Supporting information

EXPERIMENT SECTION

Material and measurements:

Nanopure water (18.2 MΩ; Millpore Co., USA) was used in all experiments. Graphite was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). $AgNO_3$ was purchased from Alfa Aesar. All other reagents were of analytical reagent grade and used as received. The UV-Vis absorption spectra and the fluorescence spectra were recorded using a JASCO V-550 UV/Visible and a JASCO FP6500 spectrophotometer (JASCO International Co. LTD., Tokyo, Japan). The ζ-potential the GQDs was measured in a Zetasizer 3000HS analyzer. TEM images were recorded using a JEOL 1011 transmission electron microscope operating at 200 kV. AFM imaging was performed in the tapping mode on a Multimode V using NP-S tips (Veeco Inc.).The synthesis was performed on a WBFY-201 Microwave Oven equipped with atmospheric reflux device (Gongyi Yu Hua Instrument Co. Ltd., Gongyi, China).

Preparation of fluorescent graphene quantum dots:

Graphene oxide (GO) was synthesized from natural graphite powder by Hummers method.[1] Following synthesis of GO, Graphene quantum dots was synthesized referring to a previous report.[2] Briefly, GO solution (30 mL, 0.14 mg/mL) was firstly mixed carefully with concentrated HNO_3 (8 ml) and H_2SO_4 (2 ml). Then the mixture was heated and refluxed under microwave irradiation for 8-10h in microwave oven operating at a power of 650 W. The product contained brown transparent suspension and black precipitates. After cooling to room temperature, the pH of the mix was tuned to 8 with Na_2CO_3 in an ice-bath. The suspension was filtered through a 0.22 μm microporous membrane to remove the large tracts of GO and a deep yellow solution was separated. The deep yellow filter solution was reduced with $NaBH_4$ under stirring at room temperature for 10h. Then HNO_3 solution was added dropwise to terminate the reaction and tune the pH to 8. The mixture solution was further dialyzed in a dialysis bag (retained molecular weight: 1000 Da) and blue fluorescent GQDs were obtained.

Assay procedure:

10 μL of GQDs stock solution (20 μg/mL) was mixed with 1000 μL of 10 mM Tris-HNO_3 buffer. 2 μL of different concentration of Ag (I) was added, and equilibrated for 5 min at room temperature before the spectral measurements. The fluorescence spectra were recorded under excitation at 340 nm. For the Cys detection, 2 μL of different concentration of Cys were added to the above mixture solution. After 5 min, the fluorescence spectra were recorded.

Determination of Binding Constants[3]:

Binding constants were measured by fluorescence titration methods, in which fixed concentrations of Ag^+ titrated with increasing biothiols concentrations.

According to the 1 : n binding mode, the binding reaction can be described as:

$P + M = PM_n$

Where P denotes Ag^+, M denotes biothiols, and PM denotes silver-thiols conjugates.

So, the binding constant can be described as:

$K_b = [PM_n]/[P][M]^n$

With

$[P] = [P_0]-[PM_n]$

$[M]=[M_0]-n[PM_n]$

Where $[P_0]$ is the concentration of Ag^+ and $[M_0]$ is the concentration of biothiols

So,

$$Kb = [PM_n]/\{[P_0] - [PM_n]\}\{[M0]-n[PM_n]\}_n$$

The formation of silver-thiol conjugates PMn can be quantitated by the fluorescence signal that satisfies the following equation:

$$F=F_0 + (F_\infty - F_0)[PM_n]/ [P_0]$$

So

$$K_b=\{\Delta F\times[P_0]/ \Delta F_{max}\} /\{ [P_0] - \Delta F\times[P_0]/\Delta F_{max} \}\{ [M_0]-n\Delta F\times[P_0]/ \Delta F_{max} \}^n$$

Where $\Delta F= F - F_0$, $\Delta F_{max}= F_{max}- F_0$

Fluorescence titration was used to determine the quantitative binding constants. Nonlinear least-squares fit of the data yields the binding constants of 1.09×10^8, 2.14×10^8 and 2.43×10^8 for Cys, Hcy and GSH with Ag^+, respectively.

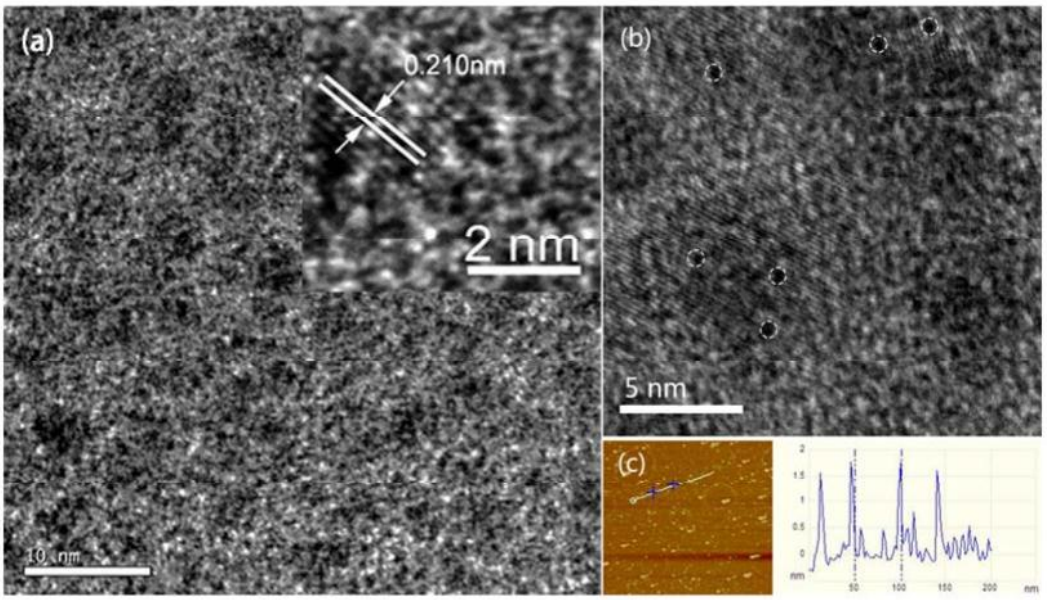

Fig. S1 (a) Transmission electron microscopy (TEM) images (a) of GQDs. Inset is the high-resolution TEM. (b) TEM images of AgNPs supported on GQDs. (c) Atomic force microscopy (AFM) images (b) of GQDs.

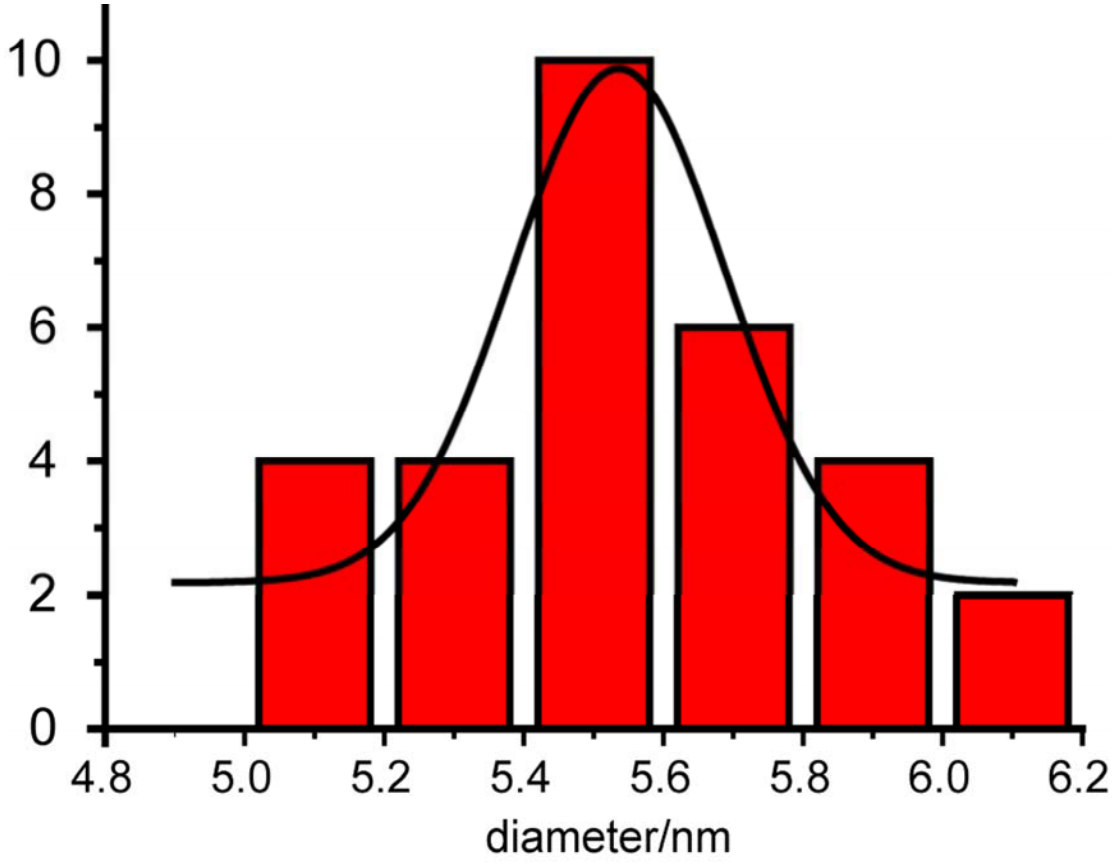

Fig. S2 Particle size statistics and Gauss fit of graphene quantum dots.

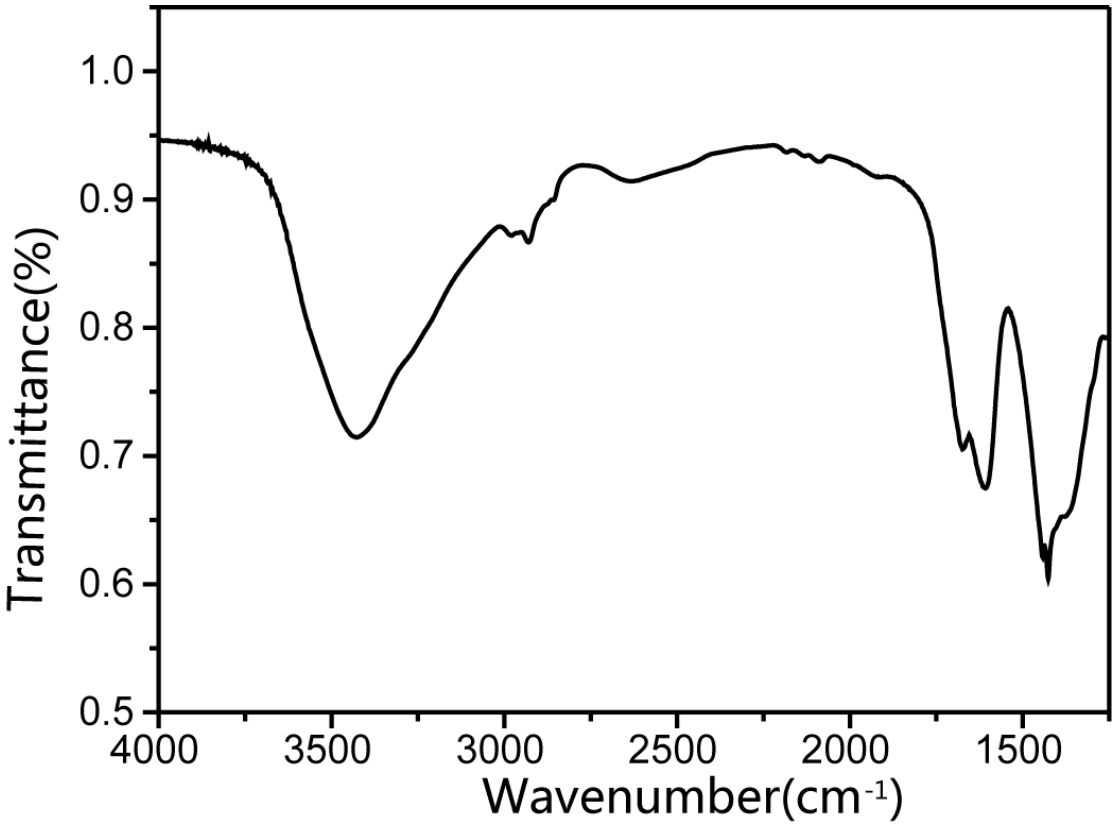

Fig. S3 Frourier transform infrared (FTIR) spectrum of GQDs.

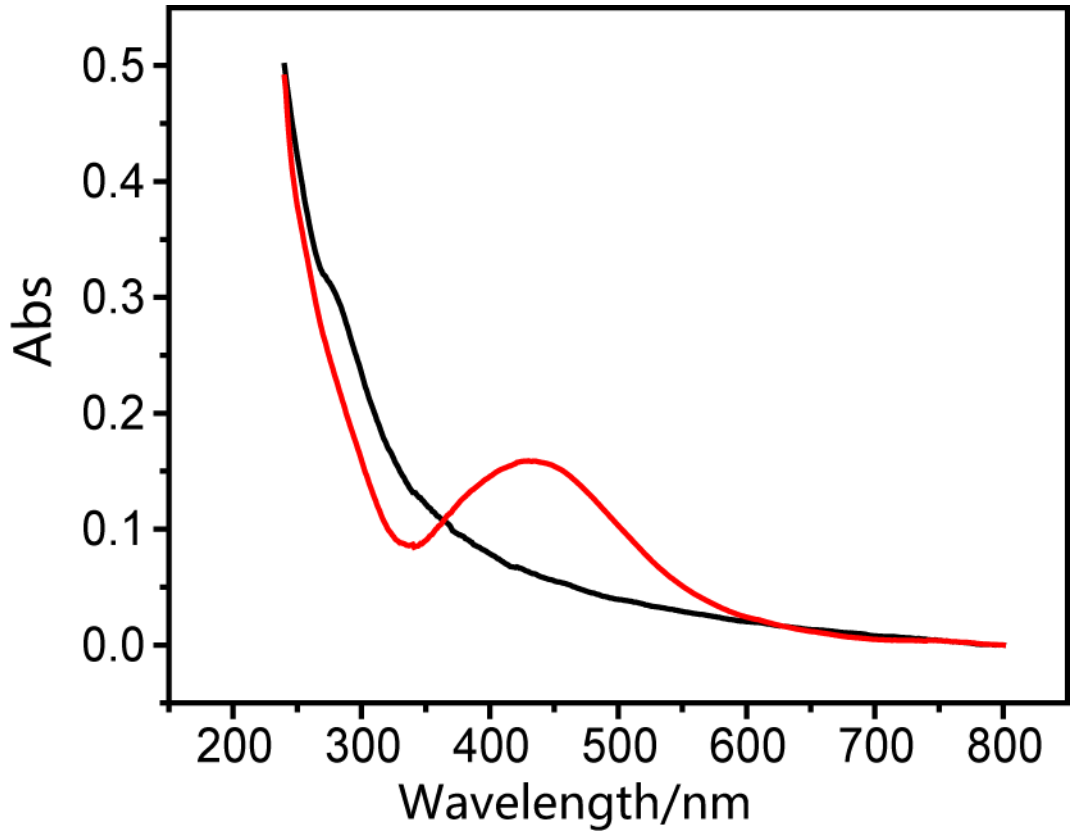

Fig. S4 UV-Vis spectra of GQDs in the absence of Ag^+ (black line) and the presence of Ag^+ (red line) in 10mM Tris-HNO_3 buffer.

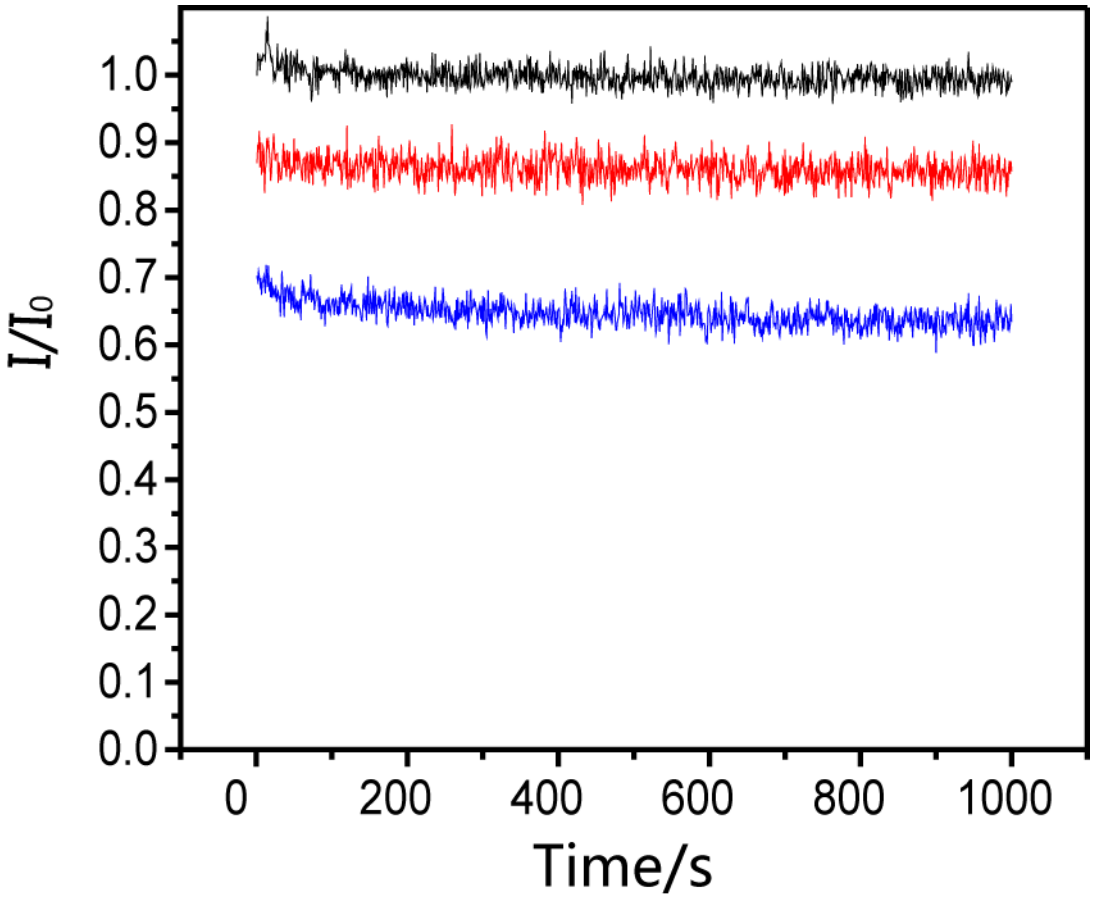

Fig. S5 Time course curves of GQDs in the absence of Ag^+ (black line) and the presence of Ag^+ (red line) and the FL quench of AgNPs/GQDs in the present of Cys (blue line) in 10 mM Tris-HNO_3 buffer.

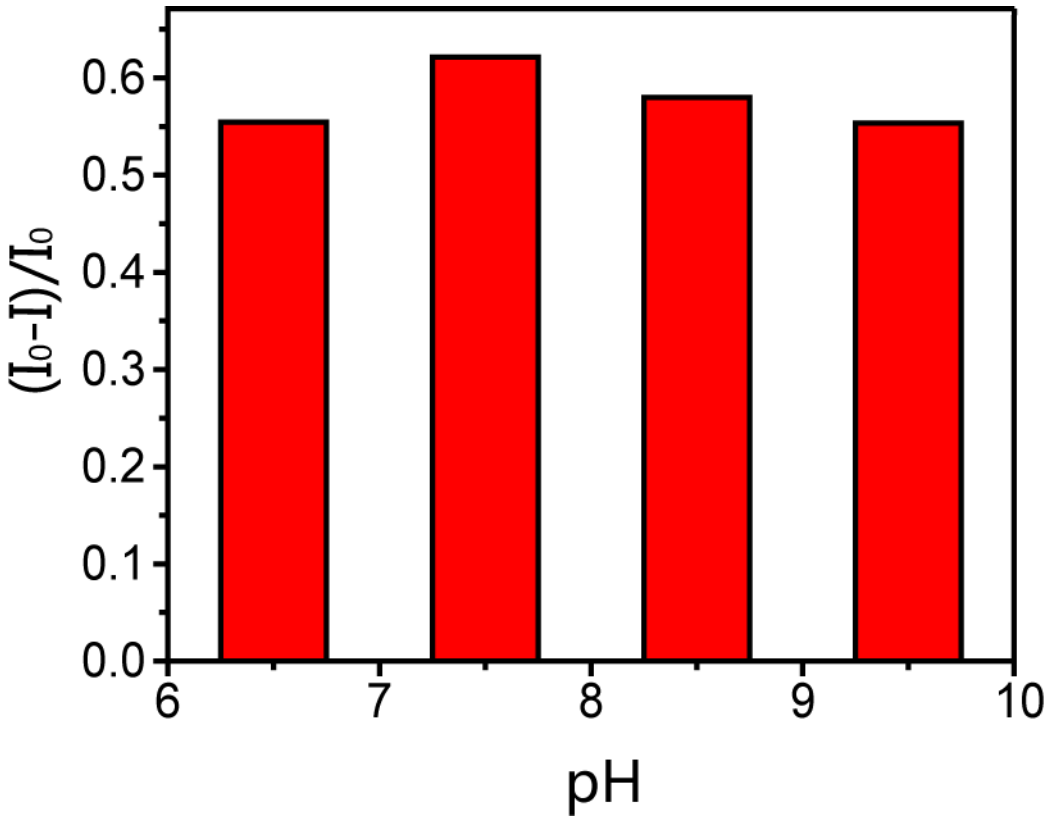

Fig. S6 Effect of different pH on the FL quench of AgNPs/GQDs based assay for cysteine.

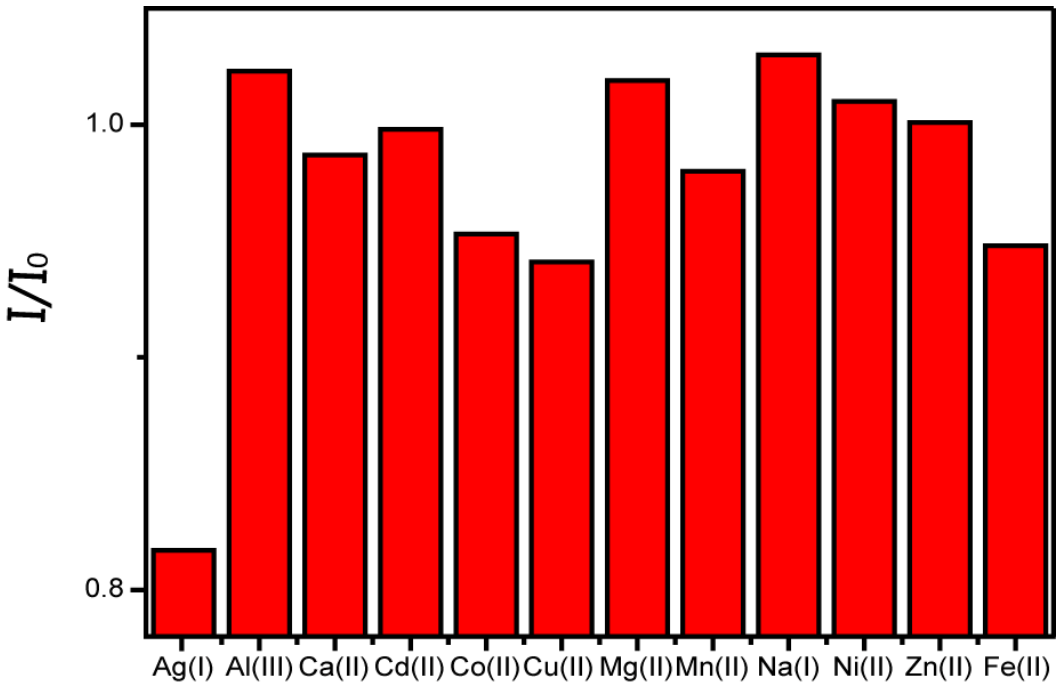

Fig. S7 Selectivity of the Ag^{+} sensor based on the GQDs. All competing ions were 1 μM.

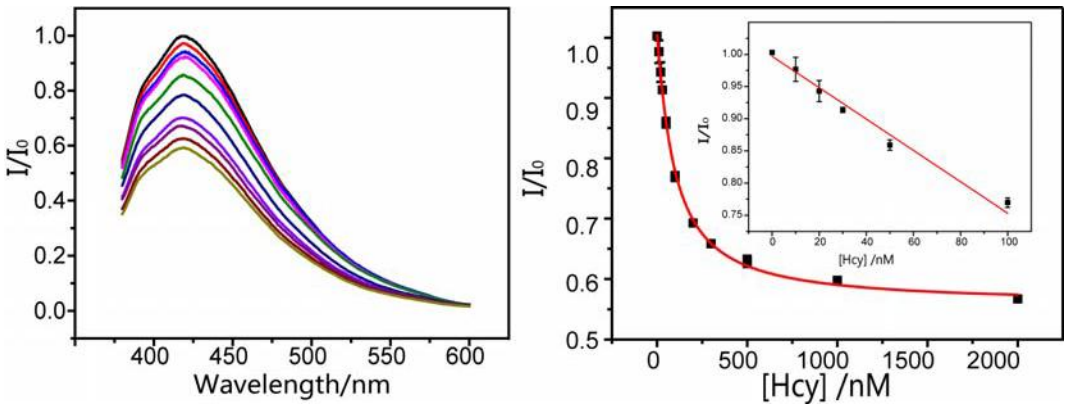

Fig. S8 (a) FL emission spectra of GQDs containing Ag^+ (1 μM) in the increasing of Hcy concentrations (0-2 μM). (b) The relationship between FL of GQDs and the Hcy. The error bars represent the standard deviation of three measurements. Inset is a linear region. I and I_0 is the FL intensity of the AgNPs/GQDs at 420 nm in the presence and absence of Hcy, respectively.

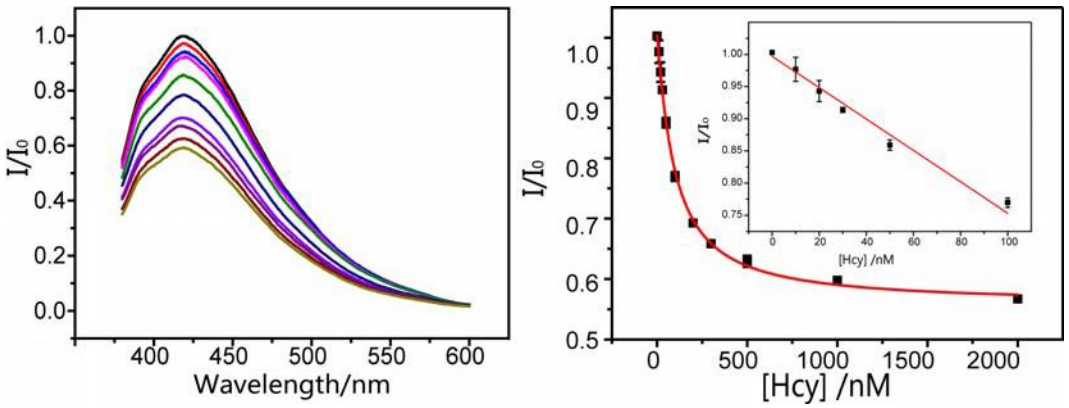

Fig. S9 (a) FL emission spectra of GQDs containing Ag^{+} (1 μM) in the increasing of GSH concentrations (0-2 μM). (b) The relationship between FL of GQDs and the GSH. The error bars represent the standard deviation of three measurements. Inset is a linear region. I and I_0 is the FL intensity of the AgNPs/GQDs at 420 nm in the presence and absence of GSH, respectively.

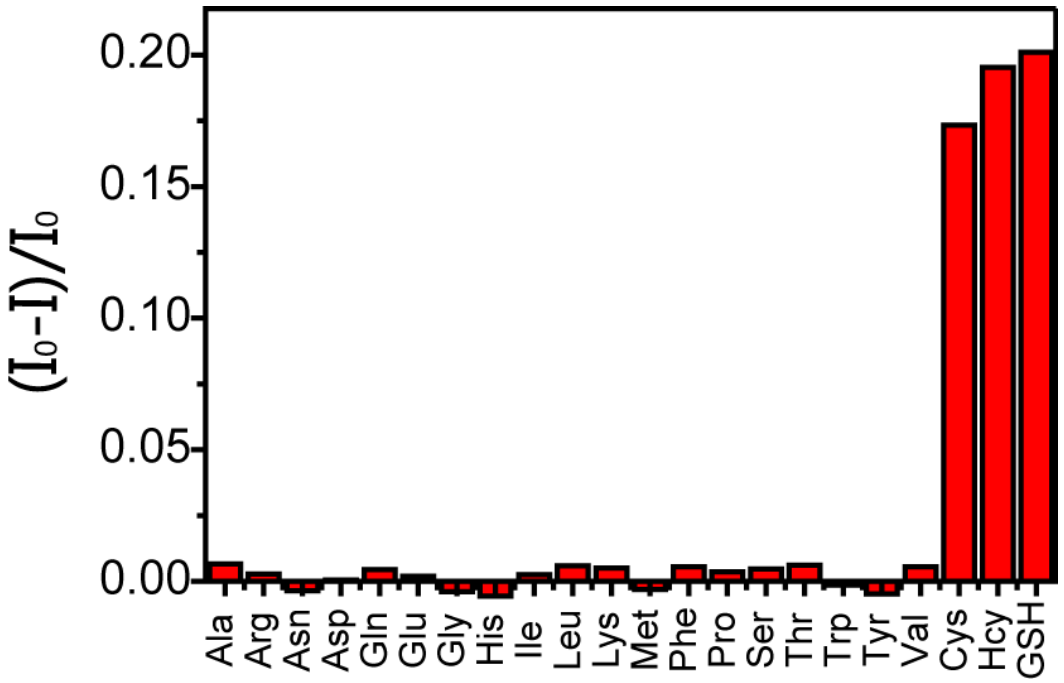

Fig. S10 Fluorescence response of the AgNPs/GQDs in the presence of other amino acids (1 μM), Cys, Hcy and GSH.

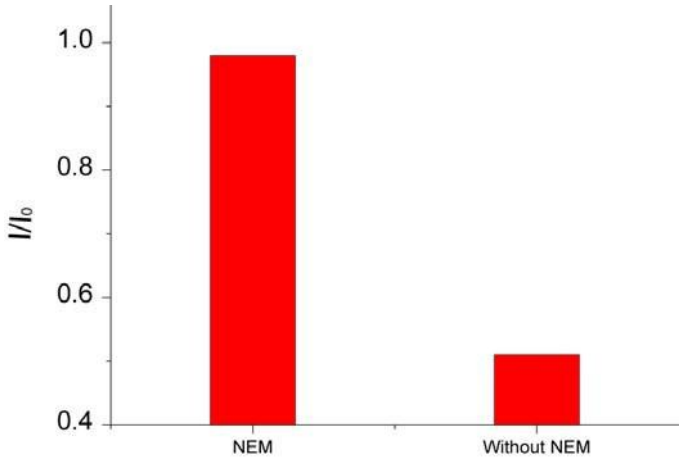

Fig. S11 FL response of AgNP/GQDs to plasma with or without pretreatment by thiol blocking agent, NEM.

Table S1 Determination of biothiols in human plasma (human plasma was diluted with buffer before detection)

Samples	Determined thiol compound(μM)	Add Cysteine(μM)	Found(μM)	Recovery(%)	RSD(n=3,%)
1	515.2	200	718.1	101.5	2.17
		500	1215.8	100.0	1.60
2	547.3	200	743.6	98.2	2.48
		500	1246.2	99.8	4.92

References:

1. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. L. L. Li, J. Ji, R. Fei, C. Z. Wang, Q. Lu, J. R. Zhang, L. P. Jiang, J. J. Zhu, *Adv. Funct. Mater.*, 2012, **22**, 2971.
3. C. Xu, C. Zhao, J. Ren, X. Qu, *Chem. Commun.*, 2011, **47**, 8043.