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Shape-Controlled Pd Nanocrystal-Polyaniline Heteronanostructures with Modulated Polyaniline Thickness for Efficient Electrochemical Ethanol Oxidation

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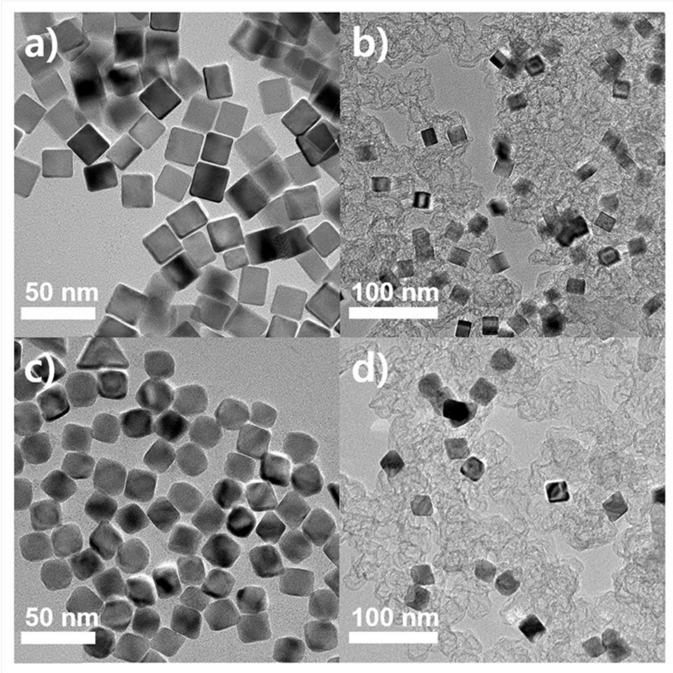

Fig. S1 TEM images of (a) cubic Pd NCs, (b) cubic Pd NCs on carbon support, (c) octahedral Pd NCs, and (d) octahedral Pd NCs on carbon support.

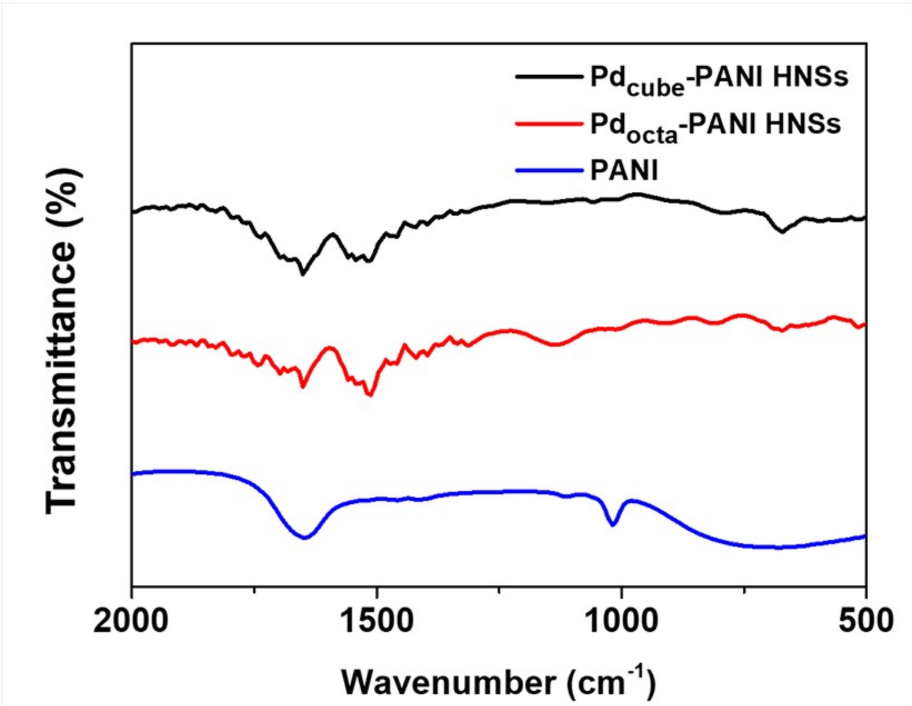

Fig. S2 FTIR spectra of Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, and PANI.

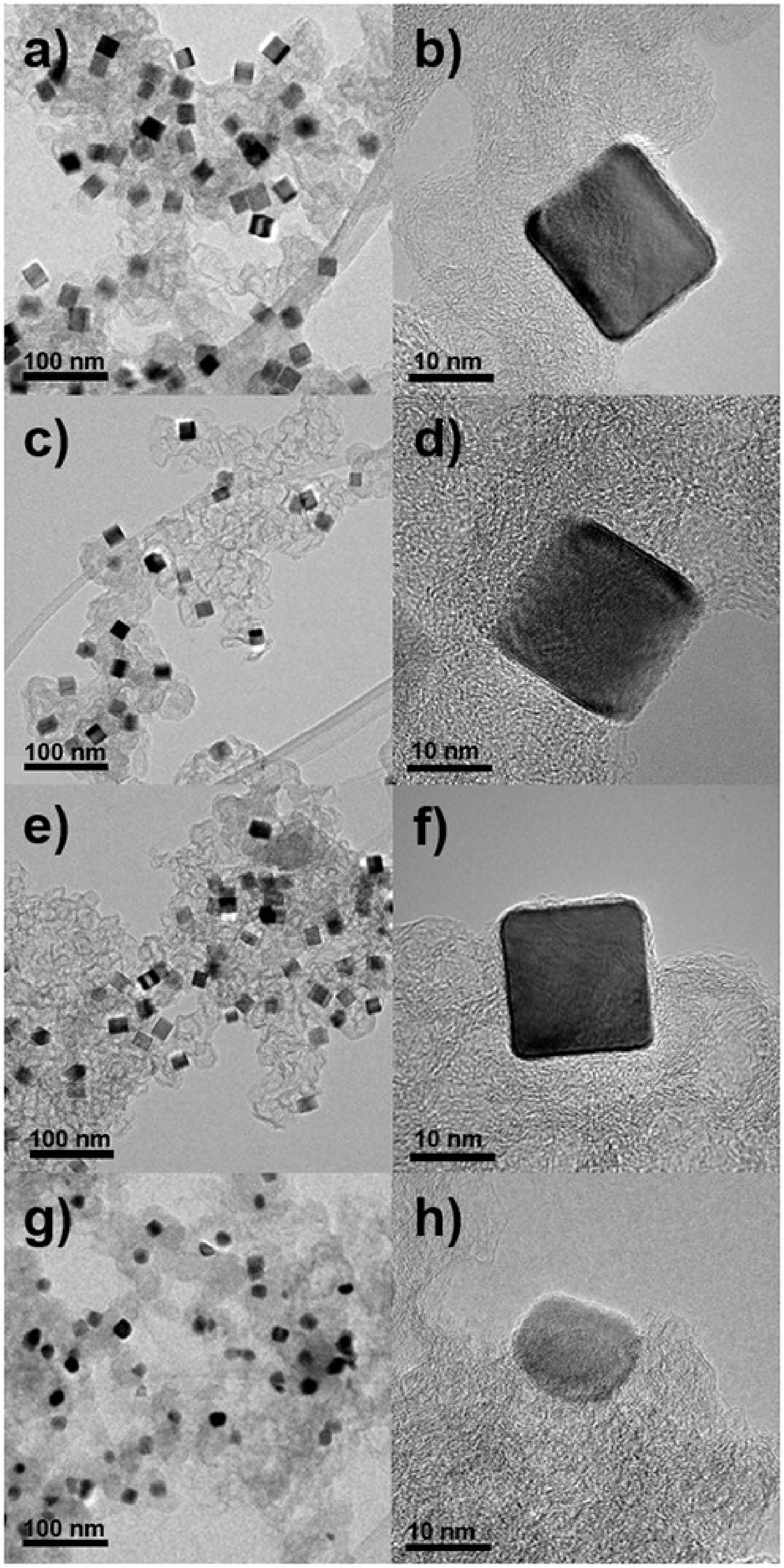

Fig. S3 (a,c,e,g) Low- and (b,d,f,h) high-magnification TEM images of products synthesized under pH (a,b) 7, (c,d) 6, (e,f) 4, and (g,h) 1.

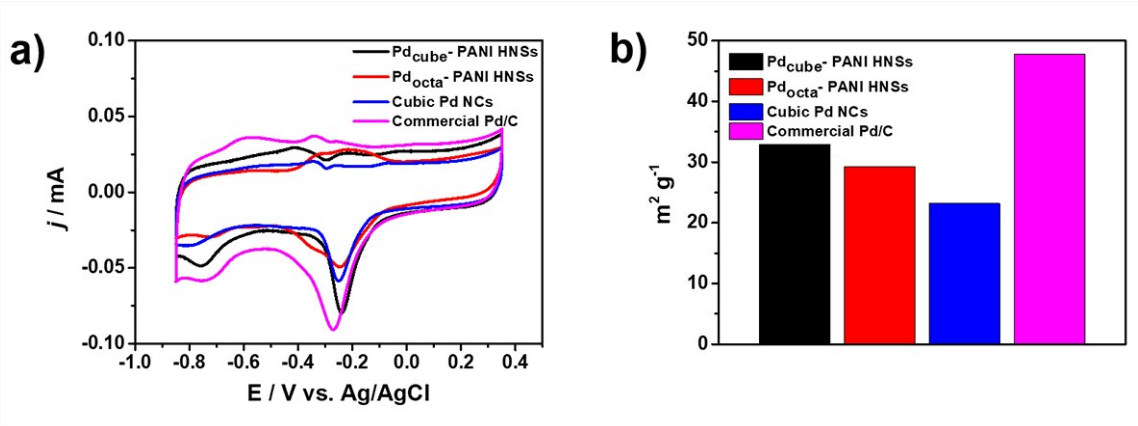

Fig. S4 (a) CVs of the Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, cubic Pd NCs, and commercial Pd/C in 0.1 M KOH at a scan rate of 50 mV s^{-1} and (b) corresponding ECSAs of different catalysts.

Current values were normalized with respect to the electrochemically active surface areas (ECSA). ECSA was estimated by the following equation; ECSA = Q_o/q_o, where Q_o is the surface charge that can be obtained from the area under the CV trace of oxygen desorption (-0.4 ~ -0.1 V) and q_o is the charge required for desorption of monolayer of oxygen on the surface of catalysts (424 μC/cm^2, ref.: Woods, R. In Electroanalytical Chemistry: A Series of Advances (vol.9); Bard, A. J., Ed.; Marcel Dekker: New York, 1974; pp 1-162).

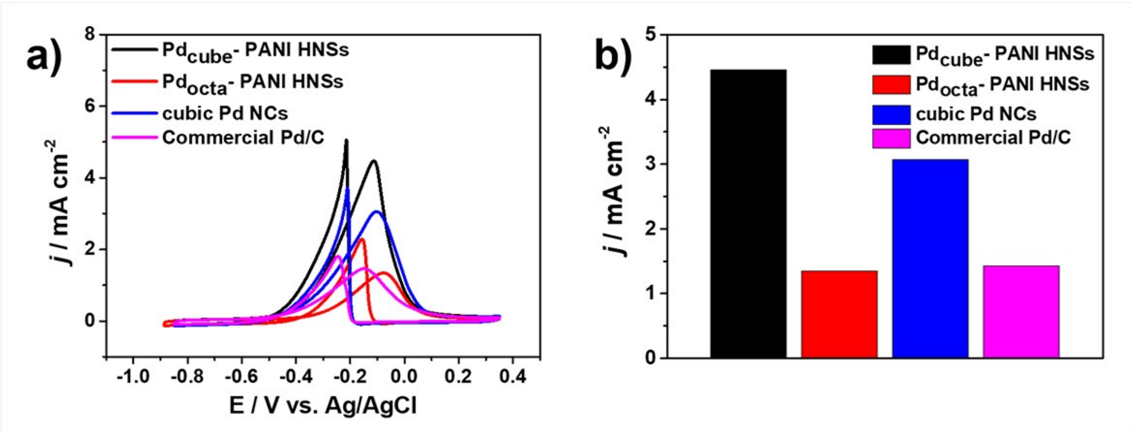

Fig. S5 (a) CVs of the Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, cubic Pd NCs, and commercial Pd/C in 0.1 M KOH + 0.5 M ethanol at a scan rate of 50 mV s^{-1} and (b) corresponding catalytic activities of different catalysts.

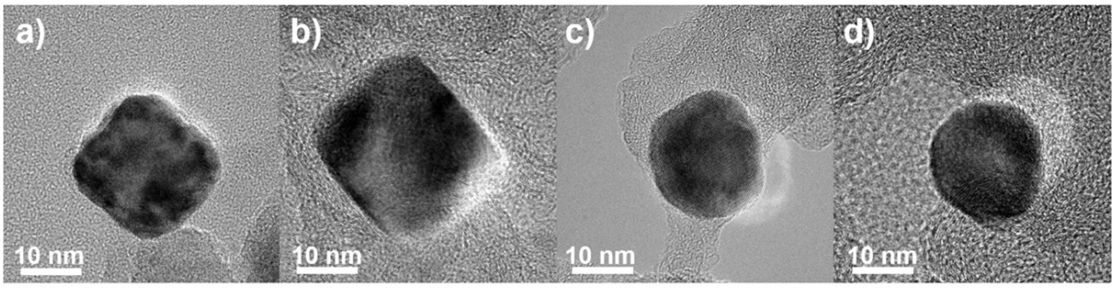

Fig. S6 TEM images for (a) Pd_{cube}-PANI HNSs, (b) Pd_{octa}-PANI HNSs, (c) cubic Pd NCs, and (d) Pd/C catalysts after ADT (500 cycles).

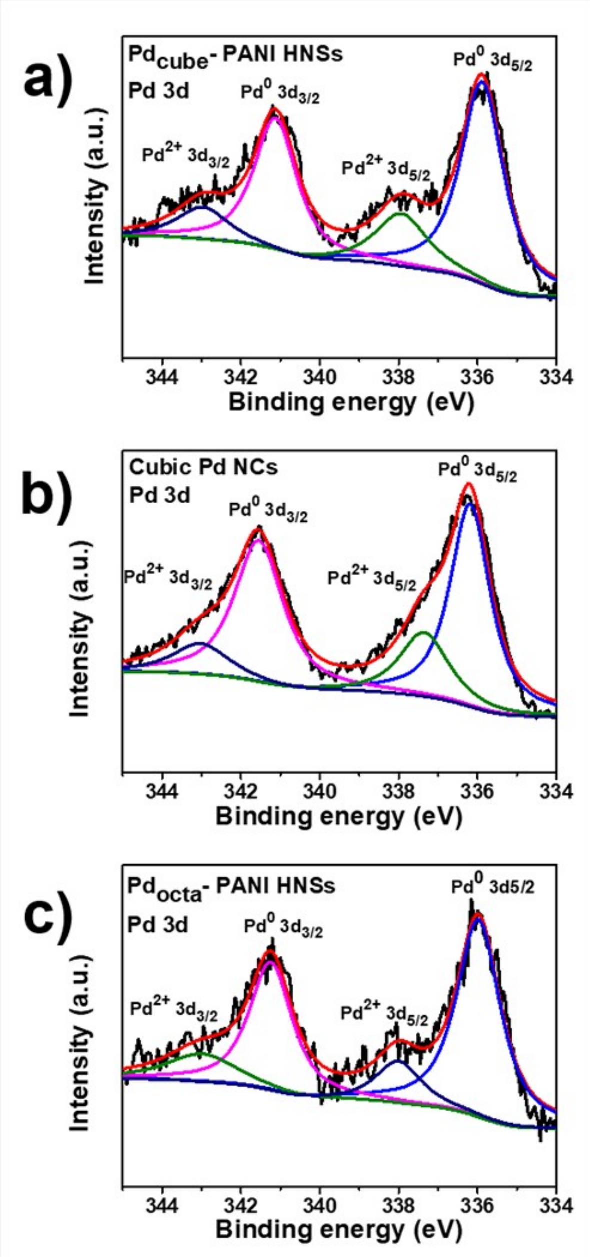

Fig. S7 XPS spectra for the Pd 3d core-level for (a) Pd_{cube}-PANI HNSs, (b) cubic Pd NCs, and (c) Pd_{octa}-PANI HNSs.

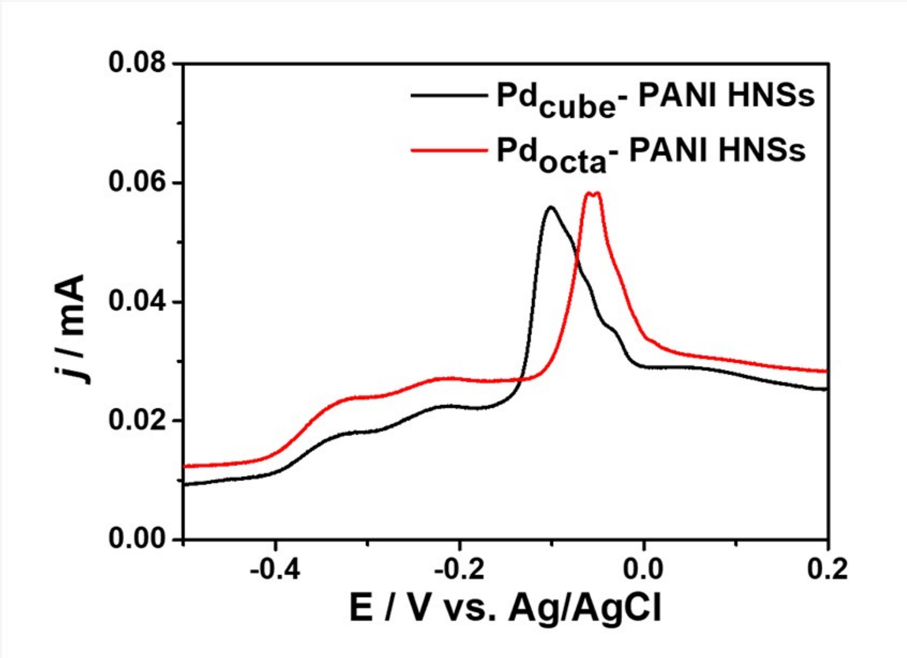

Fig. S8 CO stripping measurements of Pd_{cube}-PANI and Pd_{octa}-PANI HNSs.

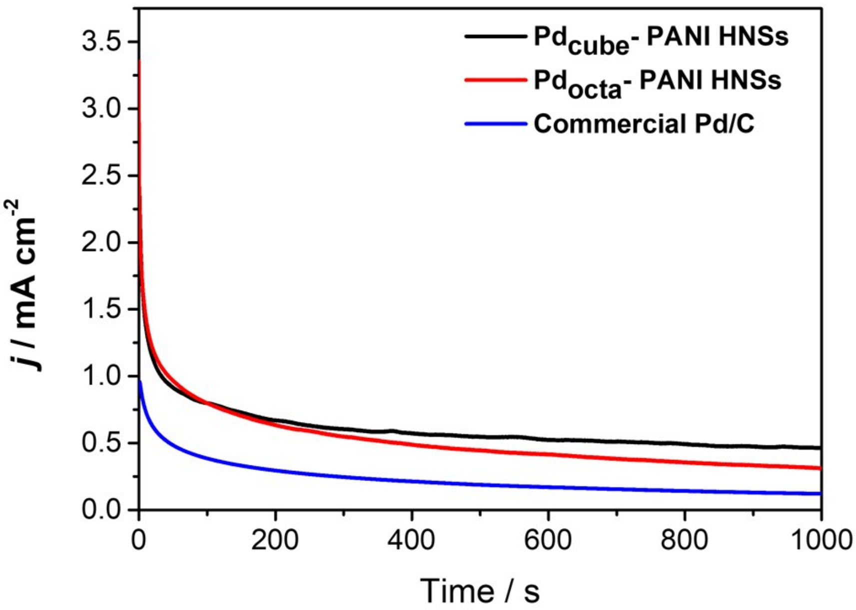

Fig. S9 Chronoamperometric curves of the Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, and commercial Pd/C at -0.15 V vs. Ag/AgCl.

Table S1 Comparison of the electrochemical performances of Pd_{cube}-PANI HNSs, Pd_{octa}-PANI HNSs, cubic Pd NCs, commercial Pd/C, and other reported Pd-based conductive polymer electrocatalyst for EOR.

Sample Name	**ECSA (m^2 g^{-1})**	**Electrolytes**	**Mass activity (mA mg^{-1})**	**Ref.**
Pd_{cube}-PANI HNSs	33	0.1 M KOH + 0.5 M ethanol	1472.6	This work
Pd_{octa}-PANI HNSs	29.3	0.1 M KOH + 0.5 M ethanol	402.9	This work
cubic Pd NCs	23.2	0.1 M KOH + 0.5 M ethanol	707.1	This work
commercial Pd/C	47.9	0.1 M KOH + 0.5 M ethanol	697.9	This work
PANI-Pd composite	25.2	1.0 M NaOH + 1 M ethanol	433	[S1]
AgPd(1:2)/PANI/GCE	-	0.5 M NaOH + 1 M ethanol	-	[S2]
Pd/Ppy	-	1 M KOH + 1 M ethanol	153.9	[S3]
$Pd_{89}Pt_{11}$/Ppy	-	1 M KOH + 1 M ethanol	368.9	[S3]
$Pd_{54}Au_{46}$/Ppy	-	1 M KOH + 1 M ethanol	374.9	[S3]
$Pd_{30}Pt_{29}Au_{41}$/Ppy	-	1 M KOH + 1 M ethanol	853.3	[S3]
Pd nanoplate in PDPB	-	1 M KOH + 1 M ethanol		[S4]
Pd/PANI/Pd SNTAs	-	1.0 M NaOH+ 1.0 M ethanol	~350	[S5]
Pd NTAs	-	1.0 M NaOH+ 1.0 M ethanol	~100	[S5]
Pd/PPy	104	1 M KOH + 1 M ethanol	-	[S6]
Pd/PEDOT	20	1 M KOH + 1 M ethanol	-	[S6]
Pd/PANI	85	1 M KOH + 1 M ethanol	-	[S6]

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