Supporting Information

Highly sensitive and selective fluorescent detection of cerebra lead (II) based on GQD-DMA/tryptophan compound system

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Experimental Section

Reagents and materials. Graphite powder, H_2O_2, $SOCl_2$ were obtained from Sinopharm Chemical Regent Company (Shanghai, China). $NaNO_3$, $KMnO_4$ were purchased from Shanghai fine chemicals Ltd. (Shanghai, China). Tryptophan (Trp) was purchased from Shanghai Bio Science & Technology Co., Ltd. (Shanghai, China). H_2SO_4, HCl, benzene, N, N-dimethyl formamide (DMF) and triethylamine were obtained from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Bis(2-chloroethyl)-amine hydrochloride, ethanethiol were purchased from Sigma-Adrich (USA). Other chemicals used were of analytical grade and purchased from Sinopharm Chemical Regent Company (Shanghai, China). All aqueous solutions were prepared with ultrapure water (>18 MΩ cm) obtained from a Milli-Q Plus system (Millipore). All solvents and chemicals in this work were used without further purification unless otherwise stated.

Instrumentation. Fluorescence experiments were carried out using a Hitachi F-7000 Fluorescence Spectrophotometer with a 150 W xenon lamp (Hitachi, Japan). Samples for absorption and emission measurements were conducted in 1 cm×1 cm quartz cuvette. The slit width of excitation and emission were both 5 nm, and the scan speed was set as 1200 nm/min. Transmission electron microscopy (TEM) images were obtained using a JEOL2100F electron microscope (JEOL, Tokyo, Japan). The FT-IR spectra were obtained with a Nexus 670 optical bench (Nicolet, USA). AFM images were taken using a multimode 8 atomic force microscope (Bruker Corporation, Germany). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out by IRIS Intrepid II XSP (Thermo Electron Corporation, USA).

Animal experiments for microdialysis. All procedures involving animals were conducted with the approval of the Animal Ethics Committee in ECNU, China. Male rats (weight ranges from 250 to 300 g) were purchased from Shanghai SLAC Laboratory animal Co. Ltd and acclimatized for 4 days. Then the rats were anesthetized with chloral hydrate (initial dose of 300 mg/kg (i.p.) with additional doses of 50 mg/kg (i.p.) as needed to maintain anesthesia) and wrapped in a homeothermic blanket (Beijing Tide-Gene Biotechnology Development Center). The rats were placed in a stereotaxic frame (Beijing Tide-Gene Biotechnology Development Center) with the incisor bar set at 5 mm above the interaural line and appropriately placed holes were drilled through the skull. The microdialysis probe (CMA/110/111 Tub) was implanted in the striatum at the site of 2.5 mm anterior to bregma, 2.5 mm lateral from midline, and 7.0 mm below dura. In order to reduce the injury to the rat, the microdialysis probe should be implanted into the striatum of rats

slowly within 30 min with special care. The microdialysis probes were implanted into the striatum of rats and perfused with aCSF solution at 2.0 μL/min for at least 90 min for equilibration and the injury recovery. After that, 50 μL of brain microdialysates were collected from the anesthetized rat brain striatum.

Synthesis of GO. GO was prepared using a modification of Hummers and Offeman's method[1] from natural graphite powders. In the reaction, 0.5 g of graphite powders, 0.5 g of $NaNO_3$, and 23 mL of concentrated H_2SO_4 were mixed together and stirred in an ice bath for several minutes. Then, 3 g of $KMnO_4$ was slowly added (in ten minutes). Subsequently, the solution was transferred to a 35 °C oil bath and stirred for about 2 h. Next, 40 mL of water was added dropwise under room temperature, and the solution was stirred for 30 min while the temperature was raised to 90 ± 5 °C. Finally, 100 mL of water was added, followed by the slow addition of 3mL of H_2O_2 (30%), turning the color of the solution from dark brown to yellow. After that the solution was filtered and washed with 200 mL of 1 mol/L HCl and 200 mL of water for two times respectively. The final sediment was dried under 60 °C for 24 h.

Synthesis of 3,9-Dithia-6-monoazaundecane (DMA). Under a nitrogen atmosphere, 4.6 g of sodium was dissolved in 200 mL of ethanol, and 7.44 g of ethanethiol was added to the solution. An 100 mL ethanol solution of 7.14 g bis(2-chloroethyl)-amine hydrochloride was added dropwise with refluxing, and the reaction mixture was refluxed for 2 h under a nitrogen atmosphere. After the reaction was completed, the solvent was evaporated in vacuo and then water was added to the residue. The product was extracted with chloroform for twice, and the extract was dried over $MgSO_4$. After removal of the solvent, the crude product was distilled in vacuo under 170-180 °C to obtain a colorless liquid .[2]

Synthesis of GO-DMA. Briefly, 0.1 g of GO, 10 mL of $SOCl_2$, 2 mL of benzene were mixed together and stirred under 70 °C for 24 h.[3] At the end of the reaction, the obtained solid (GO-Cl) was washed with ultra-dried tetrahydrofuran (THF) for two times and dried under 60 °C for 24h. Next, in the presence of 10 mL of DMF, 30 mg of the GO-Cl and 0.5 mL of triethylamine were allowed to react with 9.2 mg DMA under 130 °C for 72 h to obtain the GO-DMA. After the reaction, the solution was cooled to room temperature and centrifuged to remove the supernate. The excess DMA and other impurities were removed through three washing cycles that included sonication, filtration (discarding the filtrate), re-suspending the solid in 5 mL of DMF each time. The precipitate was washed with a small quantity of H_2O to remove $Et_3N\cdot HCl$.

Synthesis of GQD-DMA. 15 mg of GO-DMA was dispersed in 12 mL of ultra-pure water. Then the solution was transferred to a 20 mL of poly (tetrafluoroethylene) (Teflon)-lined autoclave and heated under 200 °C for 24 h. After the reaction was completed, the reactor was cooled to room temperature. The product was filtered to obtain light yellow transparent solution and the black precipitates were discarded. The solid samples can be obtained by evaporating the solvents.

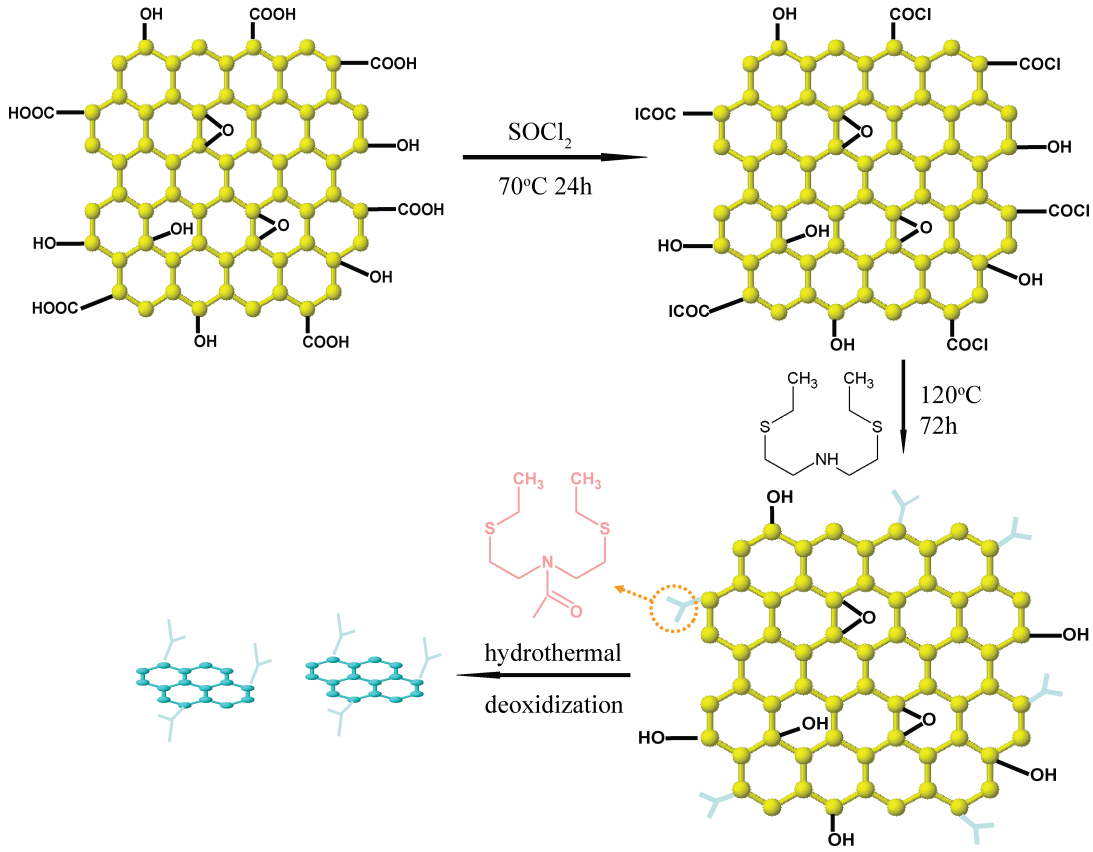

Fig. S1 Schematic Illustration of the Synthetic Steps.

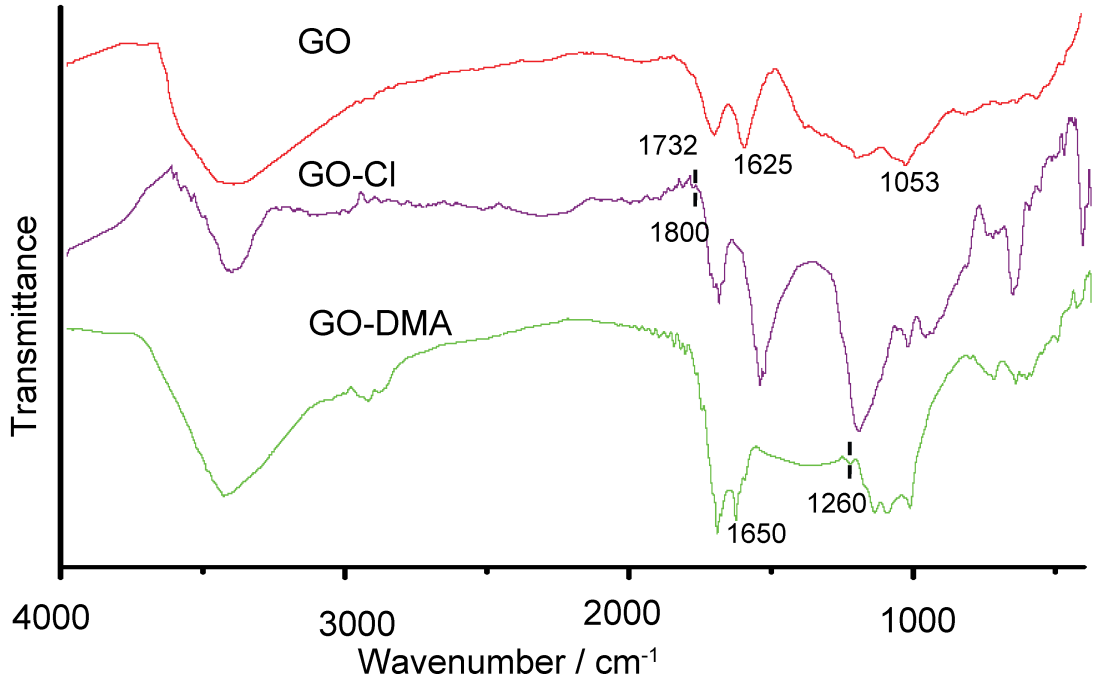

Fig. S2. I-R spectra for GO, GO-Cl, GQD-DMA.

The modification in each synthesized procedure was confirmed by fourier transform infrared spectrometer (FT-IR) spectroscopy. Fig. S2 shows FTIR spectra of GO, GO-Cl, and GQD-DMA. In the spectrum of GO, the broad peak at 3000-3700 cm-$^{-1}$ corresponds to the –OH of the hydroxyl group, the peaks at 1732 cm^{-1} and 1625 cm^{-1} are attributed to the C=O stretching mode of COOH groups, the peaks at 1053 cm^{-1} is ascribed to alkoxy C-O functional groups. In the spectrum of GO-Cl, the broad peak at 3000-3700 cm^{-1} almost disappeared and a new broadband emerged at 1800 cm^{-1} indicates the reaction between COOH and $SOCl_2$. In the spectrum of GQD-DMA, the stretching band of amide C-N peak appears at 1260 cm^{-1} and the stretching band of C=O peak appears at 1650 cm^{-1}. These results clearly indicate that the GQD-DMA has been covalently bonded to the GQD via the amide linkage.

Samples	The present methods mean ± S.D. (μM)	ICP-AES Mean ± S.D. (μM)
Rat 1	0.25 ± 0.04	0.26± 0.05
Rat 2	0.26± 0.02	0.26 ± 0.02

Table S1. Sensing of Pb^{2+} in cerebral spinal fluid of rat samples using the presented method and ICP-AES.

References

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