Supplemental Information

Platinum Nanostructure via a Self-assembly of Amyloid-like Peptide: a Novel Electrocatalyst for the Oxygen Reduction

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Materials

Wang resin, Fmoc-protected amino acids, triisopropylsilane (TIS), diisopropylcarbodiimide (DIC), 1-hydroxylbenzotriazole, trifluoroacetic acid (TFA) and piperidine were purchased from GL Biochem (Shanghai, China). 4-Aminophenylacetic acid was obtained from Aladdin (Shanghai, China). $H_2PtCl_6 \cdot H_2O$ and sodium citrate was received from Sigma-Aldrich (St. Louis, MO). Organic solvents were obtained from Hengxing Co. (Tianjin, China). All aqueous solutions were prepared with deionized water (18 MΩ cm^{-1}) treated with a water purification system (Simplicity Plus, Millipore Corp., Billerica, MA).

Apparatus

Transmission electron microscope (TEM) images were obtained from a JEOL JEM-2010 microscope (Japan). Atomic Force Microscopic (AFM) images were obtained from an MFP-3D-SA microscope (Asylum Research, Santa Barbara, CA) using the tapping mode in air. Dynamic light scatter (DLS) measurement was performed at 25 ^oC with a fixed scattering angle of 173^o and ξ−potential was measured by a Malvern Nano ZS Zetasizer equipped with a He-Ne laser (633 nm, 4 mW). Electrospray mass spectrometry (ESI-MS) was conducted on a Thermo Fisher LTQ linear ion-trap mass spectrometer (San Jose, CA). X-ray photoelectron spectra (XPS) was measured on a K-Alpha 1063 Instrument (Thermo Fisher Scientific, Britain) and Electrochemical experiments were performed with CHI 660 electrochemical workstation (Shanghai CH Instruments Co., China).

Synthesis of AFP

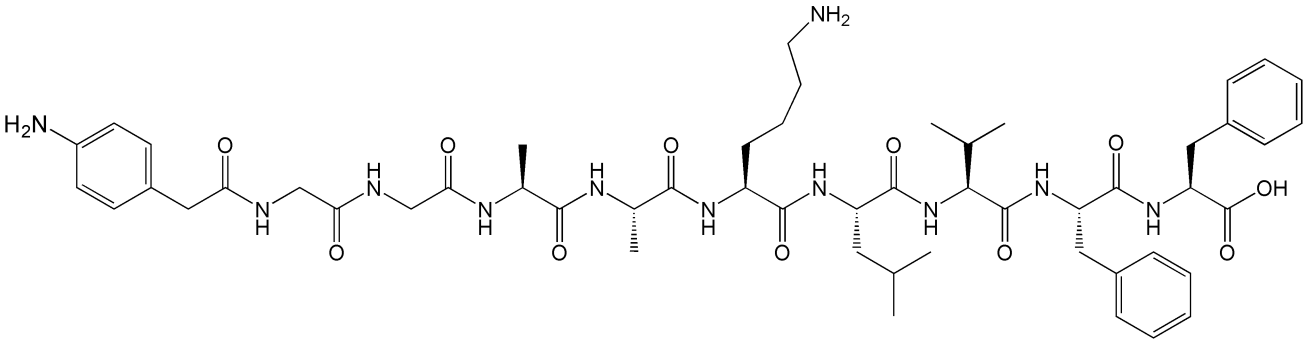
The amino acids were linked by diisopropylcarbodiimide in DMF and the Fmoc groups were deprotected with 20% piperidine in DMF (V/V) after the coupling reaction proceeded for 50 min. The peptide was cleaved from the resin using TFA/H_2O/TIS (95:2.5:2.5). The peptide was purified by semi-preparative reversed-phase HPLC (Shimadzu 6AD, Columbia, MO) using a C18 column (dimension of 250 × 4.6 mm i.d.). The mobile phases used were 0.1% trifluoroacetic acid in water (V/V, mobile phase A) and 0.1% trifluoroacetic acid in acetonitrile (V/V, mobile phase B), at a flow rate of 4.75 mL/min. The elution gradient was 20–40% B for 20 min, the AFP peptide eluted at 13.2 min.

Synthesis of Citrate-Stabilized Pt NPs

A total of 1 mL of 1% H_2PtCl_6 aqueous solution was added into 100 mL of water and then heated to boiling. Aging of the H_2PtCl_6 solution was not necessary in this synthetic procedure. Then 3 mL of a 1% sodium citrate aqueous solution was added rapidly, and the mixture was kept at boiling temperature for about 30 min.

Preparation Procedure of the Pt-AFP fibrils

Millipore filtered water (1 mL) was added to 4.5 mg of lyophilized AFP, and the sample was sonicated at 25 ^{o}C for 10 min in a bath sonicator to fully dissolve the material. The solution was then mixed using an IKA Vortex mixer for 1 h and left to rest for the following 24 h to form AFP fibrils. Then, the as-synthesised Citrate-Stabilized Pt NPs was added. Samples were incubated at room temperature with continuous shaking for 6 h.



Scheme 1S. Molecular structure of AFP

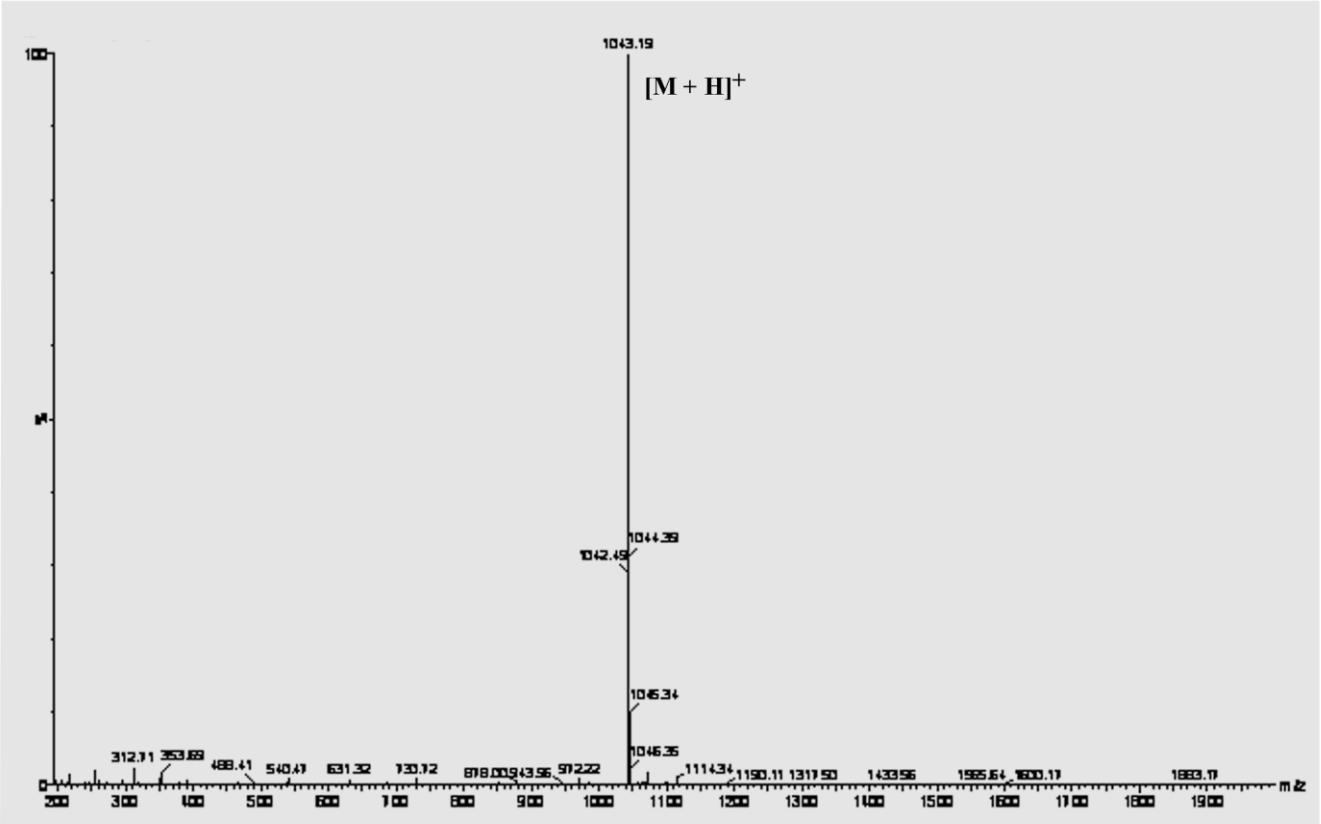


Fig. 1S. ESI-MS for AFP. m/z: calcd. for $C_{53}H_{75}N_{11}O_{11}$ $[M + H]^+$: 1043.23; found: 1043.19.

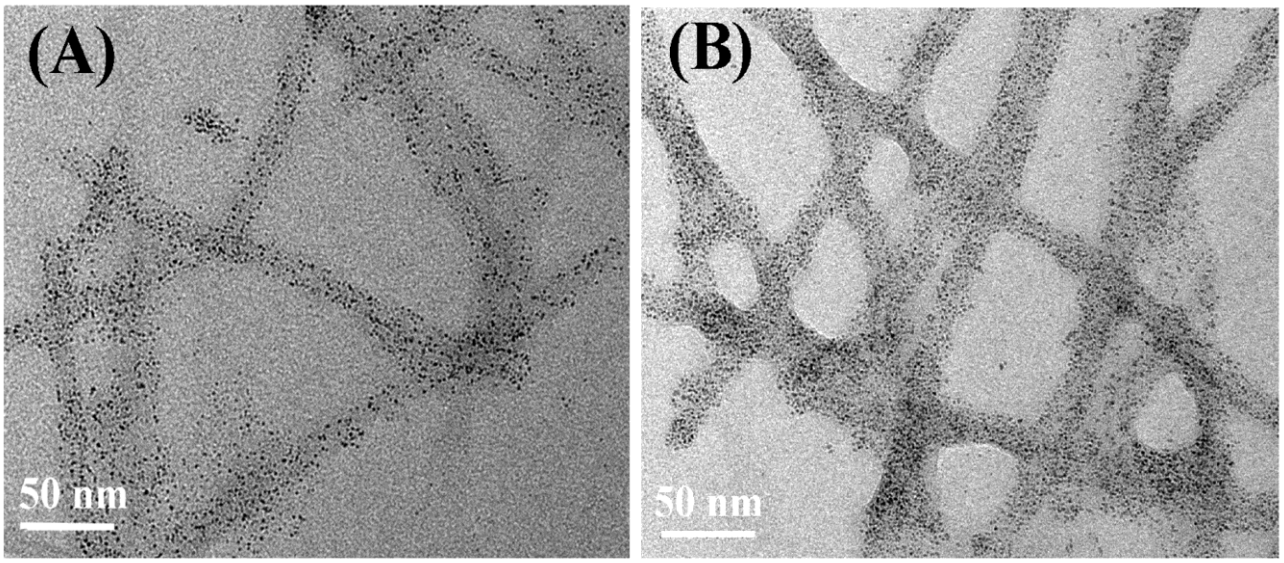


Fig. 2S. TEM micrographs for Pt-AFP fibrils. (A), The ratio of AFP fibrils to Pt NPs is 1:1 (w/w) and (B), the ratio of AFP to Pt NPs is 1:3 (w/w). AFP fibrils were co-incubated with Pt NPs at 25 ^{o}C with continuous shaking for 6 h.

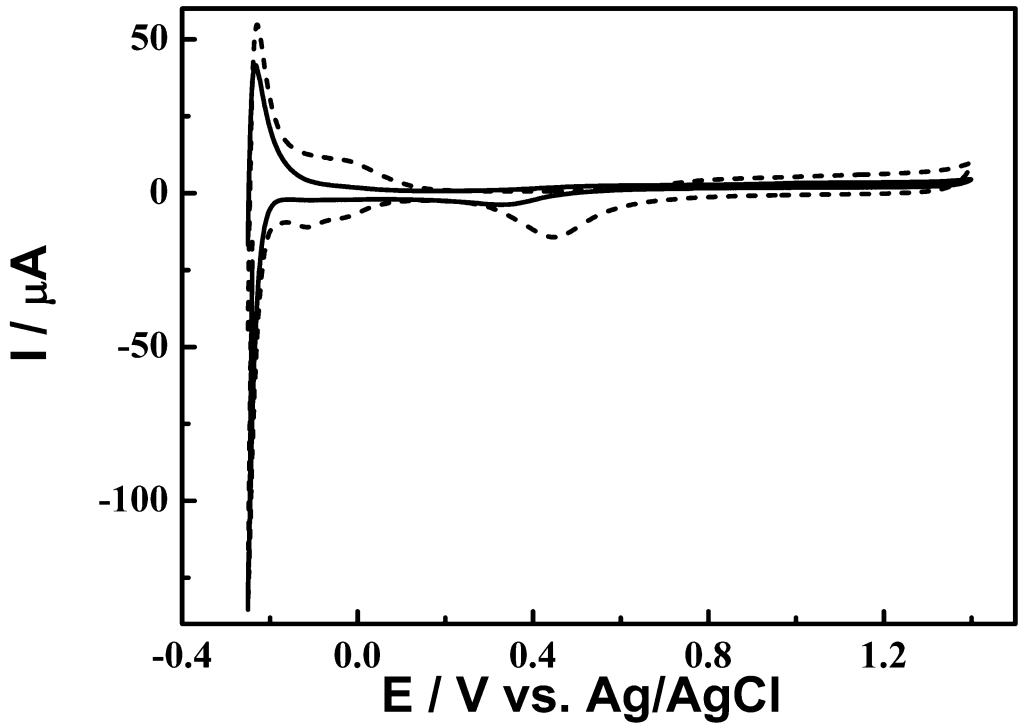


Fig. 3S. Cyclic voltammogram of a Pt-AFP fibrils (dashed line) and Pt NPs (solid line) modified GC electrode in N_2-saturated 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1}.