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Supplementary Information for

Peptide-based bimetallic nanostructures with tailored surface compositions and their oxygen electroreduction activities

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Experimental Methods

Synthesis and purification of a genetically cysteine-modified HexCoil peptide (Cys-HC). A 9-fluorenylmethoxycarbonyl (Fmoc) solid-phase reaction was carried out to synthesize the peptide, HexCoil, reported in our previous paper,[1] using an automated microwave peptide synthesizer (CEM LibertyBlue) at 0.1 mmole scales. The H-Rink amide resin (PCAS BioMatrix ChemMatrix®) was used as a solid support. For peptide coupling, a mixture of amino acid/*N*,*N′*-diisopropylcarbodiimide/ethyl 2-cyano-2-(hydroxyimino)acetate/resin with the molar ratio of 5:4.9:10:1 was used in each coupling step. Fmoc-protecting groups were removed using 20% piperidine in dimethylformamide. Products were cleaved from the resin in trifluoroacetic acid (TFA)/triisopropylsilane/deionized (DI) water with the volume ratio of 95:2.5:2.5 at room temperature for 2 h. After filtration for the removal of the resin, the solvent was evaporated under nitrogen gas. The crude peptides, precipitated with cold diethyl ether, were freeze-dried *in vacuo* and then purified by reverse phase high performance liquid chromatography (Waters 2545 Quaternary Gradient Module) using C4 column (Waters XBridge Protein BEH, 300 Å, 5 μm) and a linear gradient of buffer A (99.9% H_2O and 0.1% TFA) and buffer B (90% acetonitrile, 9.9% H_2O and 0.1% TFA). Molecular mass of peptides was verified by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (Bruker Ultraflex III, flex control 1.3).

Self-assembly of Cys-HC peptides around a single-walled carbon nanotube (SWNT) (HC/SWNT). A stock solution of SWNTs was prepared by adding 20 mg of SWNTs to 20 mL aqueous solution containing 1% glycerol by weight. The mixture was tip-sonicated (QSonica Q125, 1/8th inch tip) in an ice bath for approximately 20 min, in order to obtain homogeneous dispersion of SWNTs. 1 m L of the stock solution was taken and centrifuged at

5000 rpm for 5 min (Eppendorf Centrifuge 5430R) and the supernatant was discarded. The centrifugation was repeated twice more to remove glycerol residues, each time adding 1 mL of DI water beforehand and discarding the supernatant afterwards. The resulting SWNT precipitate was mixed with 1 mL of 1 mg/mL peptide solution in 20 mM sodium phosphate and 100 mM NaCl (pH 7.5). The mixture was then tip-sonicated in an ice bath for 20 min. The ice-bath cooling was to prevent conformational changes in protein structure due to excessive heating. The sample was warmed up to room temperature and collected using centrifugation at 5000 rpm for 10 min.

Nucleation and growth of AuPt nanocrystals on the HC/SWNT (AuPt/HC/SWNT). The HC/SWNT suspension prepared as above was treated with 1 mM of tris(2-carboxyethyl)-phosphine hydrochloride to reduce the sulfhydryl group of cysteine, followed by purification via centrifugal filtration (Amicon® Ultra-4 centrifugal filters, Ultracel-10 membrane). The purified sample was dispersed in 100 μL of buffer solution (20 mM sodium phosphate and 150 mM NaCl). Two precursor aqueous solutions of 100 mM $HAuCl_4$ and 100 mM H_2PtCl_6 were successively added to the purified HC/SWNT solution and incubated at 4 ºC for ~30 min. Here, the volume ratio of $HAuCl_4$/ H_2PtCl_6 was adjusted to be 4 μL/16 μL, 6 μL/14 μL and 10 μL/10 μL, in order to obtain different Au/Pt ratios of samples. Then, 40 μL of 100 mM $NaBH_4$, as a reducing agent, was slowly injected into the solution and kept at 4 ºC for 72 h to slowly grow nanoparticles.

Sample characterization. The morphological images of AuPt/HC/SWNT samples were obtained using transmission electron microscopy (TEM, JEOL JSM-2100F, 200 kV). For the sampling, a few drop of the sample solution ultrasonically dispersed in DI water was dropped and dried in air on a carbon-coated copper grid. The atomic structure of AuPt nanoparticles grown on the peptide template was characterized by high-resolution TEM and powder X-ray diffraction (XRD, Rigaku D/Max-2000, Cu Kα radiation (λ = 1.5415 Å)). The chemical state of AuPt nanoparticles was analyzed using X-ray photoelectron spectroscopy (XPS) equipped with concentric hemispherical analyzer (SPECS PHOIBOS-HAS 3500) and monochromatic X-ray source (Mg Kα, 1253.6 eV). The Au 4f and Pt 4f core-level binding energies were calibrated with respect to the adventitious carbon C 1s binding energy of 284.5 eV. For XRD and XPS, the sample was freeze-dried completely. The elemental composition of AuPt was analyzed by energy-dispersive X-ray spectroscopy (EDS) attached to high-angle annular dark-field scanning TEM (HAADF-STEM, JEOL JEM ARM 200F) equipped with a spherical aberration corrector.

Electrochemical characterization. All electrochemical experiments were carried out in a three-electrode cell at room temperature using a potentiostat (Ivium Compactstat) equipped with a rotating disk electrode (RDE) and a motor controller (Metrohm Autolab). 5 μL of the as-prepared AuPt/HC/SWNT solution was dropped and dried naturally onto a glassy carbon RDE (ø = 3 mm), as the working electrode, and 5 μL of a 0.05 wt% Nafion (dissolved in ethanol) solution was then dropped onto the RDE surface to fix the sample. A Pt net and a commercial Hg/HgO/20% KOH electrode (BAS RE-6A) were used as the counter electrode and reference electrode, respectively. All the measured potentials are converted into those with respect to a reversible hydrogen electrode (RHE).

Cyclic voltammetry (CV) was performed in a N_2-saturated 0.1 M KOH aqueous solution at a sweep rate of 50 mV s^{-1}, in order to obtain the electrochemical surface areas (ECSAs) of Pt and Au ($ECSA_{Pt}$ and $ECSA_{Au}$). For the Pt surface in KOH, one electron participates in the adsorption/desorption of hydrogen species ($Pt + H_2O + e^- \rightleftarrows Pt{-}H + OH^-$).[2] Therefore, the charge, $Q_{\mathrm{H,Pt}}$, is calculated from the CV curve by integrating the area associated with hydrogen desorption region after the double-layer correction as

$$Q_{H,Pt} = \frac{\int i\,dE}{1 \cdot v}$$

with the current i, the potential E, and the sweep rate v.[3] The ECSA$_{\mathrm{Pt}}$ (cm^2) can be then calculated as

$$ECSA_{Pt} = \frac{Q_H}{210\ (\mu C\ cm^{-2})}$$

where the value of 210 μC cm^{-2}, which is used as the conversion factor, is the charge density of full coverage for the surface of polycrystalline Pt by the adsorbed hydrogen species.[4] The ECSA$_{\mathrm{Au}}$ can also calculated by the same method used to calculate the ECSA$_{\mathrm{Pt}}$. For Au in KOH, one electron is transferred during the electro-oxidation of Au. The conversion factor is 390 μC cm^{-2}, which corresponds to the charge density for the formation of a monolayer of OH species on polycrystalline Au.[5]

Polarization curves for the oxygen reduction reaction were obtained by sweeping the potential from 1.1 V to 0.2 V versus RHE in an O_2-saturated 0.1 M KOH electrolyte at a sweep rate of 10 mV s^{-1} and a rotation rate of 1600 rpm.

Supplementary Figures

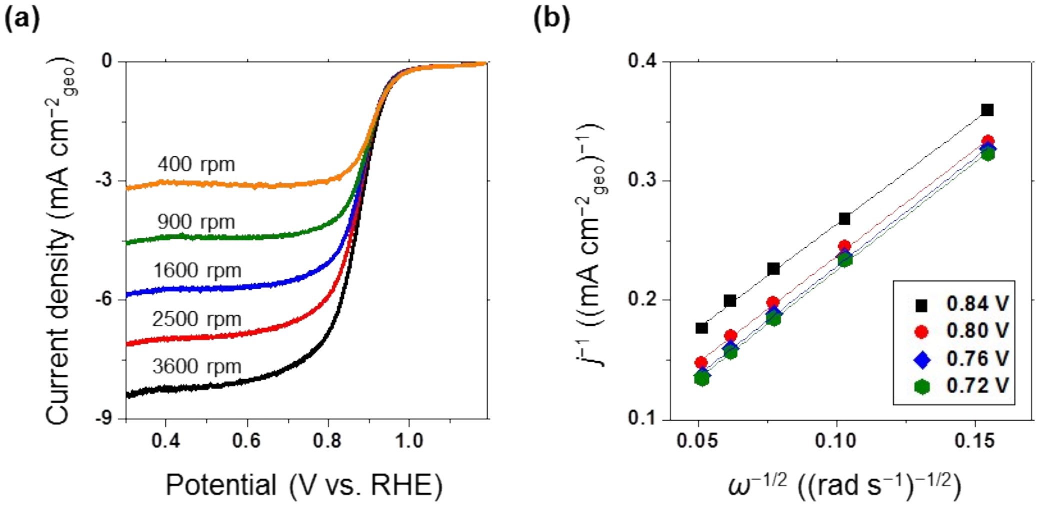

Fig. S1 (a) Rotation-rate-dependent ORR polarization curves of the $Au_{50}Pt_{50}$/HC/SWNT electrocatalyst on a rotating disk electrode in O_2-saturated 0.1 M KOH aqueous solution at a sweep rate of 10 mV s^{-1}. (b) Koutecký−Levich plots from the curves at different potentials within the mixed kinetic/diffusion regime. The measured current (i) can be expressed by the Koutecký−Levich equation, $1/i = 1/i_k + 1/i_d$, where i_k and i_d are the kinetic current and the diffusion-limited current, respectively. The kinetic current represents the current that is not affected by mass-transfer effects. The i_d term can be obtained from the Levich equation, $i_d = 0.62nFAD^{2/3}\omega^{1/2}\upsilon^{-1/6}C^*$, where n is the number of electrons participating in the reaction, F is the Faraday's constant (96485 C mol^{-1}), A is the electrode surface area (cm^2), D is the diffusion coefficient of electroactive species (cm^2 s^{-1}), ω is the angular velocity (s^{-1}), υ is the kinematic viscosity of the electrolyte (cm^2 s^{-1}) and C^* is the concentration of electroactive species (mol cm^{-3}). Here, the ω term is described using the relationship, $\omega = 2\pi f/60$, where f is the rotation speed in revolutions per minute (rpm).[6] In order to calculate the n term in this study, we used literature values, D_{O2} of 1.9×10^{-5} cm^2 s^{-1} and C_{O2} of 1.2×10^{-6} mol cm^{-3} in 0.1 M KOH solution and υ_{KOH} of 0.01 cm^2 s^{-1}.[7]

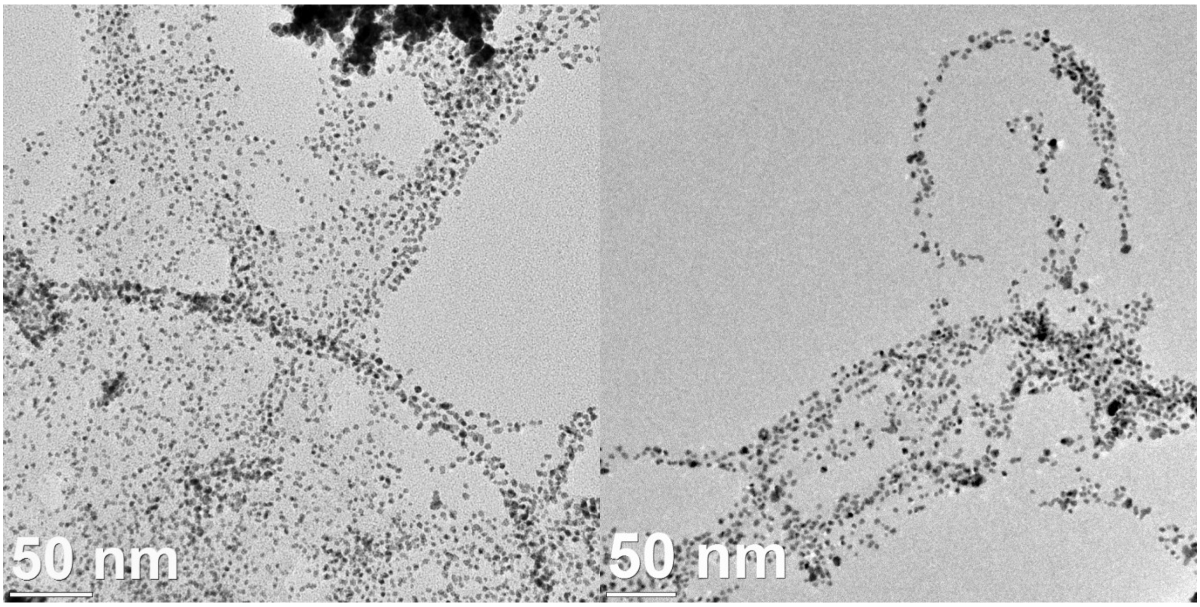

Fig. S2 TEM images of $Au_{20}Pt_{80}$/HC/SWNT after imposing the potential of 0.4 V for 30000 s.

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