-8} M of target is used for the target detection.[3]

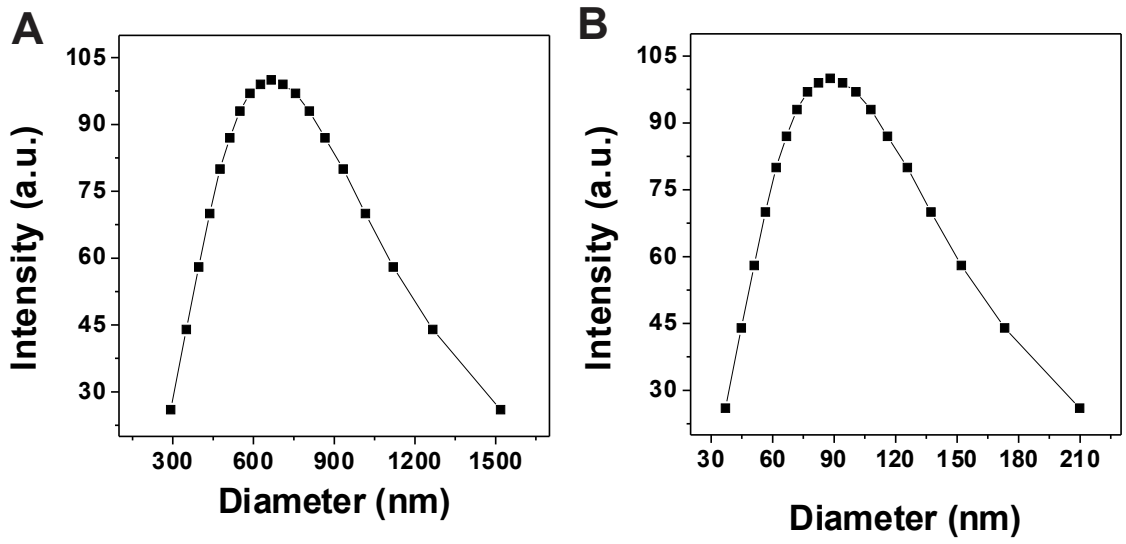

Fig. S1. (**A**) Particle size distributions of micro-sized GO and (**B**) nano-sized GO solution used for reduction.

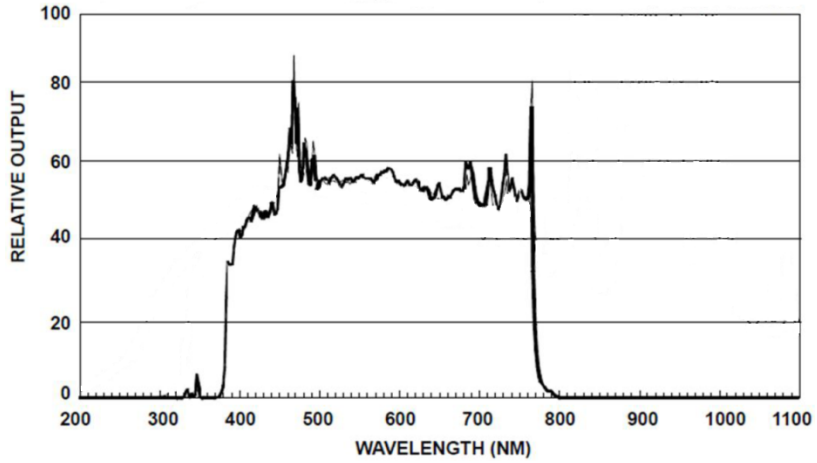

Fig. S2. The output spectra of Xe-lamp used for visible light source (Ceramax®, Waltham, USA) (PE300BFA).

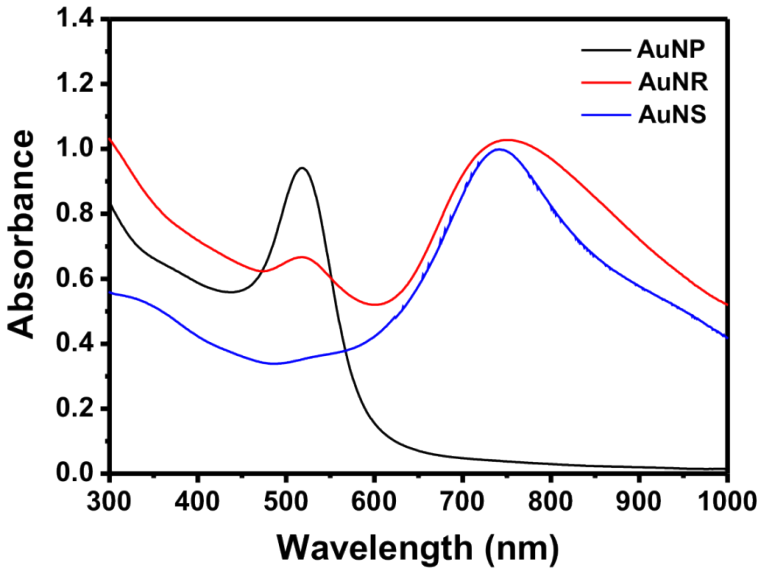

Fig. S3. The UV-Visible spectra of AuNP (black line), AuNR (red line), and AuNS (blue line).

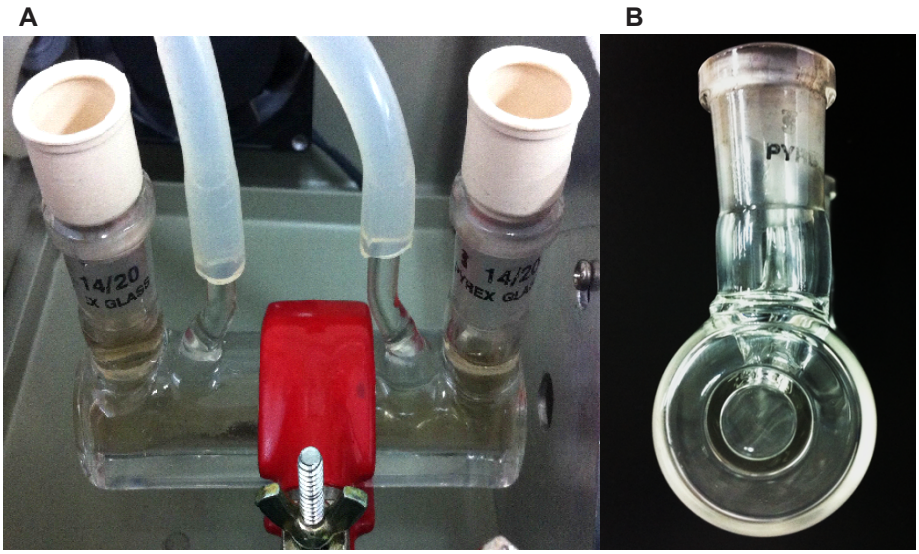

Fig. S4. The photographs of (**A**) reaction apparatus equipped with water circulation jacket, (**B**) the reaction apparatus window. (Pyrex, reaction volume = 10 ml, window diameter = 11 mm).

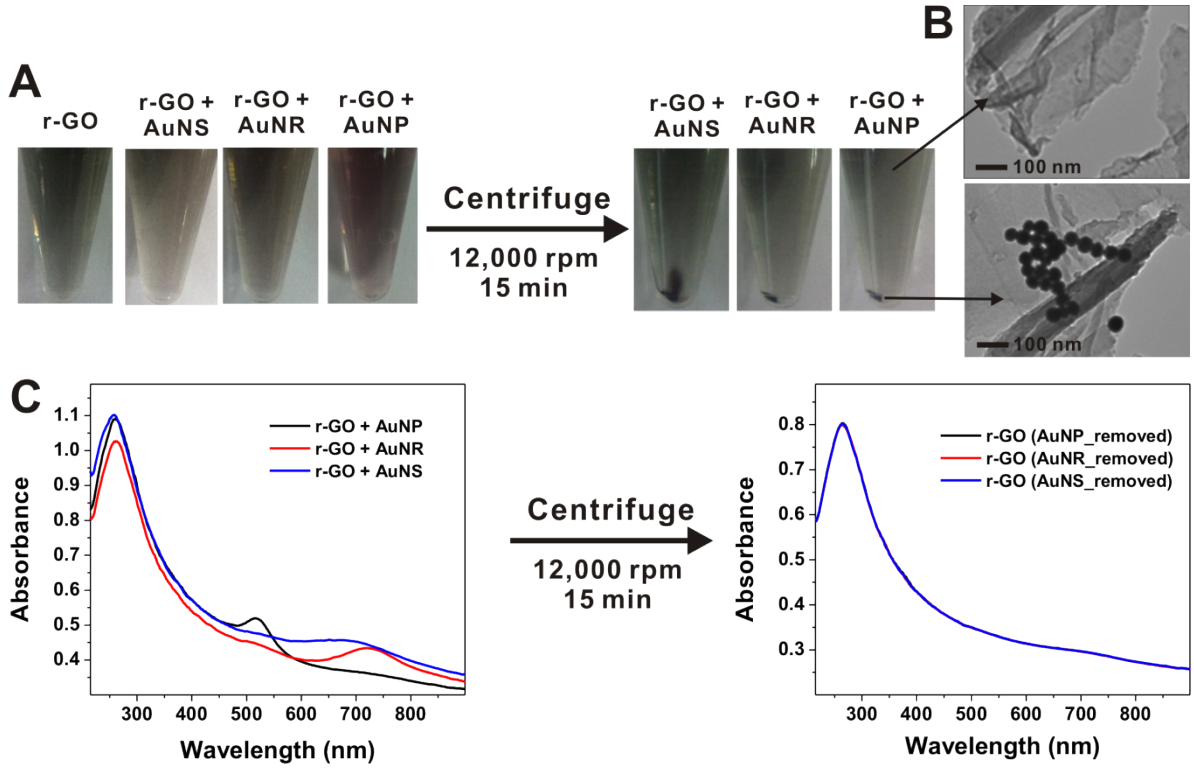

Fig. S5. (**A**) The photographs of GO, GO + AuNP, GO + AuNR, GO + AuNS solution before and after centrifugation (12,000 rpm/15 min), (**B**) HR-TEM images of GO solution and precipitates, (**C**) the UV-Vis spectra of r-GO + AuNP mixture, r-GO + AuNR mixture, and r-GO + AuNS mixture before and after centrifugation.

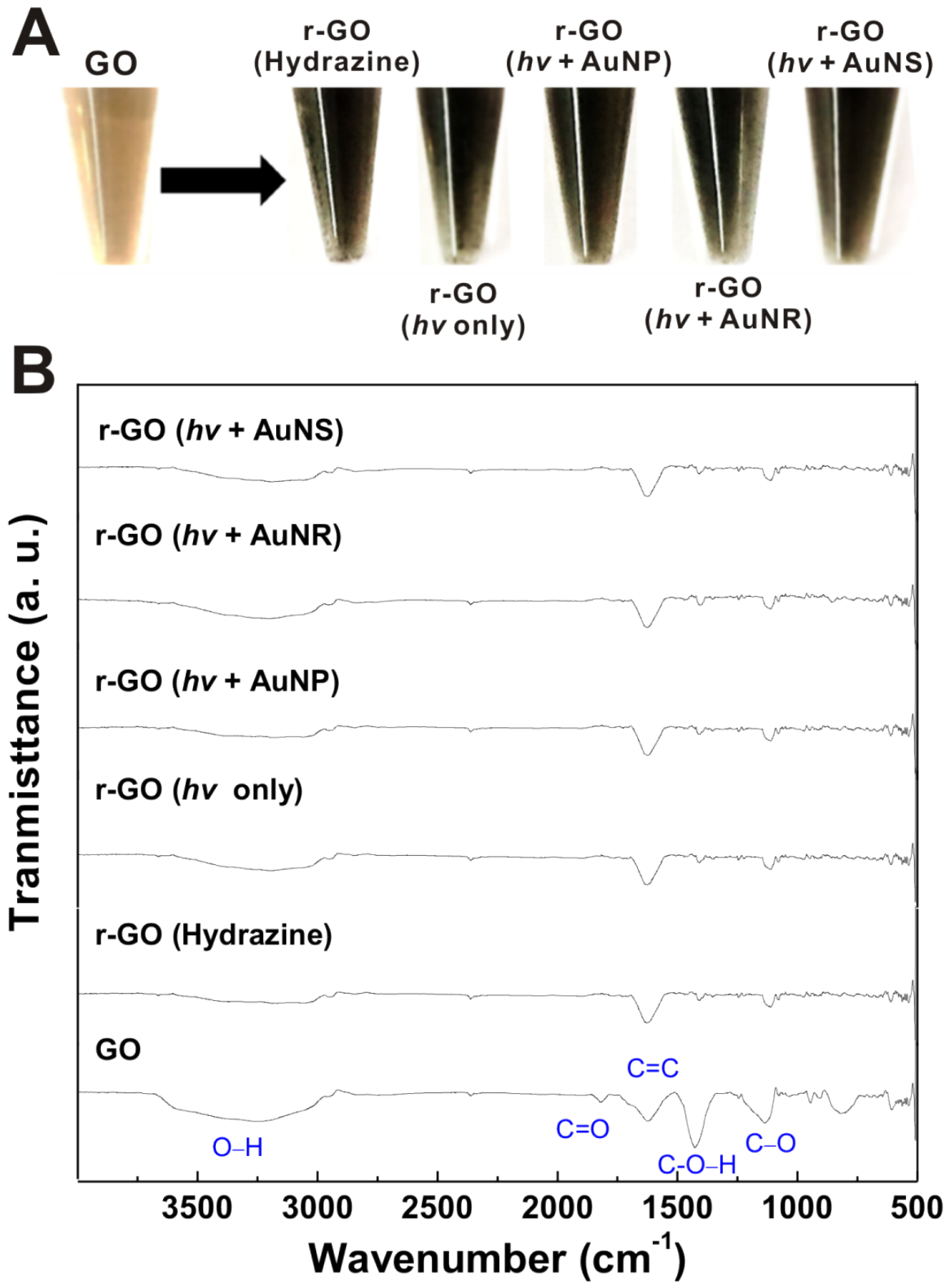

Fig. S6. (**A**) Solution color changes of GO from light yellow-brown to black after reduction into r-GO, (**B**) FT-IR spectrum of GO or r-GO prepared from different methods such as chemical reduction (hydrazine), and light induced method (*hv* only, or in the presence of AuNP, AuNR, and AuNS).

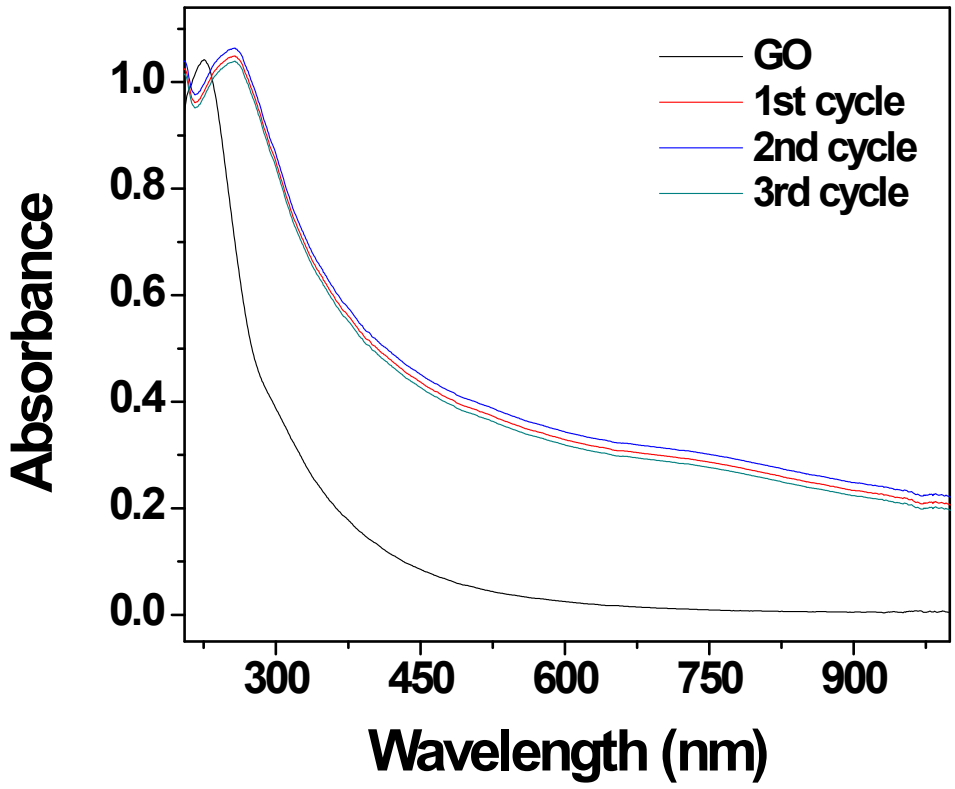

Fig. S7. UV-Visible spectra of GO solution, r-GO solutions prepared using recycled AuNP.

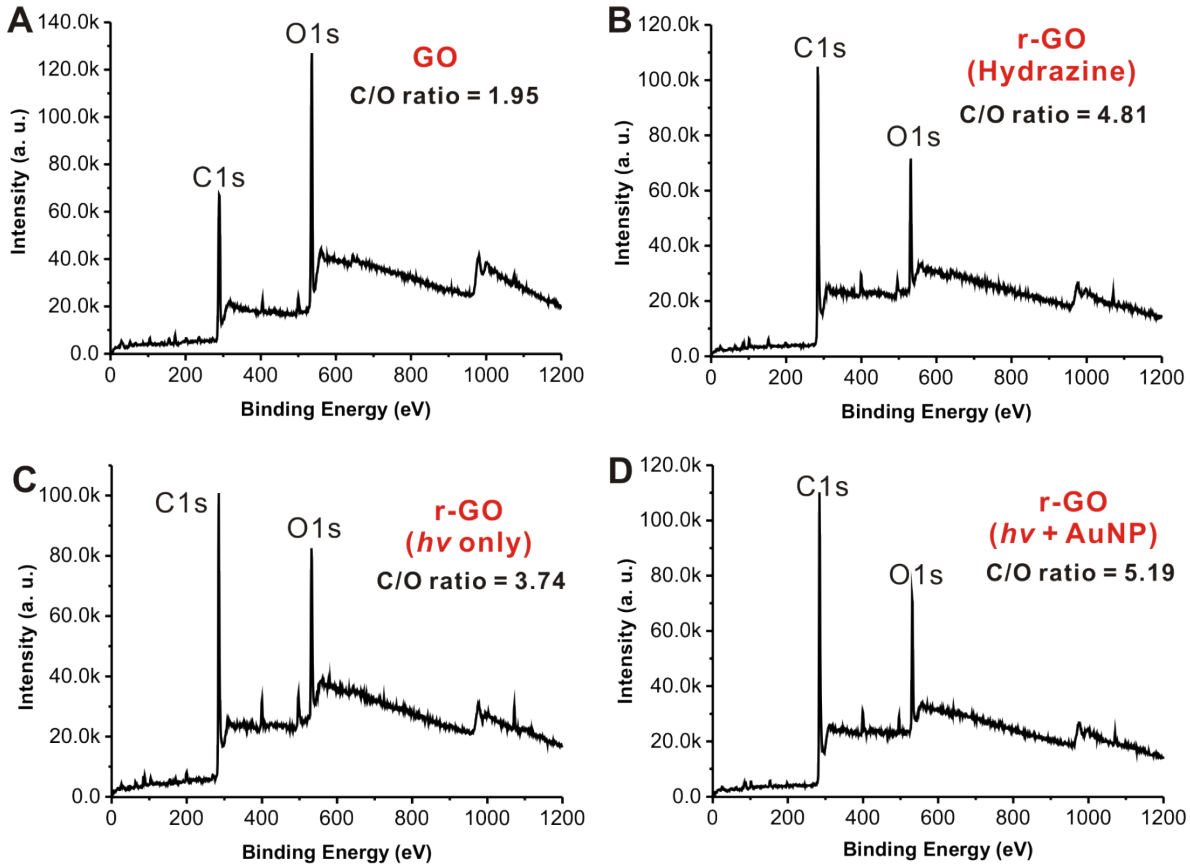

Fig. S8. The XPS analysis of GO solution (**A**), r-GO solutions prepared with chemical method (**B**), and light-induced method without AuNP (**C**) or with AuNP (**D**).

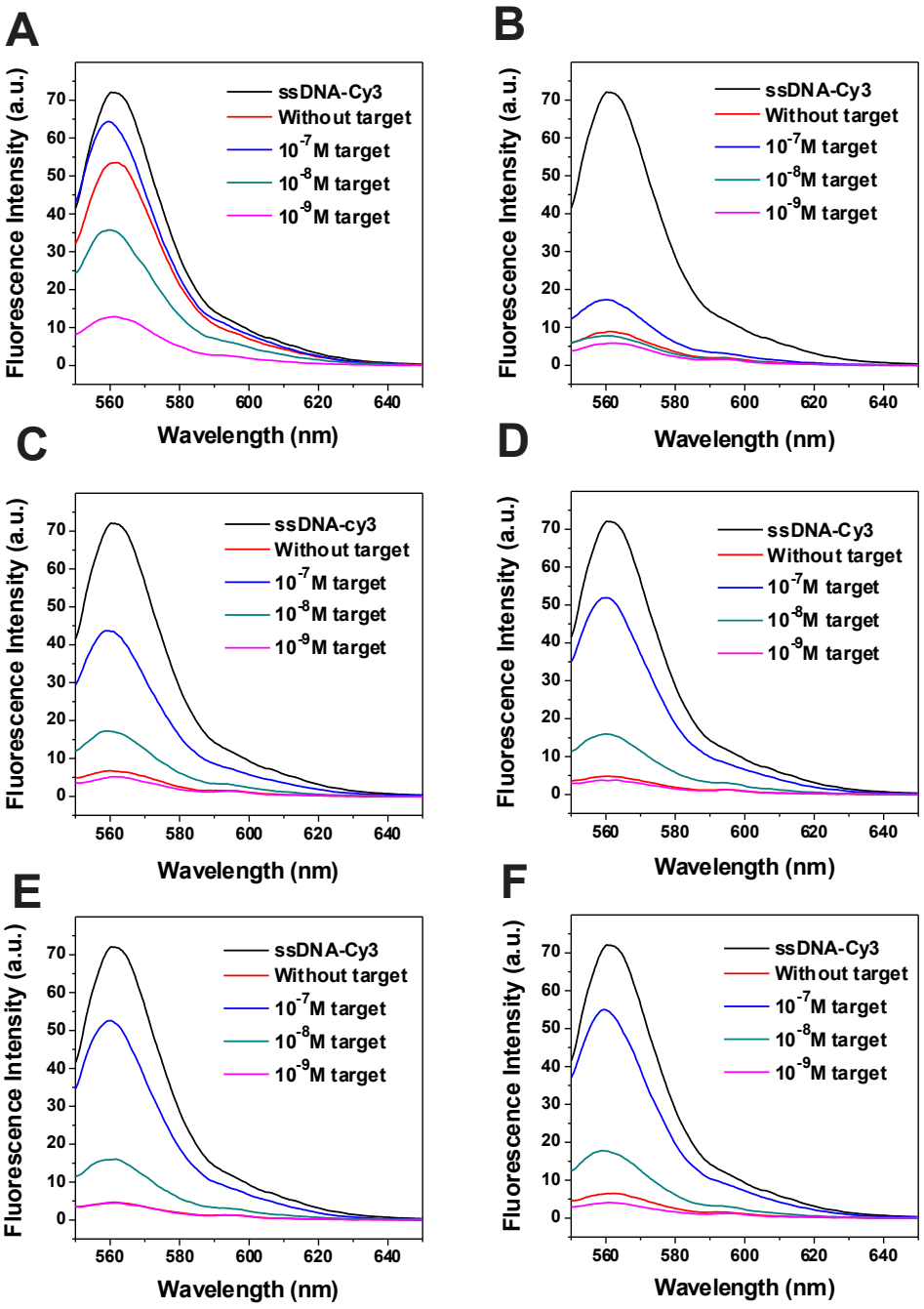

Fig. S9. Fluorescence recovery of ssDNA-Cy3 in the presence of varying concentration of target DNA (10^{-7} M, 10^{-8} M and 10^{-9} M) for (**A**) GO, (**B**) r-GO (hydrazine), (**C**) r-GO (*hv* only), (**D**) r-GO (*hv* & AuNP), (**E**) r-GO (*hv* & AuNR) and (**F**) r-GO (*hv* & AuNS).

References:

1 J. Xie, J. Y. Lee and D. I. C. Wang, *Chemistry of Materials*, 2007, **19**, 2823.

2 T. Ming, L. Zhao, H. Chen, K. C. Woo, J. Wang and H.-Q. Lin, *Nano Letters*, 2011, **11**, 2296.

3 J. Kim, L. J. Cote, F. Kim and J. Huang, *Journal of the American Chemical Society*, 2009,

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