Electronic supplementary information

Transition metal doping boosting paper-based photoelectrochemical immunosensing for neurofilament light chain protein detection

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Experimental Characterization. The confirmation of morphology was obtained under a transmission electron microscope (TEM, FEI Talos F200s). UV-vis absorption spectra were recorded by the Infinite M200 Pro NanoQuant (Tecan, Switzerland).

Preparation of mAb_1-Coated Microplate. Monoclonal antibodies to NEFL were prepared and bonded in microtiter plates as follows. The purchased mAb_1 (50 μL per well, 10 μg mL^{-1}) was added into a high-binding 96-well microplate containing sodium carbonate buffer (0.05 M, pH 9.6), and then incubated 24 h at 4 °C. A plastic film is wrapped over the microplate to prevent evaporation of the liquid. The completed incubated microplates were removed and washed three times with buffer (pH 7.4) buffer containing 0.05% Tween 20 (v/v). This was followed by incubation for 1 h by adding closure buffer (300 uL of PBS solution per well (10 mM, pH 7.4) including 1.0 wt % BSA). The aforementioned prepared microtiter plates were prepared for the NEFL assay.

Preparation of Glucose Oxidase and Detection Antibody-Conjugated Au NP (GOx-Au NP-pAb_2). GOx-Au NP-pAb_2 conjugates were prepared according to our previous reports. Firstly, gold colloids (5.0 mL, 5.0 ng mL^{-1}) were adjusted to pH 9.5 by using 0.1 M Na_2CO_3 aqueous solution. Then, 200 μL of GOx (0.5 mg mL^{-1}) and 50 μL of pAb_2 (0.5 mg mL^{-1}) were injected into colloidal gold nanoparticles and gently shaken for 60 min at room temperature on a shaker (MS, IKA GmbH, Staufen, Germany). 100 μL of polyethylene glycol (1.0 wt %) was added into the suspension and the mixture was further incubated for 12 h at 4 ℃. Finally, GOx-Au NP-pAb_2 conjugates were obtained by centrifugation at 4 ℃ (10 min, 13 000 g), and dispersed in 1.0 mL of 2 mM sodium carbonate solution ($C_{[Au\ NP]} \approx 25$ ng mL^{-1}) containing 1.0 wt % BSA and 0.1 wt % sodium azide, pH 7.4, and stored at 4 ℃ for further use.

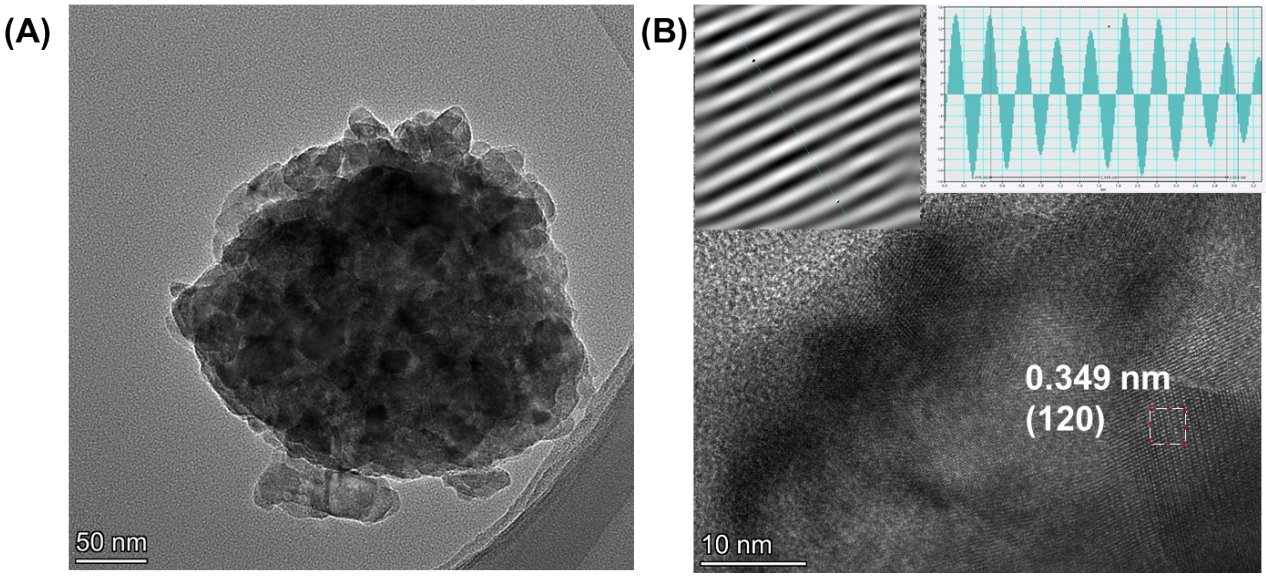

Figure S1. (A) TEM image of synthesized self-assembled TiO_2 nanoparticles and (B) corresponding high-resolution TEM image.

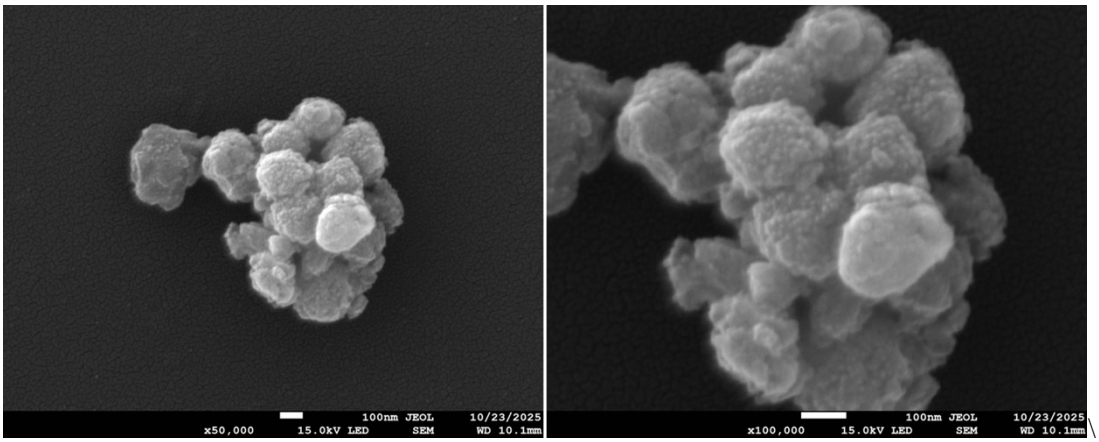

Figure S2. SEM image of synthesized self-assembled TiO_2 nanoparticles and corresponding high-resolution (10000×) SEM image.

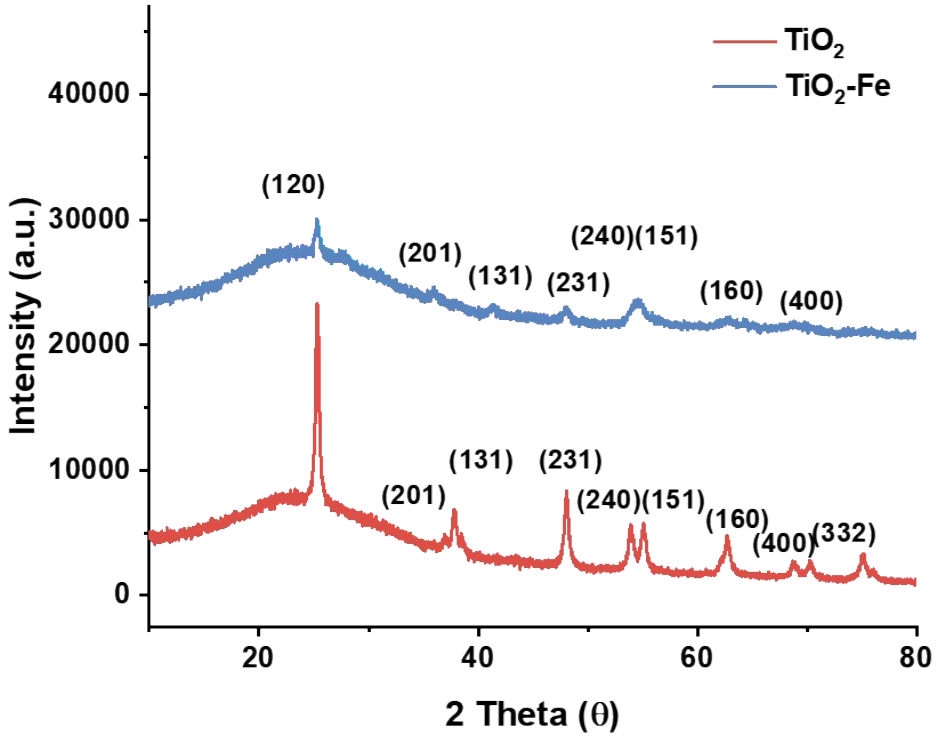

Figure S3. XRD patterns of synthesized self-assembled TiO_2 nanoparticles and TiO_2-Fe.

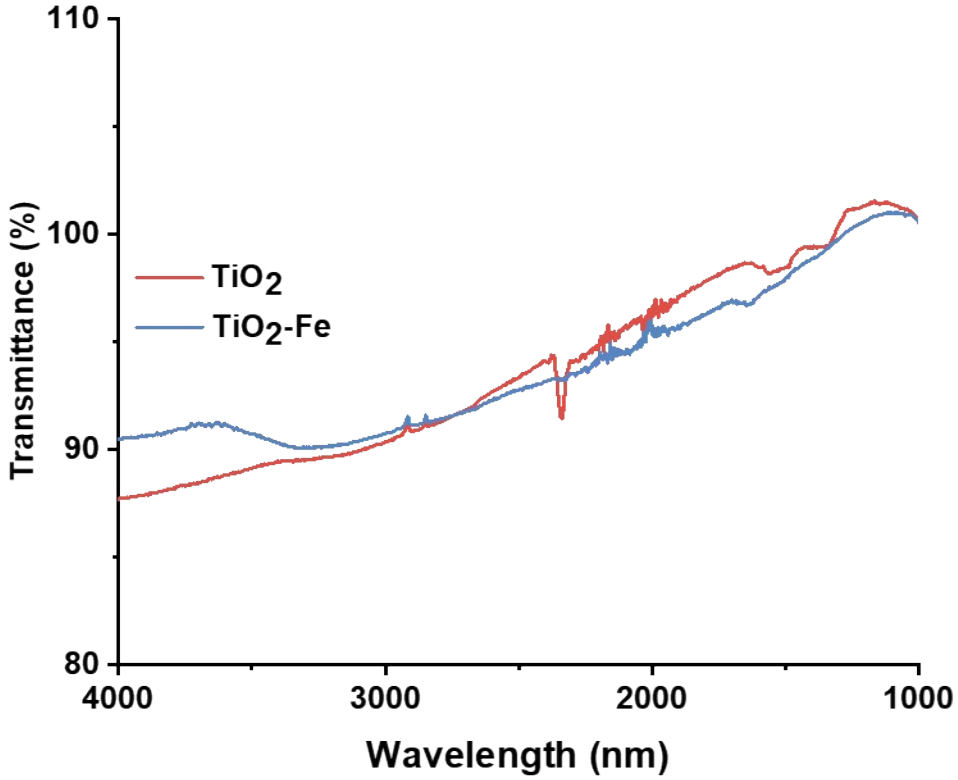

Figure S4. FT-IR spectra of synthetically self-assembled TiO_2 nanoparticles and TiO_2-Fe.

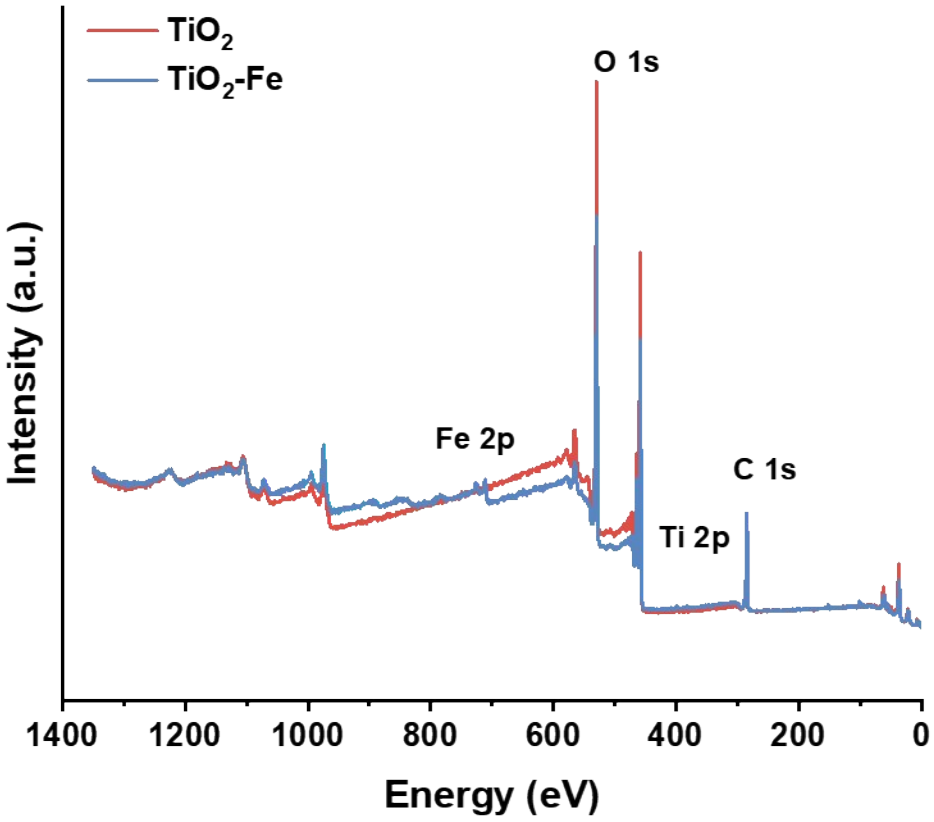

Figure S5. XPS spectra of synthesized self-assembled TiO_2 nanoparticles and TiO_2-Fe.

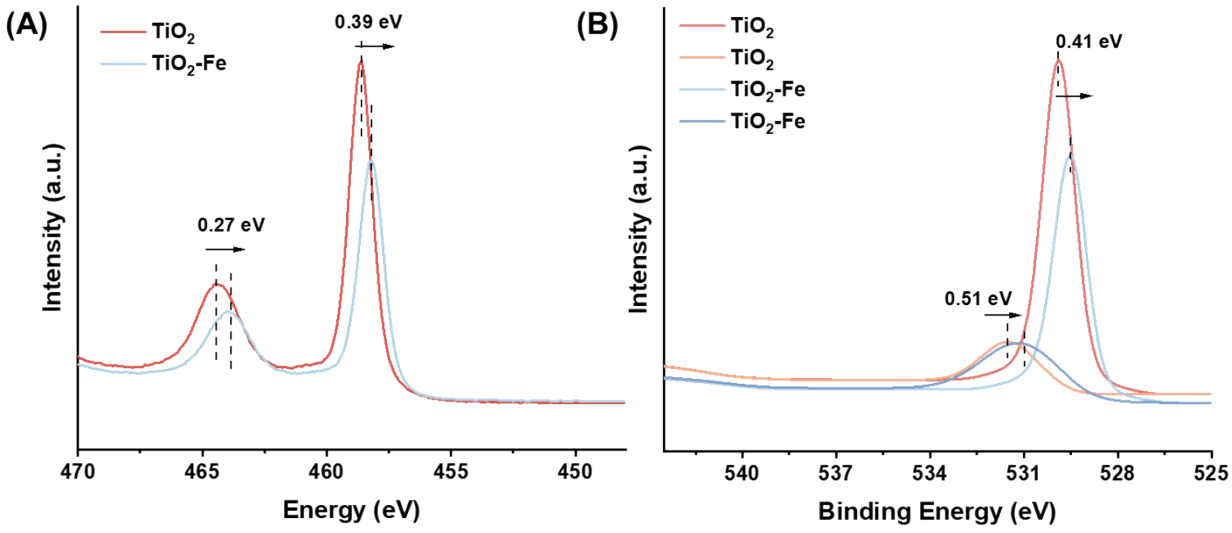

Figure S6. High-resolution XPS spectra of (A) Ti and (B) O.

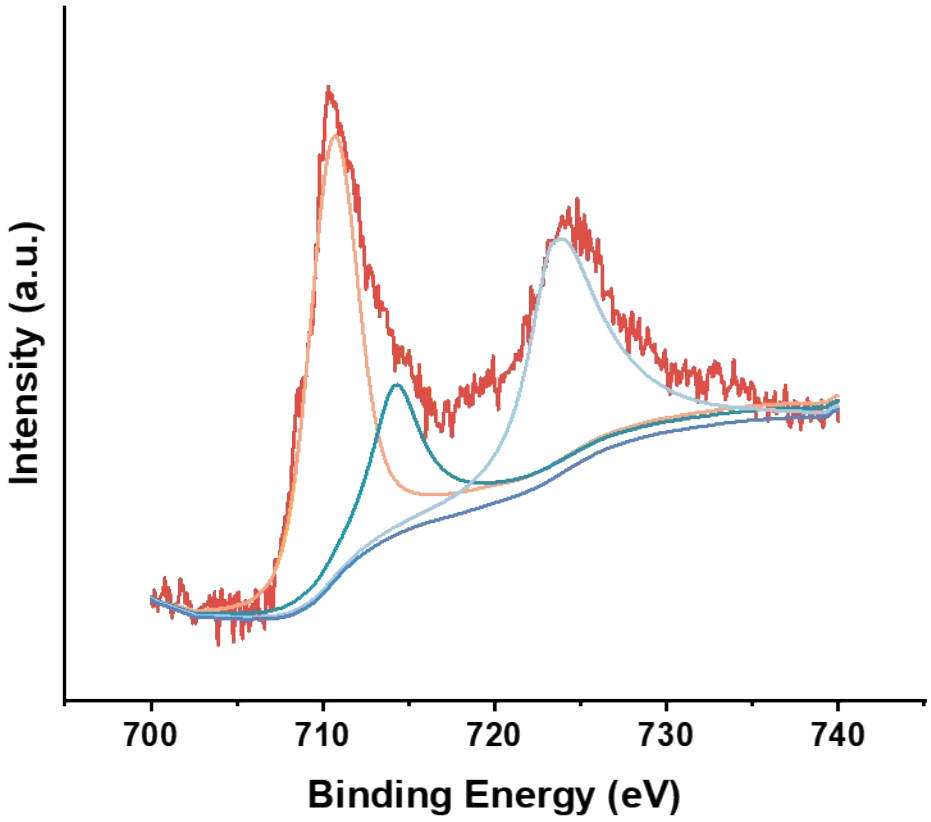

Figure S7. High-resolution fine-scale XPS spectra of the Fe 2p orbital.

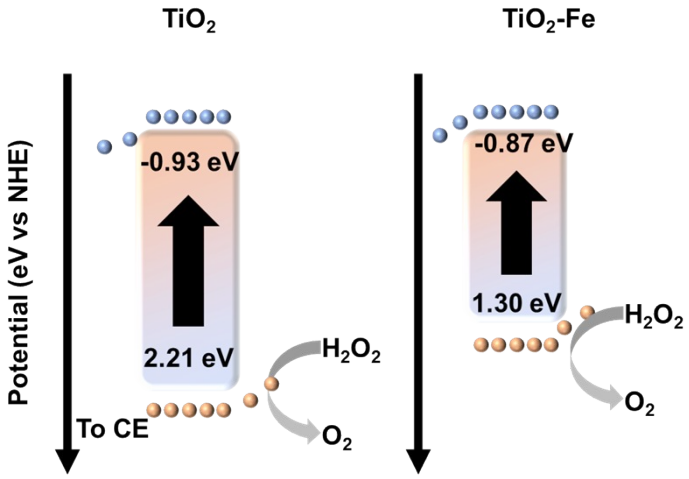

Figure S8. Schematic diagram of energy level orbitals for the synthesized photocatalyst.

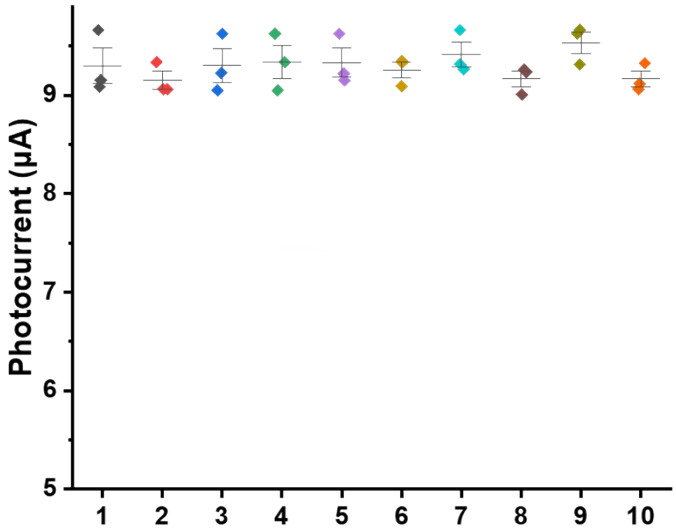

Figure S9. Photocurrent stability after repeated bending cycles, measured at the peak photocurrent excitation value.

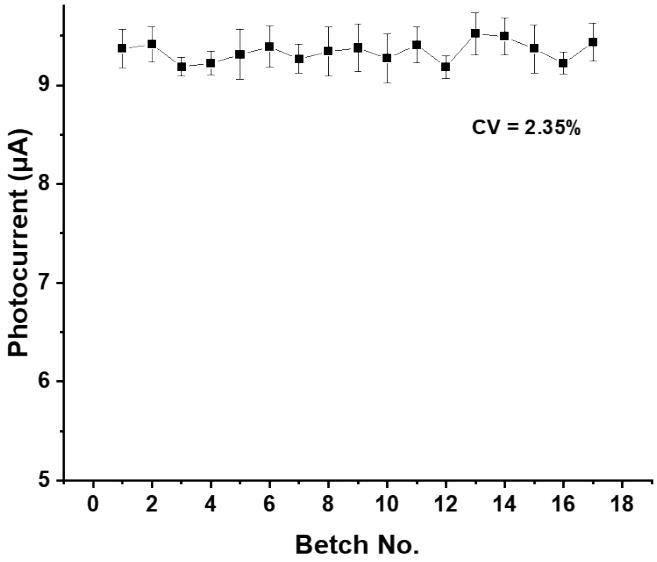

Figure S10. Batch-to-batch stability data.

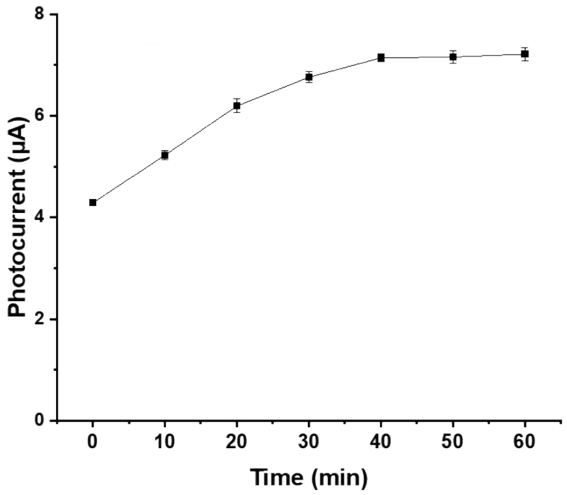

Figure S11. Optimized data for enzyme reaction catalysis time, using a 1 ng/mL sample as an example.

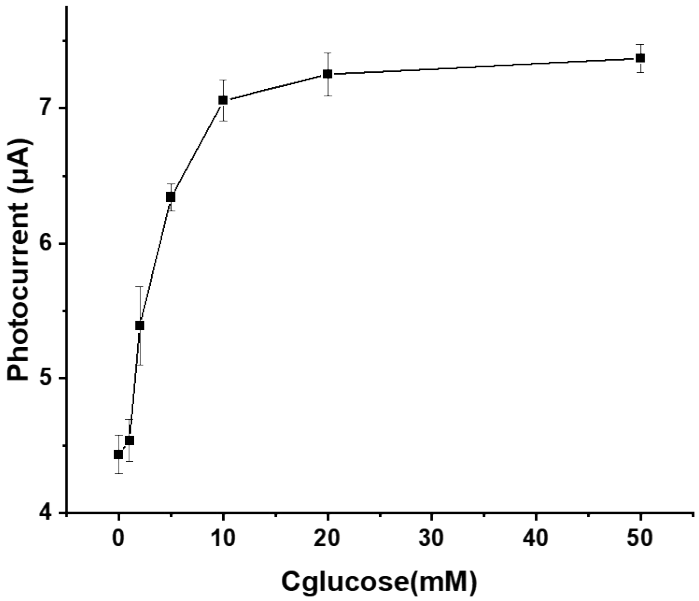

Figure S12. Optimization data for enzyme reaction substrate concentration, using a 1 ng/mL sample as an example.

Table S1. Comparison table of dynamic response range and LOD values for neurofilament light chain protein detection methods.

Detection method	Dynamic range	LOD	Ref.
Fluorescent Immunoassay Sensor	125 - 1500 pM	24 fM	[1]
ELISA	39 – 5000 pg mL^{-1}	-	[2]
Electrochemical	5.22 – 1000 pg mL^{-1}	5.22 pg mL^{-1}	[3]
Electrochemical	0.01 – 1.5 ng mL^{-1}	0.01 ng mL^{-1}	[4]
Fluorescence	0.05 - 1000 pg mL^{-1}	0.012 pg mL^{-1}	[5]
Electrochemical	0.01 - 200 ng mL^{-1}	7 ng mL^{-1}	This work

Reference

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