Electronic Supplementary Material (ESI) for Analyst.


# Supporting Information

# Sensing Ultra-trace Dopamine by Restoration of Fluorescence on Locally Acidified Gold Nanoparticles

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**Silicon nanoparticles (SiNPs)-based method.**

SiNPs (2.3 nM) with diameter of 24 nm was added to hydrochloric acid to activate overnight. The obtained SiNPs were washed two times by centrifugation at 12000 rpm for 15 min and re-suspended in 3 mL water. After adjusting the pH to 9.0, cyanuric chloride (120 μL, 100 mM) was then dropped into the solution and keeping pH at 9.0 to incubate in the ice bath for 1.5 h. The obtained cyanuric chloride modified SiNPs were washed two times via centrifugation (12000 rpm, 15 min) to remove excess cyanuric chloride, and redispersed in 1.5 mL ultrapure water. Then, 4-hydroxyphenylboronic acid (HBA, 1.5 mL, 54 mM) was dropped into the solution, adjusted pH to 9.0 and then incubated overnight at 25 °C. The obtained HBA modified SiNPs was washed three times using water by centrifugation (12000 rpm, 15 min) to remove unreacted 4-hydroxyphenylboronic acid, and redispersed in 3 mL PB buffer (pH 6.5). Then 450 μL of the above solutions were added into the mixture of Neu5Ac (5 nM) and DA (10 nM) solution and shaken in the dark for 3 h at room temperature. The obtained SiNP-HBA-Neu5Ac|DA were obtained by centrifugation (12000 rpm, 15 min) to remove the supernatant and re-suspended in 460 μL Tris-HCl buffer (pH 9.0). Then 10 μL of 0.100 μg / mL fresh FITC solution was added and shaken in the dark for 1 h. After addition of 200 μL Tris-HCl buffer and ultrasonic for 2 s, the fluorescence spectra were measured. For comparison, GNPs (2.3 nM) with same diameter of 24 nm were used. The fluorescence spectra were measured and fluorescence restoring degree ($D_{rF}$) was compared in Figure. S1.

**Optimizing the concentration of MBA.**

The influence of the concentration of MBA on fluorescence intensity was investigated by mixing 1 mL as-prepared GNPs with 3 μL MBA at different concentrations ranging from 0 mM to

10 mM at room temperature for 4 h. The obtained GNP-MBA was washed two times with water via centrifugation (12000 rpm, 15 min) and re-suspended in Tris-HCl buffer (pH 9.0). Then 10 μL of 0.100 μg/mL fresh FITC solution was added to 450 μL GNPs-MBA and shaken at room temperature for 1 h. After addition of 200 μL Tris-HCl buffer and ultrasonic for 2 s, its fluorescence spectra were measured. The resulted fluorescence intensity varies with the concentration of MBA, as shown in Figure. S2, and saturation takes place above 3 mM. So in order to provide a close shield to suppress the non-specific adsorption and more binding sites for DA and Neu5Ac, the concentration of MBA is optimized and constant at 3 mM to realize the compact assemble

**Absorption spectra of the bare and modified GNPs.**

The absorption spectra of all the modified GNPs in every step, including bare GNPs, GNPs modified with 3 mM MBA (GNP-MBA), GNP-MBA modified with 5 nM Neu5Ac (GNP-MBA-Neu5Ac), GNP-MBA modified with 5 nM Neu5Ac and 10 nM DA (GNP-MBA-Neu5Ac|DA), and GNP-MBA-Neu5Ac|DA modified with 0.100 μg / mL FITC (GNP-MBA-Neu5Ac|DA-FITC), were measured as shown in Figure. S4.

**Selection of Neu5Ac.**

Different freshly prepared boron binding molecules (10 μL, 5 nM), such as ascorbic acid, glucose, 2-hydroxypropanoic acid, epinephrine, norepinephrine, chondroitin sulfate sodium salt, heparin sodium, and Neu5Ac were added into 450 μL of the previous GNP-MBA dispersed in PB buffer (pH 6.5), respectively, and shaken in the dark for 3 h at room temperature. The obtained particles were centrifuged at 12000 rpm for 15 min to remove the supernatant and re-suspended in 460 μL Tris-HCl buffer (pH 9.0). Then 10 μL of 0.100 μg / mL fresh FITC solution was added

and shaken in the dark for 1 h. After addition of 200 μL Tris-HCl buffer and ultrasonic for 2 s, the fluorescence spectra were collected timely in Figure. S5.

**Optimizing the amount of FITC.**

The influence of the concentration of FITC was investigated, and as shown in Figure. S6, the fluorescent intensity variation between 0 nM and 10 nM DA increases first with the concentration of FITC and then turns to a plateau at ca. 0.100 μg / mL (Figure. S6). FITC 0.100 μg / mL was adopted as probing concentration to compromise measuring cost and measuring stability.

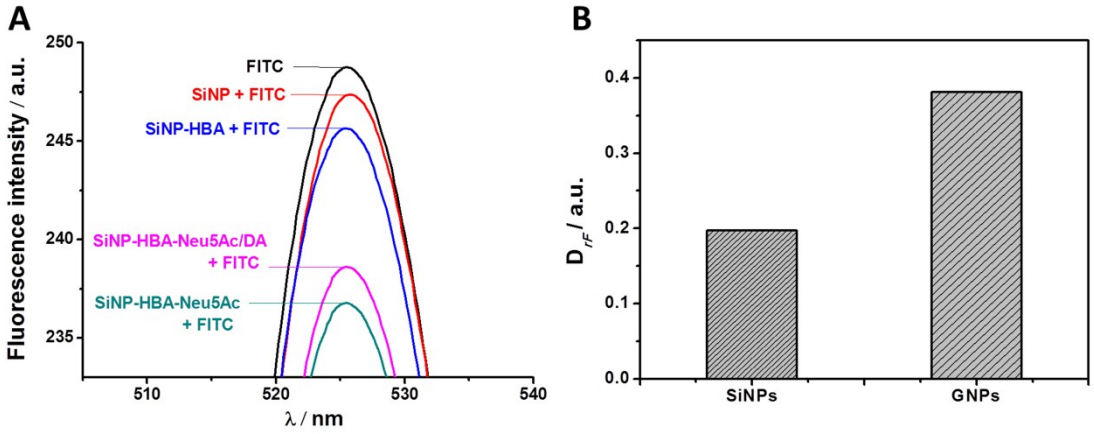


**Figure S1.** (A) Restoration of FITC fluorescence by DA after local acidification on HBA-coated silicon nanoparticles (SiNPs) with Neu5Ac; (B) Comparison of restoring degree, $D_{rF}$, by DA between HBA-coated silicon nanoparticles (SiNPs) and MBA-coated gold nanoparticles (GNPs) after acidification with Neu5Ac. The $D_{rF}$ is calculated by $\mathbf{D}_{rF} = (\mathbf{I}_{DA\text{-}added} - \mathbf{I}_{DA\text{-}free}) / \mathbf{I}_{DA\text{-}free}$, where **I** denotes the measured fluorescent intensity while the subscript "DA-added" means the addition of DA, and "DA-free" is meant without any addition of DA.

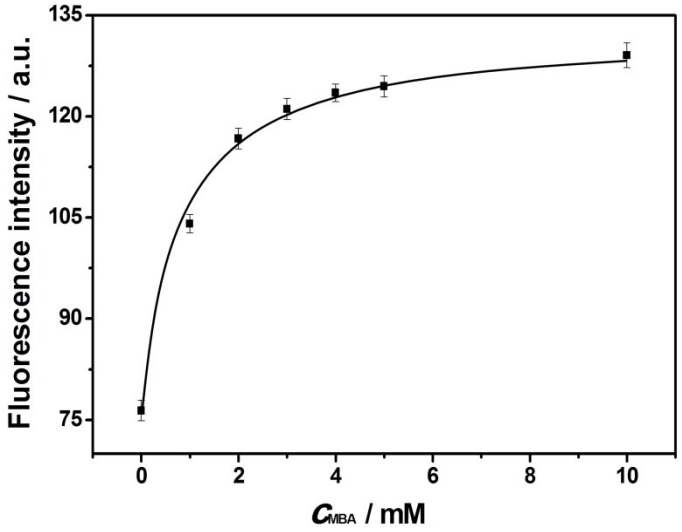


**Figure S2.** Plot of fluorescent intensity *vs.* concentration of MBA reacted with GNPs at 2.3 nM.

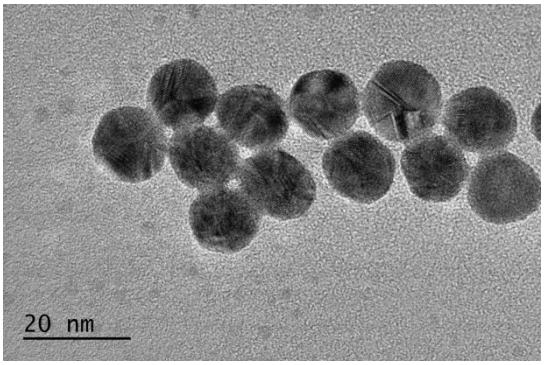


**Figure. S3** Transmission electron microscopy (TEM) of prepared GNPs.

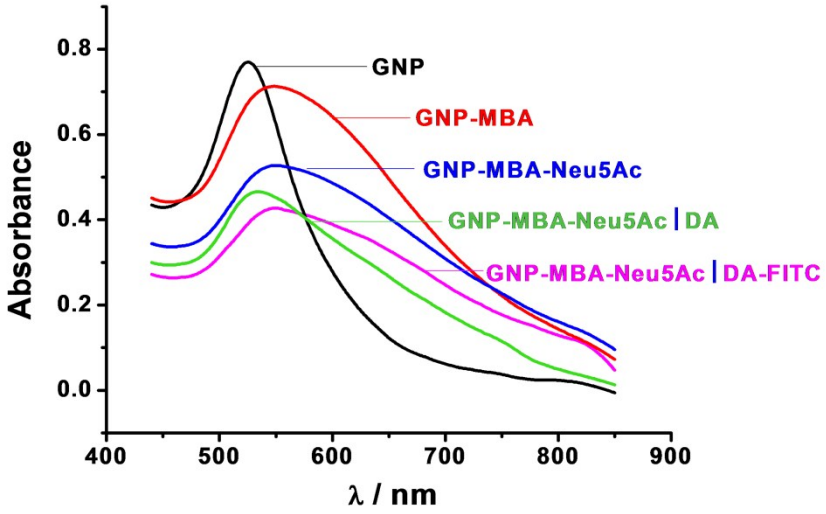


**Figure S4.** Absorption spectra of GNPs modified layer by layer measured in 10 nM PB at pH 6.5.

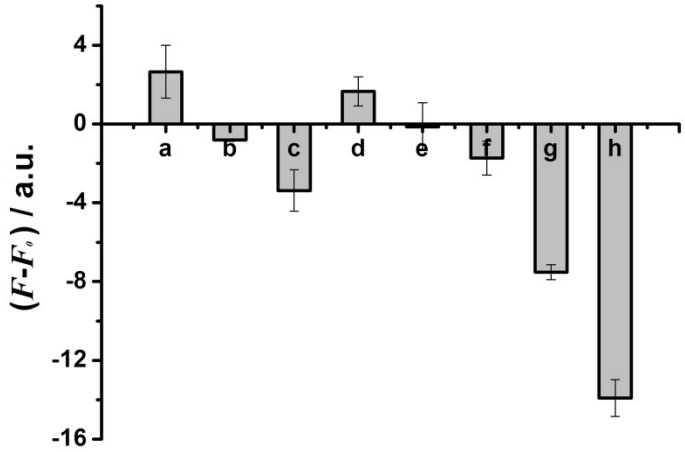


**Figure S5.** Fluorescence intensity change of sensor between different molecules modified (*F*) and nonmodified ($F_0$) GNP-MBA. (a) ascorbic acid, (b) glucose, (c) 2-hydroxypropanoic acid, (d) epinephrine, (e) norepinephrine, (f) chondroitin sulfate sodium salt, (g) heparin sodium, and (h) Neu5Ac with 5 nM concentration.

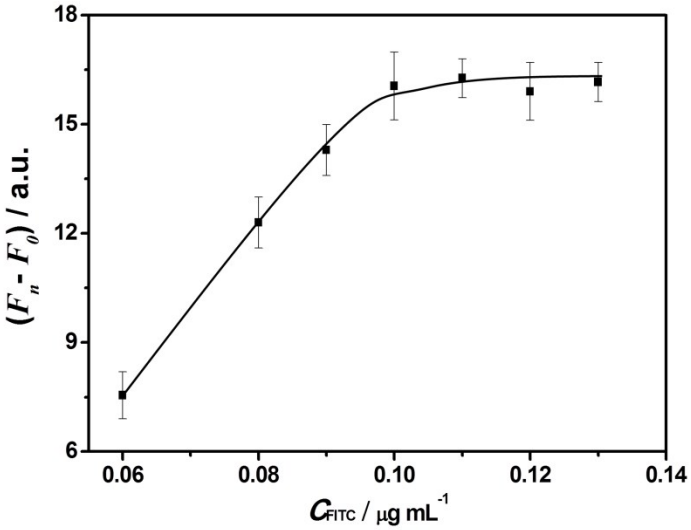


**Figure S6.** Plot of fluorescence intensity change $F_n$-$F_0$ ($F_n$ measured at 10 nM DA and $F_0$ measured at 0 nM DA) *vs.* the concentration of FITC.

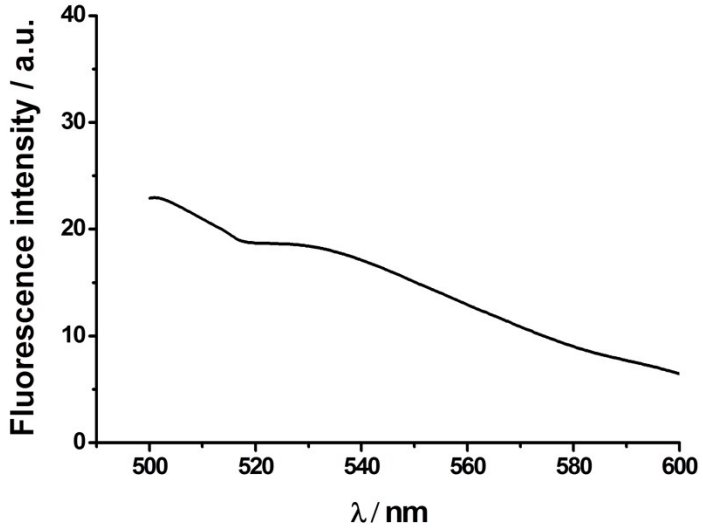


**Figure S7.** Fluorescent spectrum measured from washed mixture of MBA-coated GNPs, 5 nM Neu5Ac and 10 nM DA.

**Table S1** Comparison of this method with other fluorescent methods for DA detection [1-9].

| Method | Linear range | Detection limit | Reference |
|---|---|---|---|
| CDots-GNCs Fluorescence | 5 nM–180 nM | 2.9 nM | 1 |
| pDA NPs Fluorescence | 10 nM–5 μM | 5.5 nM | 2 |
| g-$C_3N_4$ NSs Fluorescence | 50 nM–8 μM | 18 nM | 3 |
| GODs-Fluorescence | 20 nM–200 nM | 15 nM | 4 |
| Synthesis of Fluorescence | - | 10 nM | 5 |
| pDA-GODs Fluorescence | - | 8 nM | 6 |
| InP/ZnS QDs Fluorescence | 5 nM–100 nM | 0.87 nM | 7 |
| APTMS-SiNPs Fluorescence | 5 nM–10 μM | 0.3 nM | 8 |
| Reactional Fluorescence | 10 nM–20 μM | 1.8 nM | 9 |
| GNP-Fluorescence | 0.1 nM–0.1 μM | 0.05 nM | This work |

**CDots-GNCs**: carbon dots-gold nanoclusters hybrid; **pDA NPs:** polydopamine nanoparticles
**g-$C_3N_4$ NSs**: graphite-like carbon nitride nanosheets; **GODs**: graphene quantum dots
**InP/ZnS QDs:** indium sulphide/zinc sulfide quantum dots
**APTMS-SiNPs:** (3-Aminopropyl) trimethoxysilane-modified silicon nanoparticles

## References


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