Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

NIR fluorescence detection of dopamine using 3-aminophenyl boronic acid-functionalized and lysozyme-templated gold nanoclusters

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Experimental Section

Chemicals and Apparatus. 1-(3-dimethylaminoporopyl)-3-ethylcarbodiimide hydrochloride (EDC), N-hydroxyl succinimide (NHS), Chloroauric acid hydrate ($HAuCl_4$), lysozyme, 3-aminophenylboronic acid monohydrate (APBA), glucose were purchased from sigma-aldrich. Dopamine, lysine, arginine, glycine and histidine were purchased from J&K Scientific Ltd. Ultrapure water was obtained from a Millipore water purification system (18.2 MΩ; Millipore Co., Billerica, MA). Human blood samples were collected from several healthy volunteers in the first people's hospital of Chenzhou, Chenzhou, China. All experiments were in accordance with the guidelines of the Pharmacopoeia of China (2015), and approved by the institutional ethical committee (IEC) of the first people's hospital of Chenzhou, Chenzhou, China. Informed consent was obtained for any experimentation with human subjects. All of the fluorescence spectra were recorded on a PTI-QM4 Fluorescence System (Photo Technology International, Birmingham, NJ) exciting at 375 nm and measuring emission from 570 to 730 nm. UV-Vis absorption spectra were recorded in 1.0 cm path length quartz cuvettes on a Hitachi U-4100 UV/Vis spectrophotometer (Kyoto, Japan). Transmission electron microscopy (TEM) images were obtained with a JEM-2010 instrument (JEOL, Japan).

Synthesis of APBA-Lys-Au NCs. Au NCs were prepared by lysozyme reduction of $HAuCl_4$.[1] A 300 μL aqueous solution consisting of 100 μL of lysozyme (10 mg mL^{-1}) and 100 μL of $HAuCl_4$ (4.0 mM) were stirred in a round-bottom flask for 5 min, and then 10 μL of NaOH solution was added rapidly to the solution and incubated at 37 °C overnight. And the lysozyme-protected gold nanoclusters (Lys-Au NCs) were obtained by dialysis, which were kept at 4°C for further use.

100 μL of APBA solution (5.0 mM) was added to the obtained Lys-Au NCs solution, followed with EDC and NHS (the mole ratio of APBA to EDC, NHS was 1 : 3 : 3), and then the APBA functionalized Lys-Au NCs (APBA-Lys-Au NCs) were obtained by stirring for 2 h, following by centrifugation at 10

000 rpm for 10 min. The supernatant, that is APBA-Lys-Au NCs solution, was diluted to 100 times as stock solution for the further detection of dopamine.

Spectroscopic studies. 4 mL aqueous solution containing 1 mL APBA-Lys-Au NCs stock solution was treated with equal volume of various concentration of DA solution. After incubation at room temperature for 20 min, the fluorescence emission spectra were recorded by excited at 375 nm with emission wavelength from 570 nm to 730 nm.

Detection of human blood samples. Human blood samples were collected from several healthy volunteers in the first people's hospital of Chenzhou. After 2 h's standing, the obtained human blood samples were centrifuged at 10 000 rpm for 10 min. Then, the mixture of 1 mL of supernatant and 1 mL of CH_3CN were brought to a vigorous stirring for 2 min, followed by centrifugation at 10 000 rpm at 4°C for 10 min.[2] The supernatant was filtrated for two times, followed by adjusting to neutral and dilution to 10 times as stock solution. After treatment with various concentration of DA for 20 min, the fluorescence emission spectra were recorded by excited at 375 nm with emission wavelength from 570 nm to 730 nm.

Table S1 The comparison of the proposed method with other reported methods of dopamine determination

anlyticla methods	linear range	Detection limit	Ref.
APBA-Lys-Au NCs	1~10 μM	0.72 μM	This work
HPLC	0.8~48 ng/mL	0.4 ng/mL	7
spectrophotometry	1.2~50 μg/mL	0.4 μg/mL	8
electrochemistry	0.1~205 μM	35.5 nM	9
electrochemistry	10 ~220 μM	1 nM	10
electrochemistry	4 ~100 μM	2.64 μM	11
electrochemistry	10 nM ~10 μM	1 nM	12
fluorescence	0 ~200 nM	6 nM	15
fluorescence	1 nM ~10 μM	0.1 nM	17
fluorescence	0 ~20 μM	40 nM	19
colorimetric assay	~175 nM	0.5 nM	20

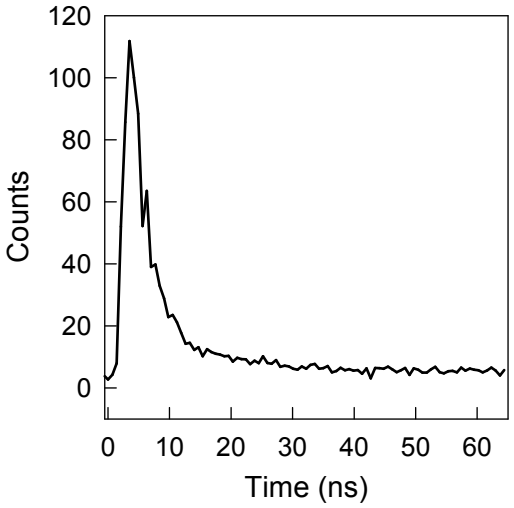

Fig. S1 Time-resolved decay of APBA-Lys-Au NCs. Life-time values obtained is plotted in the inset.

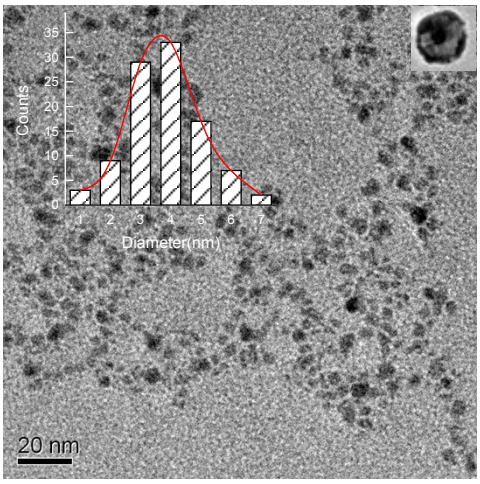

Fig. S2 TEM image of APBA-Lys-Au NCs. Inset: HRTEM image and size-distribution of APBA-Lys-Au NCs.

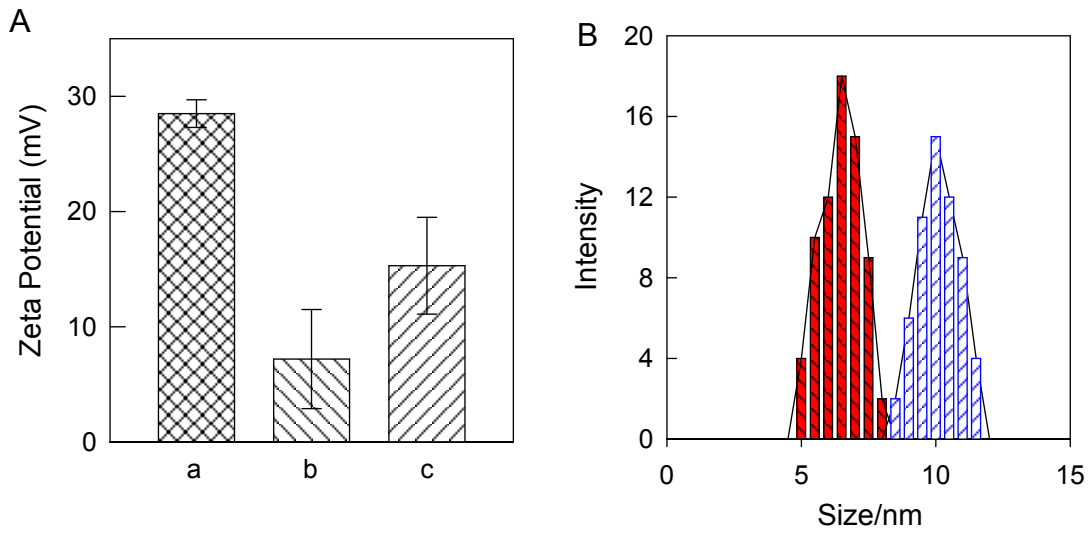

Fig. S3 (A) Zeta potential of Lys-Au NCs (a), APBA-Lys-Au NCs (b), and (b) + DA. (D) DLS of Lys-Au NCs (red) and APBA-Lys-Au NCs (blue).

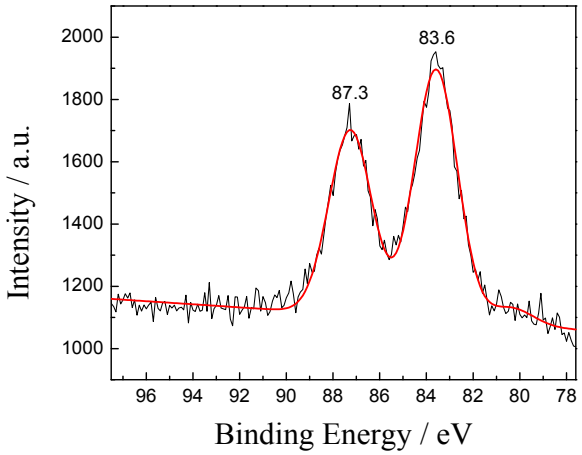

Fig. S4 XPS image of APBA-Lys-Au NCs.

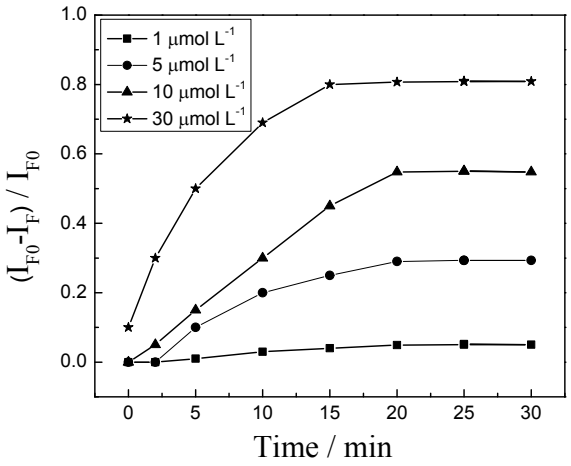

Fig. S5 The fluorescence intensity of APBA-Lys-Au NCs in the presence of various DA concentrations as a function of incubation time. Emission wavelength was 675 nm.

References

1 H. Wei, Z. Wang, L. Yang, S. Tian, C. Hou, Y. Lu, *Analyst*, 2010, **135**, 1406-1410.

2 S. Liu, F. Shi, X. Zhao, L. Chen and X. Su, *Biosens. Bioelectron.*, 2013, **47**, 379-384.