Electronic Supplementary Information

Section 1. Instruments and Reagents

The indium tin oxide (ITO) glass, purchased from Guluo Glass Electronics Co. Ltd. (Luoyang, P. R. China), was cut into 5.0 cm × 1.0 cm pieces to serve as the substrate electrode. The ECL experiments were carried out with a lab-built instrument which is reported in previous work.[1] The equipment is an embedded system mainly included software drove digital pulse generator, DAD interface, potentiostat, ECL detector (a photomultiplier tube, powered with a -1000V voltage) and a three electrode system). The electrochemical part provides pulsed voltage for electrolysis of ECL probe, where the upper/lower limiting potentials and the duration are all set by the computer. The photomultiplier tube detected ECL photocurrent is amplified, i-V transferred and converted via the DAD interface into computer. An S-4700 scanning electron microscope (SEM) (Hitachi, Japan) and a Tecnai G20 transmission electron microscope (TEM) (FEI, USA) were applied to observing the size, morphology and distribution of the nanomaterials. X-ray diffraction (XRD) spectra were recorded on D2 Phaser (Bruker, Germany) with Cu Kα radiation (λ=1.542 Å). A Nicolet 550 Spectrometer (Thermo Fisher Scientific, USA) carried out the Fourier transform infrared (FTIR) spectroscopy. The diffusive reflected UV-Visible spectra was recorded by MPC-3100 instrument (Shimadzu, Japan). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were performed with an RST-5200 Electrochemical Workstation (Risetest Instruments Co. Ltd., Suzhou, P. R. China).

Recombinant human α-synuclein protein aggregation was purchased from Abcam PLC (Cambridge, UK). The thiolated α-syn oligomer aptamer (5’-HS-$(CH_2)_6$-

TTTTTGGTGGCTGGAGGGGGCGCGAACG-3’) and carboxylated α-syn oligomer aptamer (5’-HOOC-TTTTTGGTGGCTGGAGGGGGCGCGAACG-3’) were custom made in Sangon Biotech. Co., Ltd. (Shanghai, P. R. China). Luminol was purchased from Fluka Chem. Co. (USA). Polyvinylpyrrolidone K30 (PVP) was supplied from Dalian Meilun Biotechnology Co., Ltd. (Dalian, P. R. China) and 2-aminoterephthalic acid (NH_2-H_2BDC) was provided by Chemsoon Co., Ltd. (Shanghai, P. R. China). Copper nitrate-trihydrate ($Cu(NO_3)_2$) was offered by Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, P. R. China). 3-aminopropyltrimethoxysilane (APTMS) was bought from Aladdin Industrial Co., Ltd. (Shanghai, P. R. China). Glutaraldehyde was provided by Alfa Aesar (China) Chemical Co., Ltd. (Shanghai, P. R. China). 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) was purchased from Yeasen Biotech Co., Ltd. (Shanghai, P. R. China) and N-hydroxysuccinimide (NHS) were supplied by Shanghai Macklin Biochemical Co., Ltd (Shanghai, P. R. China). Bovine serum albumin (BSA), chloroauric acid ($HAuCl_4 \cdot 4H_2O$), tris(hydroxymethyl)aminomethane (Tris), $NaBH_4$, N,N-dimethylformamide (DMF) and other chemicals were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P. R. China). All reagents were put to use as received without further purification.

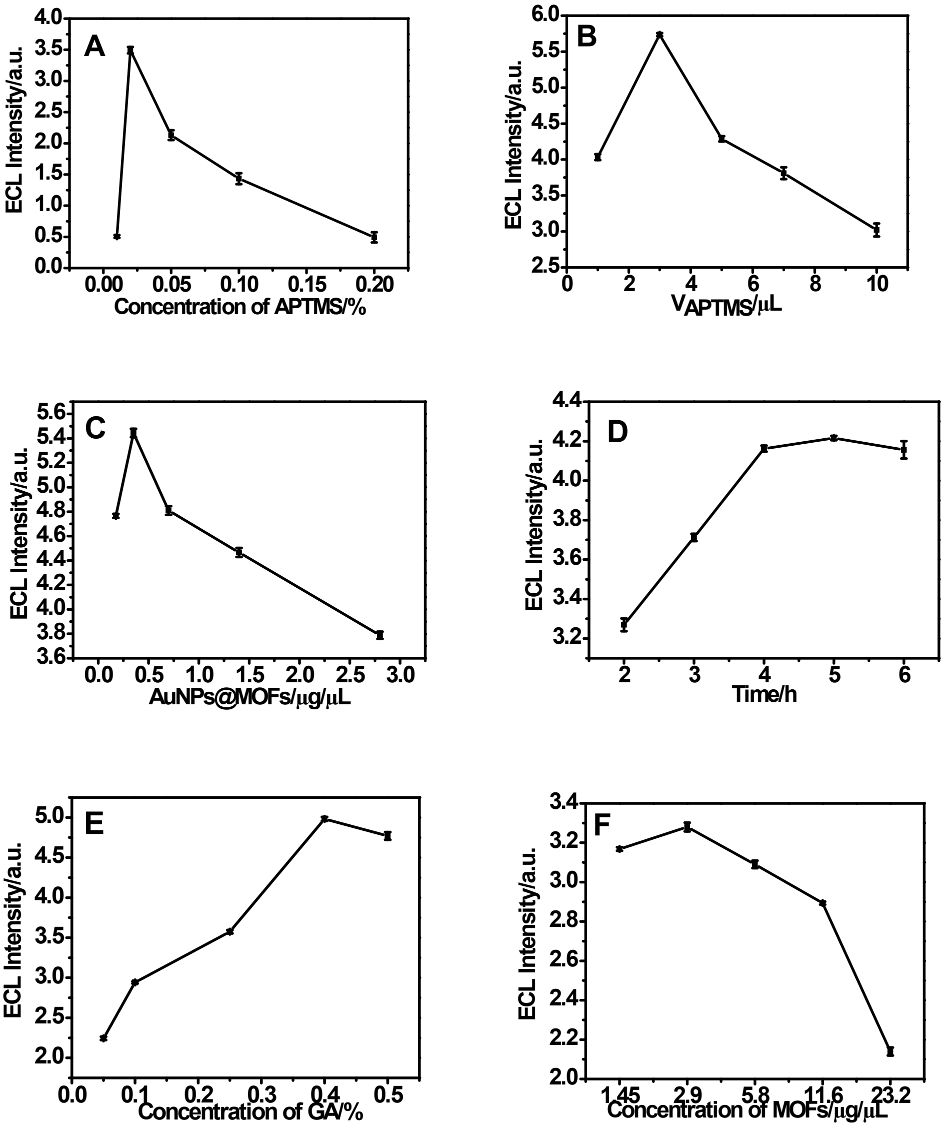
The formulation of the buffer served for α-syn oligomer is 0.15 M NaCl - 20 mM Tris (pH = 7.5). 1×10^{-5} M luminol diluted with 0.2 M phosphate buffer (pH = 8.0) was used for ECL detection. Glutaraldehyde was diluted by 0.2 M phosphate buffer (pH = 7.4). Ultrapure water (18.2 MΩ·cm of resistivity) is used throughout the experiments obtained from an ALH-6000-U water purification system (Aquapro, P. R. China).

Section 2. Synthesis of Cu-MOFs

The synthesis and purification of Cu-MOFs are as follows. 0.2 g PVP was dissolved in the mixture of 4 mL DMF and 4 mL ethanol. Another 4 mL DMF with 18.1 mg $Cu(NO_3)_2$ and 5.4 mg NH_2-H_2BDC was merged into aforesaid solution. The entire mixed solution was sonicated for 30 minutes, then placed in a Teflon-lined autoclave container and reacted at 100 °C for 8 h. The product was centrifuged at 4000 rpm for 15 minutes and collected. The above precipitation was dispersed in 20 ml DMF and purified by distillation at 100 °C for 8 h. The finally obtained Cu-MOFs was then washed with DMF, collected by centrifugation again and dispersed in 2 ml of ultrapure water for subsequent use.

Section 3. Optimal conditions for the decoration of MOFs materials on ITO

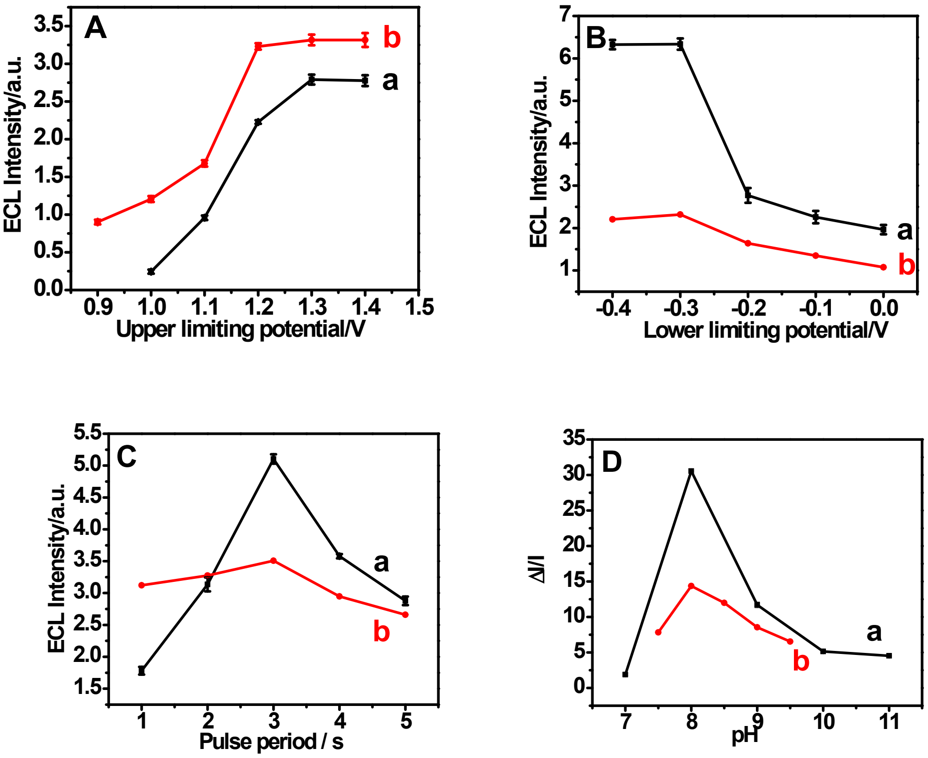
The AuNPs@Cu-MOFs or Cu-MOFs modified ITO glass was used as a basal electrode for the aptasensor, so it was necessary to optimize the conditions of their preparation. SFig. 1 shows the results of the optimization.



SFig. 1 The optimization of fabrication conditions of (A) the concentration of APTMS solution, (B) the volume of APTMS solution; (C) the solid content of AuNPs@Cu-MOFs in dispersoid and (D) the time of decoration for AuNPs@Cu-MOFs/ITO. The optimized conditions of (E) the concentration of GA solution and (F) the solid content of Cu-MOFs in dispersoid for Cu-MOFs/ITO.

Section 4. The optimization of conditions for ECL detection

There are some conditions must be optimized for obtaining best ECL signal of luminol on electrode including upper and lower limiting potentials, pulse period of electrolysis and pH value of buffer solution. SFig. 2 displays the results of the optimization.



SFig. 2 The optimization of ECL detection condition for AuNPs@Cu-MOFs/ITO (curve a) and Cu-MOFs/ITO (curve b): (A) upper /(B) lower limiting potential, (C) pulse period and (D) pH of the buffer solution.

Section 5. The band gap data of ECL enhancing materials

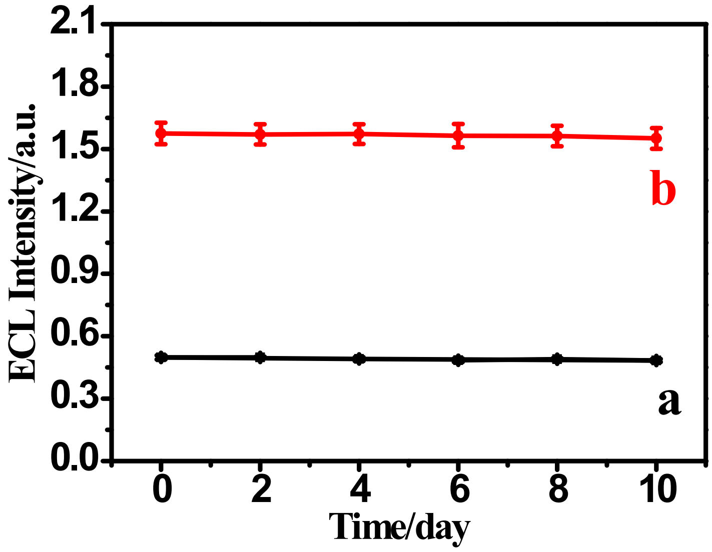
STable 1 listed the data of band gap of some materials used for ECL. It was not difficult to find through the table that ECL enhancing materials tended to have a small band gap. The conclusion from previous investigations is smaller band gap induce more significantly improved sensitivity.[1-4] Thus we can understand the causation of high sensitivity of these aptasensors using MOFs materials.

STable 1. The data of band gap of some ECL enhancing materials

Materials	Band gap	References
TiO_2	3.44 eV	[1]
Au/TiO_2	3.31 eV	[2]
AgS:Mn QDs	2.83 eV	[3]
$g\text{-}C_3N_4$	2.70 eV	[4]
Cu-MOFs	2.92 eV	This work
AuNPs@Cu-MOFs	2.69 eV	This work

Section 6. The stability of two aptasensors

In order to check the stability of the sensor, we stored it in the refrigerator for 10 days and measured their ECL signal every two days. The results are shown in the SFig. 3. It can be observed that the ECL signal has not changed significantly, which proved the good stability of two aptasensors.



SFig. 3 The ECL signal of aptasensors every two days (a: Sensor 1; b: Sensor 2).

Reference

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