Supplementary Material (ESI) for Analyst
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Fluorescent Sensing of Cocaine Based on Structure Switching Aptamer, Gold Nanoparticles and Graphene Oxide

Yan Shi, Haichao Dai, Yujing Sun, Jingting Hu, Pengjuan Ni, and Zhuang Li*

Characterization of Au NPs and Au-C2

According to Beer's law, gold nanoparticles about 13 nm give a sharp plasmon absorption band centred at 520 nm. About one month later, the UV curve had a blue shift and an absorbance decrease because of the little aggregation of bare gold nanoparticles. After the modification of DNA strand, a red shift about a few nanometers observed. DNA strands could protect nanoparticles from aggregation during stored at 4 ℃.

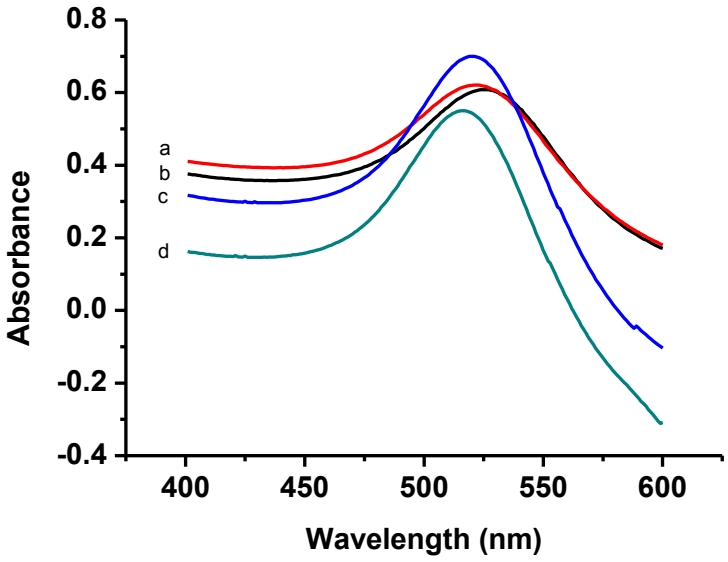

Fig. S1 UV curves of Au-C2 (a), Au NPs (c), and those after one month (b, d), respectively.

Preparation of graphene oxide (GO)

Briefly, 1.2 g of pure graphite powder (Alfa Aesar) was added to H_2SO_4 (48 mL) and $NaNO_3$ (0.75 g) in a 200 mL flask, and kept in an ice-water bath with vigorous

stirring by a magnetic stirring bar. Then, $KMnO_4$ (6 g) was added slowly with the temperature below 20 ºC. After 2 h stirring, DI water (100 mL) was added to the mixture in an ice bath, followed by slow addition of a 30 % H_2O_2 (8 mL) solution. The color was changed into brilliant yellow. The mixture was then filtered by a cellulose acetate membrane filter and washed with 1:10 aq. HCl and DI water (400 mL). To completely wash the graphite oxide flakes, the resultant graphite oxide was dissolved in water again and dialysised for one week to eliminate metal ions. After drying in air, the graphite flakes were sonicated with 100 W power in water for 0.5 h for the final store concentration of 1 mg/mL.

Elimination of noncovalent adsorbed probe C1 from go surface

The as-prepared glass slide was then immerged into 5 mM Tris buffer (pH=9.5) for 10 min. The complementary strands (C-C1, 1 μL, 9.7 μM) in 0.05 M PBS with 1 mM $MgCl_2$ were incubated for 1h at 42 ˚C, to form the double strands DNA. For that the double strands DNA have a weaker infinity than single strand DNA to GO surface, those double strands DNA of noncovalent binding were eliminated after a washing process, and the covalent binding ones were remained on GO surface. AFM images were obtained to investigate this process (Fig. S2). Before the hybridization, C1 interacted with GO in the two paths, the covalent and noncovalent modes (Fig. S2A). Once C-C1 was introduced, both covalent and noncovalent binding probe C1 formed a double strands structure (Fig. S2B). Since the adsorption strength of dsDNA was much weaker than that of ssDNA, those noncovalent probes could be eliminated through a washing process, remaining the covalent part. Therefore, the dsDNA covalent binding on GO surface were returned to ssDNA with an annealing process, through a heating step to 70 ˚C for 10 min in Tris buffer. This hybridization/dehybidization method eliminated the influence of the non-specific probe, giving more reliable results of cocaine detection. After adding C-C1, the morphology changed as the spiral double-strand DNA. Fig. S2C showed the final image of the covalent binding probe C1, which has one terminate linking on the edges or wrinkles of GO array, for that carboxy groups were proved there.

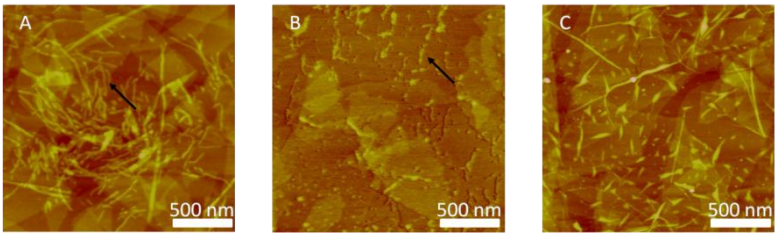

Fig. S2 The AFM images for the elimination of the noncovalent binding probe C1. (A) Probe C1 immobilized on GO surface through the two paths. (B) Double-strand DNA after the hybridization. The arrows in (A) and (B) were located on single and double strand DNA molecules. (C) The morphology of covalent binding probe C1. The scale and Z-range is 2 μm, 10 nm, respectively.

Removal of non-specific adsorption of Au-C2 from GO Surface

Similarly as above, Au-C2 also could adsorb on GO surface through π-π stacking, which makes the fluorescence intensity lower than it should be due to the quenching ability of the non-specific adsorbed Au NPs. Therefore, it is necessary to eliminate those non-specific binding Au-C2. Here, we used the complementary strand of C2 to construct double-strand DNA through hybridization/dehybidization method mentioned above, and then removed them through a washing process. Those Au NPs linked on GO surface through the recognition of cocaine and its aptamer was not affected in this step. As shown in Fig. S3A and B, a large amount of Au-NPs were adsorbed on C1 modified GO surface without cocaine, but after the interaction of C-C2, only a few Au NPs were remained. In the detection of cocaine, Au NPs could also be observed fewer through the hybridization method, shown in Fig. S3C and D.

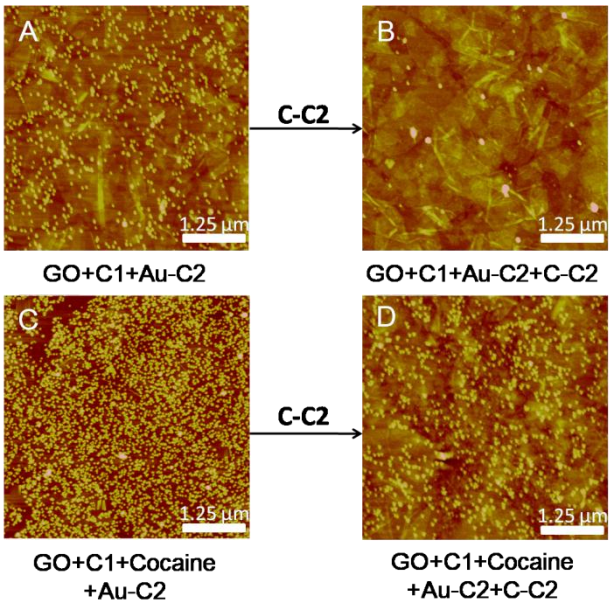

Fig. S3 AFM images of (A) C1 modified GO surfaced treated with Au-C2 complex. (B) Result after the treatment of C-C2 for the remove of non-specific interaction of Au-C2. (C)-(D) Cocaine detection without and with the treatment of C-C2. The scale for all images is 5 μm and Z-range is 30 nm.