Highly efficient dual active palladium nanonetwork electrocatalyst for ethanol oxidation and hydrogen evolution

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Physical parameters characterization

Transmission electron microscopy (TEM) images, energy-dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED) were obtained by TECNAI model FI-20 (FEI, Netherland). Brunauer-Emmett-Teller (BET) surface area and pore size distribution were obtained through the Barrett-Joyner-Halenda method by nitrogen isotherm adsorption and desorption (BelsorpII mini, BEL Japan Inc.). X-ray powder diffraction (XRD) spectra were carried out on a Rigaku D/max-2500, using filtered Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) were gained using a MultiLab 2000 with a 14.9 keV Al K X-ray source.

Electrochemical characterization

The 1 mg mL^{-1} PdNN suspension in water was prepared by sonication. A 10 μL portion of the PdNN suspension was then dropped onto the prepolished glassy carbon electrode (GCE). Other prepared catalysts, PdNPs and PdZnNN-coated GCEs were prepared by the same protocol. The 10 μL of 20% Pt/C (E-TEK) suspension in ethanol (1 mg mL^{-1} with 5 μL of 5% Nafion solution) was dropped onto GCE. The loading amount of Pd for the PdNN, PdNPs and PdZnNN catalysts was 16.9, 22.6, 25.5 μg$_{Pd}$ cm^{-2}, respectively, and Pt loading for Pt/C catalyst was 28.3 μg$_{Pt}$ cm^{-2}, normalized to the geometric electrode area (0.0707 cm^2). All electrochemical techniques were performed using a three-electrode potentiostat [CHI 700C electrochemical workstation (U.S.A.)]. A Pt wire and Ag/AgCl electrodes were used as auxiliary electrode and reference electrode, respectively. The rotating disk electrode (RDE) was used for HER using an EG&G Model 636 RDE system along with the CHI 700C. All electrochemical experiments were performed in high purity argon (Ar)-purged (for at least 30 min) 1 M KOH solutions at room temperature (RT).
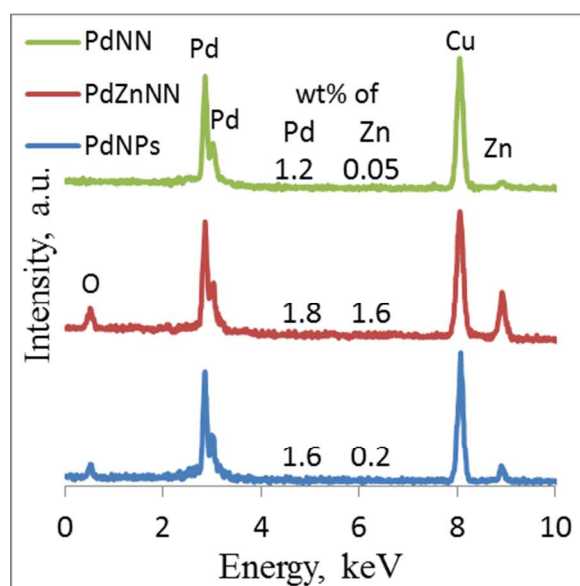
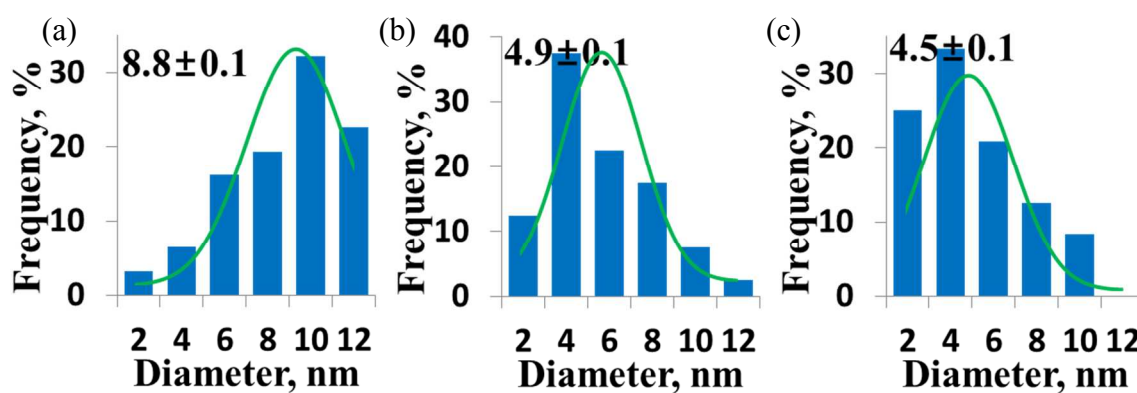**Figure S1:** EDX spectra of PdNN, PdNPs, and PdZnNN catalysts.

Figure S2: The diameter size histograms of PdNN prepared using CTAB concentrations of 40 mM (a) 80 mM (b) and 120 mM (c).
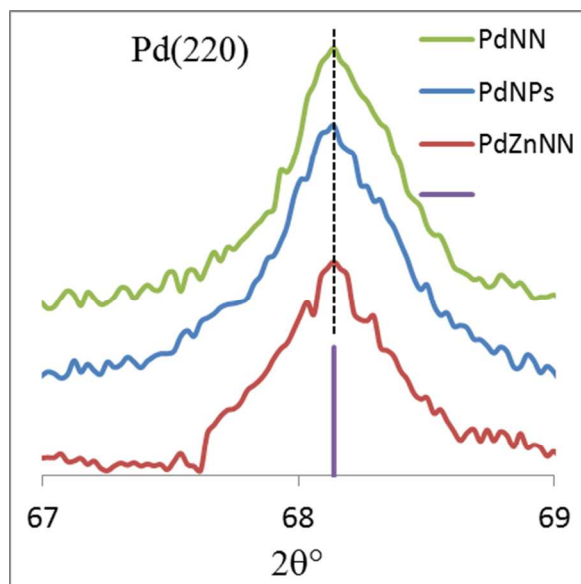
Figure S3: Enlarged XRD patterns of PdNN, PdNPs, and PdZnNN at Pd(220) region.
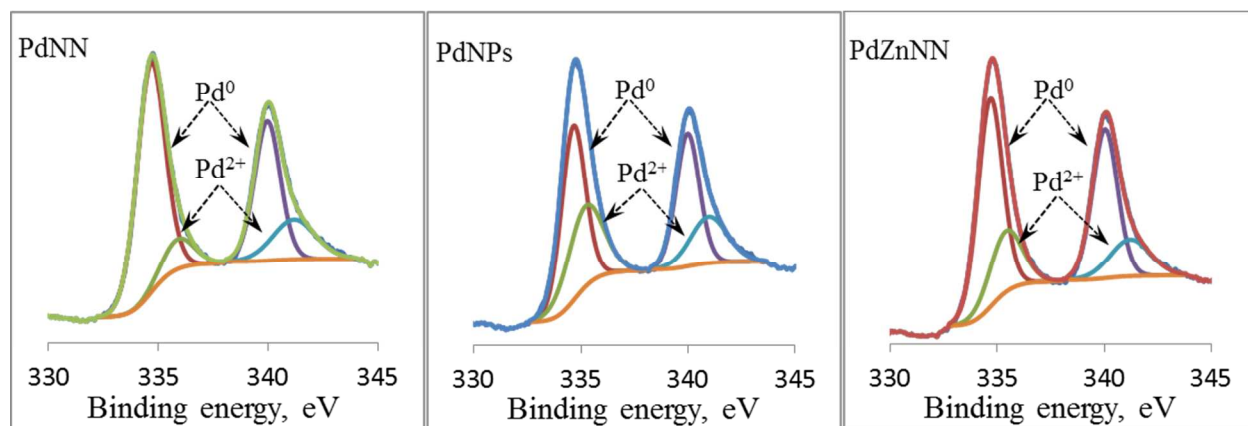

Figure S4: The core level of Pd3d XPS spectra for all samples.
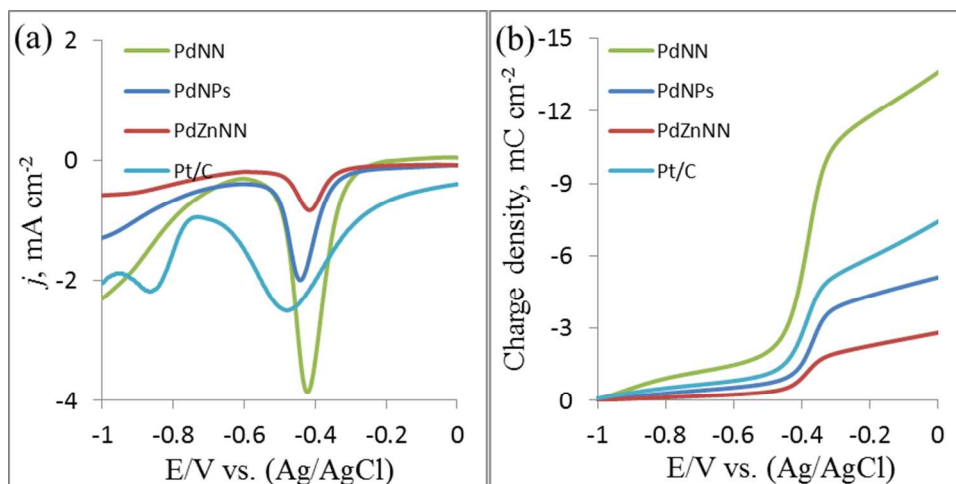
Figure S5: Backward scan of CVs on PdNN, PdNPs, PdZnNN and Pt/C recorded in Ar-saturated 1 M KOH electrolyte at a scan rate of 50 mV s^{-1} (a) and the corresponding charge density variation (b).
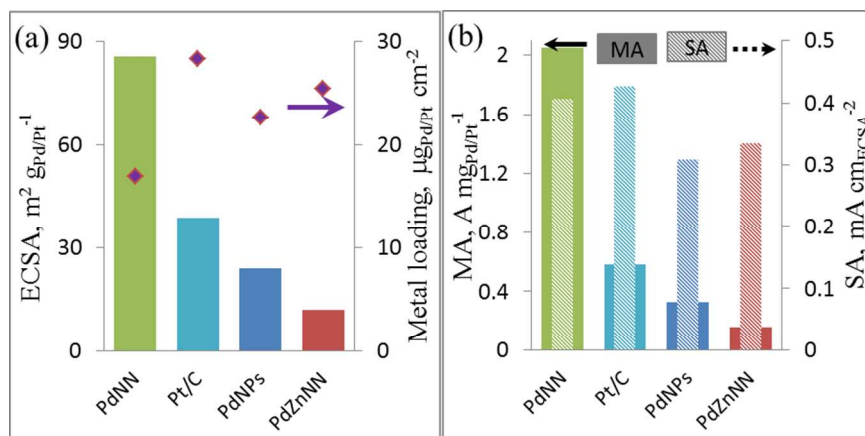

Figure S6: The plots of Pd/Pt loading and corresponding ECSA (a) and mass activity with specific activity (b) of PdNN, PdNPs, PdZnNN and Pt/C catalysts.
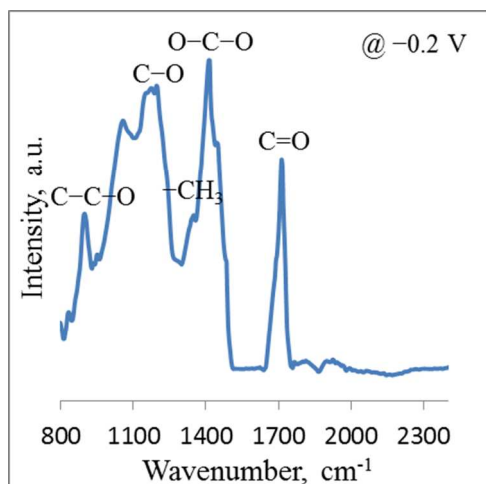
Figure S7: Single potential alteration infrared reflectance spectroscopy of the species resulting from the oxidation of ethanol in Ar-saturated 1 M KOH + 1 M ethanol solution at the PdNN.
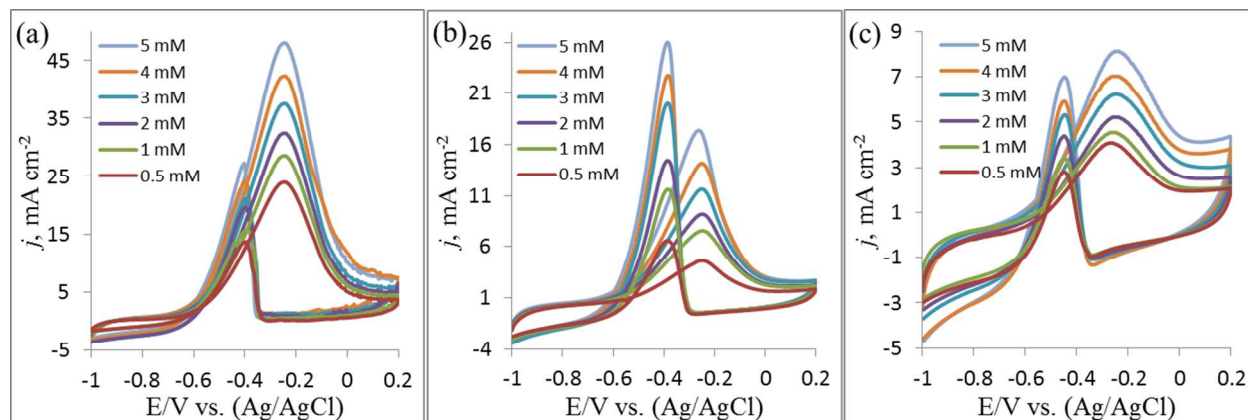

Figure S8: CVs for EOR on PdNN (a), PdNPs (b), and PdZnNN (c) recorded in Ar-saturated 1 M KOH electrolyte in presence of various concentration of ethanol at a scan rate of 50 mV s^{-1}.
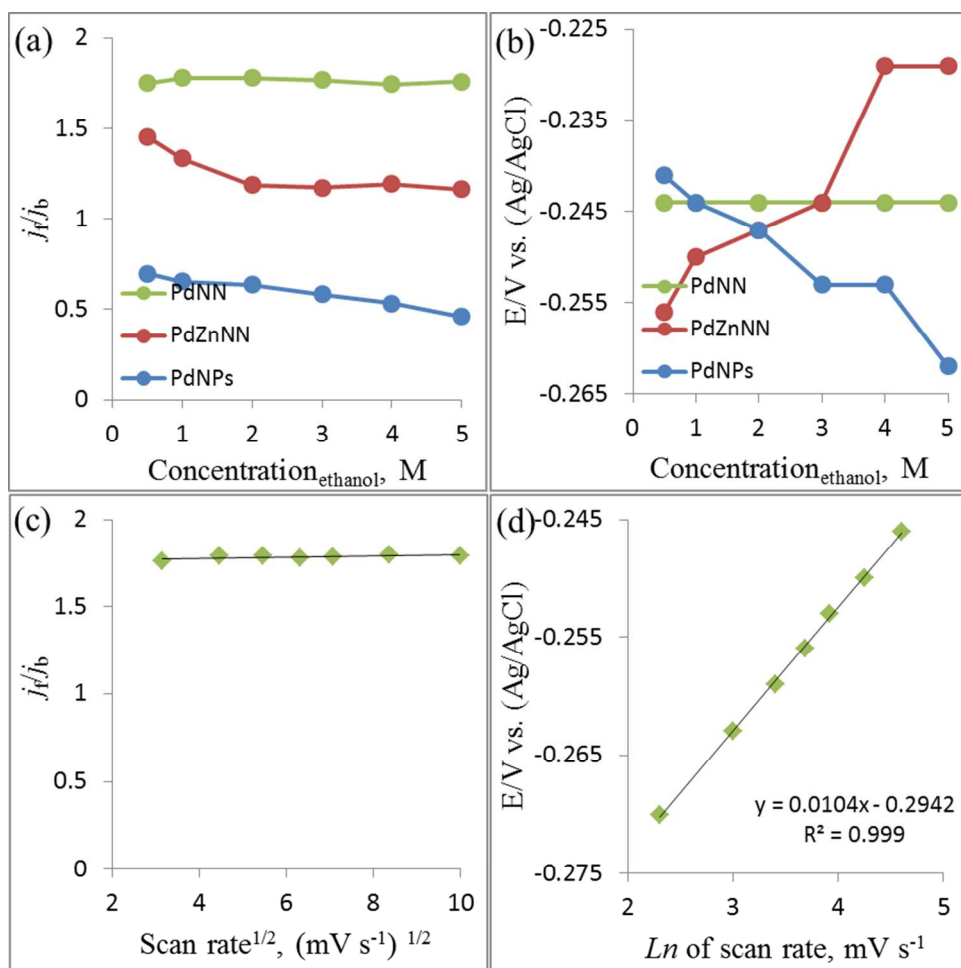
Figure S9: Plots of J_f/J_b (a) as well as J_f variation (b) as the function of ethanol concentration for PdNN, PdNPs and PdZnNN; the plot of J_f/J_b vs. square root of scan rate (c) and J_f shift vs. *ln* of scan rates (d) on PdNN-modified electrode.
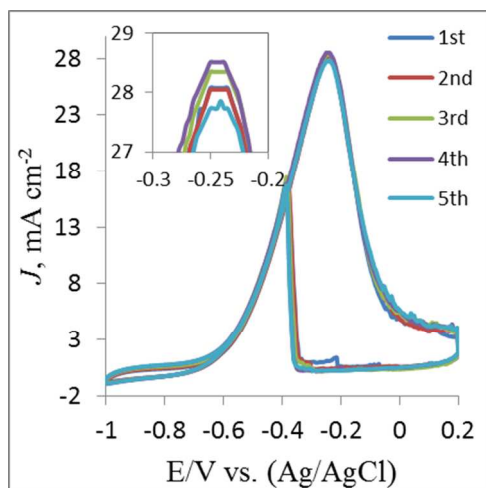
Figure S10: CV curves for EOR on five different PdNN-modified electrodes in Ar-saturated 1 M KOH electrolyte containing 1 M EtOH with current density normalized to electrode area; inset: the enlarged CV curves for better view.