Paramagnetic Relaxation Based Biosensor for Selective Dopamine Detection

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Supporting Information

Chemicals

(Trimethoxysilylpropyl)ethyldiaminetriacetic acid trisodium salt (TMS-EDTA) (35 wt% solution in water) was purchased from Gelest. Tetraethylorthosilicate (TEOS), Triton X-100 (TX-100), n-hexanol, cyclohexane, dopamine hydrochloride, ferric chloride, ammonium hydroxide (30wt%) and glacial acetic acid were from Sigma-Aldrich. All chemicals were used without further purification. Deionized (DI) water was used for the preparation of all solutions.

Synthesis of paramagnetic \( \text{Fe}^{3+} \)-chelated \( \text{SiO}_2 \) nanoparticles (\( \text{SiO}_2@\text{TMS-EDTA@Fe}^{3+} \))

Paramagnetic \( \text{SiO}_2@\text{TMS-EDTA@Fe}^{3+} \) nanoparticles were prepared in two steps using a modified version of the previously published protocol [S1]. First, \( \text{SiO}_2@\text{TMS-EDTA} \) nanoparticles with EDTA groups on surface were synthesized by mixing 1.77 g Triton X-100, 7.5 mL cyclohexane, 1.6 mL n-hexanol, and 480 µL DI water in a glass vial and stirring for 5 min. Next, 60 µL of \( \text{NH}_4\text{OH} \) was added to the microemulsion and stirred for 20 min, followed by the addition of 50 µL TEOS. The mixture was stirred at room temperature for 24 h. Then, 50 µL of TEOS was added to the microemulsion and stirred for 30 min, and finally 25 µL of TMS-
EDTA was added, followed by another 24 h stirring. Subsequently, approximately 20 mL of acetone was added to break down the microemulsion system. SiO₂@TMS-EDTA nanoparticles were recovered by centrifuging at 14000 rpm for 20 min, and then washed three times with acetone, ethanol and DI water, respectively. The resulting SiO₂@TMS-EDTA nanoparticles were dispersed in DI water.

Paramagnetic property was introduced to the SiO₂@TMS-EDTA nanoparticles by mixing excess amount of 0.1 M FeCl₃ solution and stirring overnight. Afterwards, nanoparticles were washed three times with DI water and then dispersed in acetate buffer (pH 4) for storage.

**ICP-MS measurements**

SiO₂@TMS-EDTA@Fe³⁺ nanoparticle samples were prepared in 2% trace grade nitric acid, which can release Fe³⁺ into the solution. A standard addition plot was made for SiO₂@TMS-EDTA@Fe³⁺ nanoparticle samples and acetate buffer (as control). The released Fe³⁺ concentration of each sample was measured by a triple quadrupole ICP-MS (ICP-QQQ, Agilent Technologies). Signal from the control was subtracted from that of each sample.

**Paramagnetic Relaxation Assays**

For the relaxation measurements, Carr-Purcell-Meiboom-Gill (CPMG) spin-echo pulse sequences were used to limit the effect of magnetic inhomogeneity because of instrument [S2,S3]. Transverse relaxation times (T₂) were measured at 1.41 T by a Bruker Minispec mq60
relaxometer operating at 40 °C without any washing step [S4]. Briefly, fresh dopamine stock solution was prepared and serially diluted. In a typical run, $T_2$ measurements of the SiO$_2$@TMS-EDTA@Fe$^{3+}$ nanoparticles in acetate buffer were done before target addition. Diluted dopamine solutions were added to the SiO$_2$@TMS-EDTA@Fe$^{3+}$ nanoparticle solution, and $T_2$ measurements were conducted after ~4 hr of incubation at 40 °C. The change of $T_2$ ($\Delta T_2$) was obtained. In the case of using aCSF as solvent matrix, aCSF solutions containing dopamine and the SiO$_2$@TMS-EDTA@Fe$^{3+}$ nanoparticles were prepared separately. Then calculated amounts of dopamine/aCSF solution were added into SiO$_2$@TMS-EDTA@Fe$^{3+}$/aCSF solution to obtain different concentrations of dopamine, and incubated for ~4 hr at 40 °C before $T_2$ measurement.

Figure S1. Photograph of SiO$_2$@TMS-EDTA and SiO$_2$@TMS-EDTA@Fe$^{3+}$ nanoparticles with dopamine.
Figure S2. $\Delta T_2\%$ as a function of analyte concentration for samples in acetate buffer containing dopamine, sucrose, and glucose, respectively.

REFERENCES


