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Electronic Supplementary Information

The effect of tensile strain in Pd-Ni core-shell nanocubes with tunable shell thickness

on urea electrolysis selectivity

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Materials and Methods

Section 1. Chemicals

Hexadecyltrimethylammonium bromide $(CH_3(CH_2)_{15}N(Br)(CH_3)_3)$, $\geq 99.0\%$, BioUltra, Sigma-Aldrich), hydrochloric acid (HCl, 37%, Sigma-Aldrich), palladium chloride (PdCl₂, 99.9%, Sigma-Aldrich), L-ascorbic acid (C₆H₈O₆, $\geq 99\%$, Sigma-Aldrich), potassium hydroxide (KOH, >85%, Sigma-Aldrich), hydrazine solution (N₂H₄, 35wt.% in H₂O, Sigma-Aldrich), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99.999%, Sigma-Aldrich), urea (NH₂CONH₂, >99.9%, Sigma-Aldrich) were purchased and used without further purification. Deionised water (18.2 MΩ·cm at 25 °C) purified by a Milli-Q Water Purification System was used for aqueous solution preparation.

Section 2. Synthesis of Pd@Ni nanoparticles

2.1. Pd nanoseeds

Pd nanoseeds were synthesised using a seed-mediated growth.¹ An aqueous solution of 100 mM H₂PdCl₄ was prepared by mixing 88.4 mg of PdCl₂ in 5 mL of 200 mM HCl overnight. An aqueous solution 125 mM CTAB (10 mL) was prepared at 95 °C while stirred at 800 rpm for 5 min, and H₂PdCl₄ (20 mM, 250 μ L) was added to the CTAB solution. After 5 min, ascorbic acid (100 mM, 200 μ L) was quickly injected to the mixture of CTAB and H₂PdCl₄. The solution was stirred at 95 °C for 10 min and cooled down at 30 °C for 1 h without stirring.

2.2. Pd nanocubes (NCs)

Pd NCs were grown from the Pd nanoseeds.¹ The prepared H₂PdCl₄ solution (100 mM, 1.16 mL) was added dropwisely to 8.46 mL of 210 mM CTAB at 90 °C under 800 rpm for 1–2 min, followed by adding the aged Pd nanoseed solution (6.5 mL) and ascorbic acid (1 M, 820 μ L) in sequence. The mixture was stirred at 90 °C for 1h. The product was centrifuged at 5000 rpm for 8 min, and supernatant was removed as much as possible. It was redispersed in 2 mL of deionised water by sonication.

2.3. Pd@Ni NCs with different Ni thicknesses

2.3.1. Initial attempt with different Ni precursor concentrations (Fig. S2)

The Pd NC solution (0.1 mL) was diluted by mixing 1 mL of 1.04 mM CTAB in a 1.5 mL microtube. An aqueous solution of hydrazine (210 mM, 80 μ L) was injected to the Pd NC solution at 1000 rpm in a thermomixer

(Eppendorf ThermoMixer C), followed by one-shot addition of an aqueous solution of Ni(NO₃)₂ (20 μ L) with different concentrations. Note that the reactant concentrations were calculated with respect to the final solution volume in the below table. Then, the mixture was left undisturbed at 50 °C for 1 h. The Pd@Ni solution was centrifuged at 5500 rpm for 8 min, and supernatant was removed as much as possible. It was redispersed in 0.5 mL of deionised water by sonication.

Figure number	Ni(NO3)2 (mM)	Hydrazine (mM)	CTAB (mM)	
S2a	0.09			
S2b	0.18	1.4	0.87	
S2c	0.35	14		
S2d	0.70			

2.3.2. Changes of reactant delivery method and ratio between hydrazine and Ni(NO₃)₂ (Figs. S3 and S4)

The Pd NC solution (0.1 mL) was diluted by mixing 0.5 mL of 40.8 mM CTAB in a 1.5 mL microtube. An aqueous solution of Ni(NO₃)₂ (20 μ L) with different concentrations was added to the Pd NC solution at 1000 rpm in a thermomixer (Eppendorf ThermoMixer C), followed by dropwise addition of an aqueous solution of hydrazine (35.7 mM, 400 μ L) at 0.2 mL·min⁻¹. Note that the reactant concentrations were calculated with respect to the final solution volume in the below table. Then, the mixture was left undisturbed at 50 °C for 1 h. The Pd@Ni solution was centrifuged at 5500 rpm for 8 min, and supernatant was removed as much as possible. It was redispersed in 0.5 mL of deionised water by sonication. For control experiment, the synthesis was conducted as mentioned in Section 2.3.1 with modified reactant volumes and concentrations.

Figure number	Ni(NO ₃) ₂ (mM)	Hydrazine (mM)	CTAB (mM)	Hydrazine:Ni(NO ₃)2
S3a (control)	0.35	14	10	40
S3b	0.35	14	20	40
S3c	0.18	14	20	80
S3d	0.09	14	20	160
S4	0.35	56	20	160

2.3.3. Optimised scale-up synthesis (Figs. 1 and S5)

The Pd NC solution (2 mL) was diluted by mixing 8 mL of 30.5 mM CTAB to have ~1.9 in extinction at 370 nm. An aqueous solution of Ni(NO₃)₂ (200 μ L), 0.893 mM for 0.5 nm Ni shell, 1.79 mM for 1 nm Ni shell, 2.98 mM for 1.5 nm shell, 4.46 mM for 2.5 nm Ni shell, and 17.9 mM for 10 nm Ni shell, was added to the diluted Pd NC solution in a 15 mL centrifuge tube under 1000 rpm in a thermomixer (Eppendorf ThermoMixer C), and hydrazine (2 mL) was slowly added using a syringe pump (KDS Legato 100) at 1 mL·min⁻¹. Note that the Ni shell thickness was changed by varying concentrations of Ni(NO₃)₂ and hydrazine while keeping the ratio between hydrazine and Ni(NO₃)₂ as 160. Note that the reactant concentrations were calculated with respect to the final solution volume in the below table. Then, the mixture was left undisturbed at 50 °C for 1 h. The Pd@Ni solution was centrifuged at 5500 rpm for 8 min, and supernatant was removed as much as possible. It was redispersed in 1 mL of deionised water by sonication.

Ni thickness (nm)	Ni(NO3)2 (mM)	Hydrazine (mM)	CTAB (mM)	Hydrazine:Ni(NO ₃) ₂
0.5	0.015	2.3		
1.0	0.030	4.7		
1.5	0.049	7.8	20	160
2.5	0.073	12		
10	0.29	47		

Section 3. Materials characterisation

A Hitachi S5200 scanning electron microscope (SEM) and a FEI Tecnai TF30ST transmission electron microscope (TEM) with a ZrO/W (100) Schottky emitter at 300 kV were used for imaging all the samples, and energy-dispersive X-ray spectroscopy (EDS) was conducted by the FEI Tecnai TF30ST TEM. A D8 Advanced A25 (BRUKER) was used for powder X-ray diffraction (XRD) measurement. X-ray photoelectron spectra (XPS) was recorded using a Thermo Scientific K-Alpha XPS spectrometer.

Section 4. Electrochemical measurement

The working electrode was prepared as follows. A highly concentrated Pd@Ni NC solution was first prepared by centrifuging 5 batches of Pd@Ni NC solution, which was redispersed in 100 μ L of deionised water. The concentrated solution was mixed with 50 μ L of diluted Nafion-117 (~5% in a mixture of lower aliphatic alcohols and water, Sigma-Aldrich) and sonicated for 2 min. The mixture was dropcasted uniformly onto one side of carbon paper (1 cm × 1 cm).

Cyclic voltammetry (CV) was conducted in a conventional gas-tight two-compartment cell connected to an electrochemical workstation (Biologic SP-300 or SP-50). Nickel foam was used as a counter electrode, and Ag/AgCl was used as a reference electrode. Electrolyte was purged with ultra-high purity Ar (Praxair, 99.999%) for 15 min before CV. Chronoamperometry (CA) was performed in a H-cell system equipped with an inlet and an outlet for urea oxidation reaction (UOR). Nickel coil was used as a counter electrode, and Ag/AgCl was used as a reference electrode with 1 M KOH as catholyte and 1 M KOH containing 0.33 M urea as

anolyte, which were purged with Ar for 1 or 2 h until gas chromatography (GC) displayed only trace amount of O₂ and N₂. Then, UOR was carried out at 0.55 vs Ag/AgCl and 0.7 V vs Ag/AgCl for 1 h, respectively. Any gaseous product was measured using an SRI MG-5 multiple gas analyser or an Agilent 7890B GC System. Any ionic product was analysed using a Metrohm Eco ion chromatography (IC). The current density values were normalised by electrochemically active surface area (ECSA) of Pd@Ni NCs. The ECSA was estimated from the reduction event of NiOOH at ~0.3 V vs Ag/AgCl in CV using the following equation: ECSA = $Q/257 \mu C \cdot cm^{-2.2}$



Fig. S1 (a) TEM image of Pd NCs. (b) Edge length distribution of Pd NCs. Data were obtained by measuring 200 Pd NCs. (c) UV-visible spectrum of Pd NCs in solution. Scale bar: 100 nm.



Fig. S2 (a-d) Representative TEM images of Pd@Ni NCs produced with different Ni(NO₃)₂ concentrations: (a) 0.09 mM, (b) 0.18 mM, (c) 0.35 mM, and (d) 0.70 mM. Aqueous solutions of hydrazine and Ni(NO₃)₂ were added sequentially to the Pd NC solution. The concentration values were calculated with respect to the final solution volume. The particle size was measured as 50.4 ± 2.6 nm for Pd NCs, 50.4 ± 2.9 nm for Pd@Ni NCs with 0.35 mM, and 50.2 ± 3.3 nm for Pd@Ni NCs with 0.70 mM. Scale bars: 30 nm. (e-g) Edge length distribution of Pd NCs (e), and Pd@Ni NCs prepared with 0.35 mM (f) and 0.7 mM (g) Ni(NO₃)₂ concentrations.



Fig. S3 SEM images of Pd@Ni NCs with different delivery method and molar ratio between hydrazine and Ni(NO₃)₂. (a) Control sample produced with the addition order (hydrazine \rightarrow Ni(NO₃)₂) and without dropwise addition of hydrazine. The ratio of hydrazine:Ni(NO₃)₂ was 40. (b) Pd@Ni NCs with 40 as hydrazine:Ni(NO₃)₂ after changing the addition order (Ni(NO₃)₂ \rightarrow hydrazine) with dropwise addition of hydrazine at 0.2 mL·min⁻¹. (c) Pd@Ni NCs with 80 as hydrazine:Ni(NO₃)₂ after changing the addition of hydrazine at 0.2 mL·min⁻¹. (d) Pd@Ni NCs with 160 as hydrazine:Ni(NO₃)₂ after changing the addition order (Ni(NO₃)₂ \rightarrow hydrazine) with dropwise addition of hydrazine at 0.2 mL·min⁻¹. (d) Pd@Ni NCs with 160 as hydrazine:Ni(NO₃)₂ after changing the addition order (Ni(NO₃)₂ \rightarrow hydrazine) with dropwise addition of hydrazine at 0.2 mL·min⁻¹. Scale bar: 100 nm.



Fig. S4 SEM images of Pd@Ni NCs with 5 times increased concentrations of Ni(NO₃)₂ (0.35 mM) and hydrazine (56 mM) while keeping hydrazine:Ni(NO₃)₂ as 160. The concentration values were calculated with respect to the final solution volume. Scale bar: 100 nm.



Fig. S5 Representative TEM images of Pd@Ni NCs with different Ni thickness of (a) 0.5 nm, (b) 1.0 nm, (c) 1.5 nm, (d) 2.5 nm, and (e) 10 nm. Scale bar: 50 nm.



Fig. S6 TEM image and corresponding Pd lattice spacing measurement diagram of Pd@Ni NCs with different Ni thickness of (a) 0.5 nm, (b) 1.0 nm, (c) 1.5 nm, (d) 2.5 nm, and (e) 10 nm. Scale bar: 2 nm.



Fig. S7 TEM image and corresponding Ni lattice spacing measurement diagram of Pd@Ni NCs with different Ni thickness of (a) 0.5 nm, (b) 1.0 nm, (c) 1.5 nm, (d) 2.5 nm, and (e) 10 nm. Scale bar: 2 nm.



Fig. S8 XPS spectra of Pd@Ni NCs with different Ni thickness of (a) 0.5 nm, (b) 1.0 nm, (c) 1.5 nm, (d) 2.5 nm, and (e) 10 nm (top: before electrochemical measurement, middle: after UOR at 1.55 V, and bottom: after UOR at 1.7 V). The binding energy positions were assigned as 852.5 eV for Ni⁰, 853.7 eV for Ni²⁺, and 856.6 eV for Ni³⁺.



Fig. S9 (a,b) The relative product formation rates as a function of Ni shell thickness for the electolysis of 0.33 M urea in 1 M KOH performed at 1.55 V (a) and 1.7 V(b). (c) The ratio of nitrite to N_2 as a a function of Ni shell thickness observed for the electolysis of 0.33 M urea in 1 M KOH performed at 1.55 V. (d) The ratio of O_2 to UOR products as a a function of Ni shell thickness observed for the electolysis of 0.33 M urea in 1 M KOH performed at 1.7 V.



Fig. S10 The product distribution as a function of time for long-term electolysis of 0.33 M urea in 1 M KOH performed at 1.7 V for Pd@Ni NCs with 1 nm (a) and 10 nm (b) Ni shell thickness.

Sample	$ECSA(cm^2)$
Pd@Ni0.5nm NC	60
Pd@Ni1.0nm NC	78
Pd@Ni1.5nm NC	109
Pd@Ni2.5nm NC	147
Pd@Ni10nm NC	292
Ni(OH)2 XG	908
Pd NC	269

Table S1. Estimated ECSA values of Pd@Ni NCs with Ni thicknesses and control samples.

Table S2. The performance of selected catalysts for urea electrolysis.

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Catalyst	Electrolyte	Eons (V vs RHE)	$J_{\text{geom}} (\text{mA cm}^{-2})$	Ref.
Pd@Ni10nm NC	0.33M Urea +1M KOH	1.34	32	This work
Pd@Ni0.5nm NC	0.33M Urea +1M KOH	1.34	22	This work
NiF ₂	0.33M Urea +1M KOH	1.37	20	[3]
Ni-WC/MWCNT	0.33M Urea +1M KOH	1.38	10	[4]
β-Ni(OH) ₂	0.33M Urea +1M KOH	1.37	2	[5]
Ni/Sn-dendrites	0.33M Urea +1M KOH	1.33	30	[6]
Ni ₂ P	0.33M Urea +1M KOH	1.33	86	[3]
NF@NiO	0.33M Urea +1M KOH	1.33	70	[7]
β-Ni(OH)2 Ni/Sn-dendrites Ni2P NF@NiO	0.33M Urea +1M KOH 0.33M Urea +1M KOH 0.33M Urea +1M KOH 0.33M Urea +1M KOH	1.37 1.33 1.33 1.33	2 30 86 70	[5] [6] [3] [7]

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