Electronic Supplementary Material (ESI) for Nanoscale Horizons.

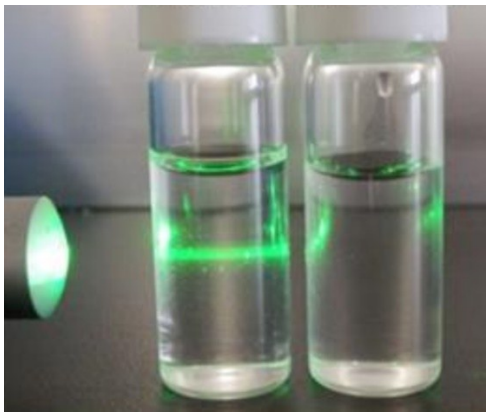

Fig. S1. A digital photograph showing the Tyndall effect in which light scattering occurred in the presence of micelles. The addition of an ethanol-water mixture induced the transformation of the free unimer (right side) into micelles (left side).

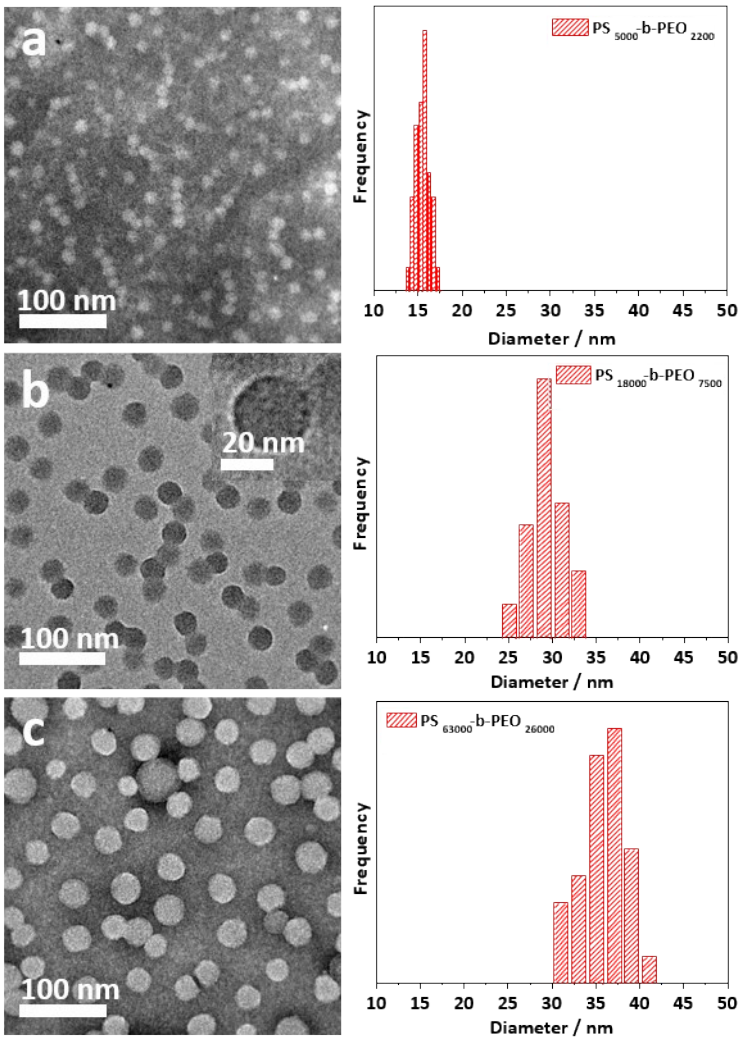

Fig. S2. TEM images (left) and diameter distribution histograms (right) of the spherical micelles made from (a) $PS_{(5000)}$-*b*-$PEO_{(2200)}$, (b) $PS_{(18000)}$-*b*-$PEO_{(7500)}$, and (c) $PS_{(63000)}$-*b*-$PEO_{(26000)}$. The micelles were stained with 1.0 wt% phosphotungstic acid. In some parts, staining agents were adsorbed on the PEO micelle surface thus appeared as a corona, as indicated on the inset in panel b (left).[S1]

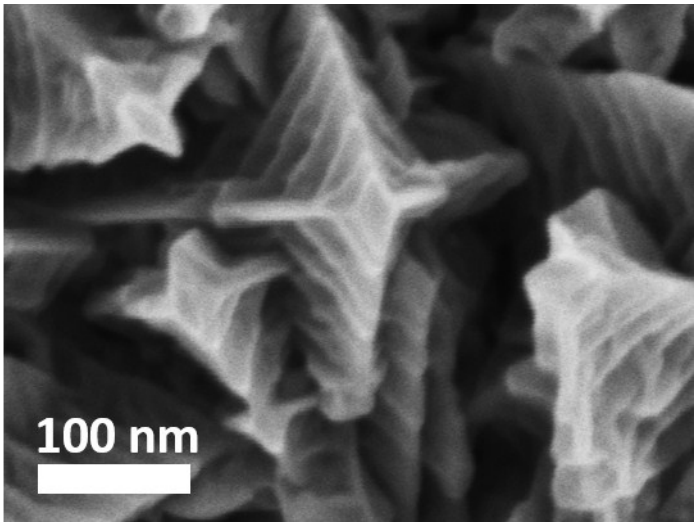

Fig. S3. A typical SEM image of the non-porous Pd film obtained in the absence of the block copolymer PS-*b*-PEO using the same electrochemical deposition process.

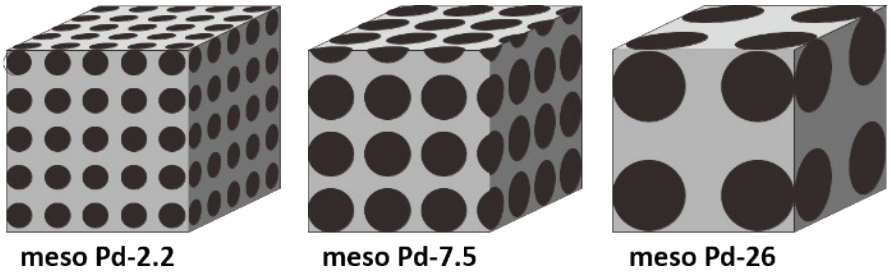

Fig. S4. Modeled pore arrangements and geometries of meso Pd-2.2, meso Pd-7.5, and meso Pd-26 for validating the calculations of the Pd surface area inside the films. To make these models, the pore sizes and the wall thicknesses were fixed to be 14 nm and 6 nm (for meso Pd-2.2), 25 nm and 6 nm (for meso Pd-7.5), 41 nm and 18 nm (for meso Pd-26), respectively.

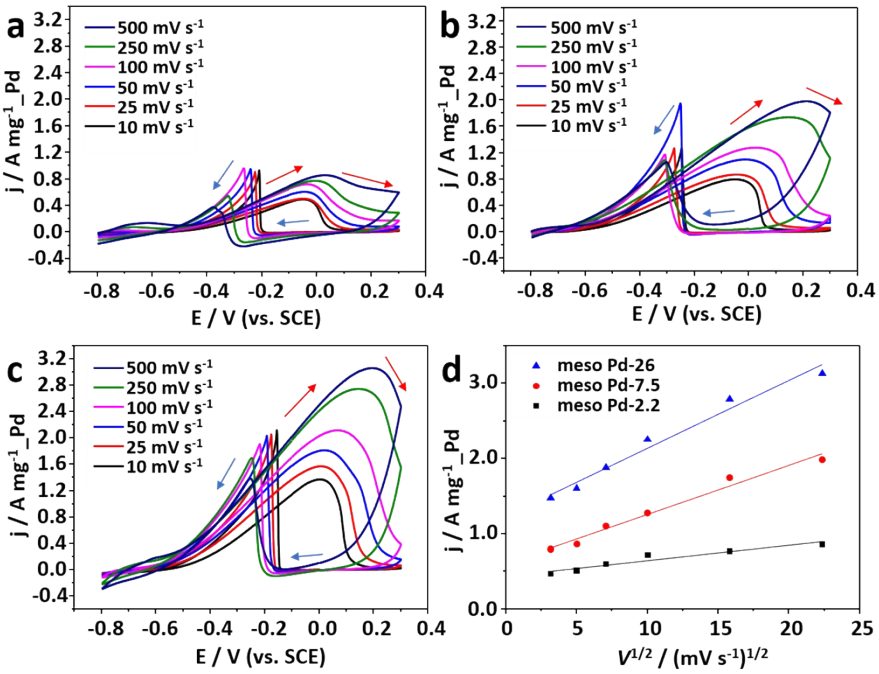

Fig. S5. (a-c) Cyclic voltammetry (CV) curves of (a) meso Pd-2.2 film, (b) meso Pd-7.5 film, and (c) meso Pd-26 film with the same film thickness (~500 nm) in 1.0 M KOH containing 1.0 M C_2H_5OH at various scan rates (10, 25, 50, 100, 250 and 500 mV s^{-1}). (d) Forward oxidation peak current density (mass activity) as a function of the square root of the scan rate for meso Pd-2.2, meso Pd-7.5, and meso Pd-26 films. The red and blue arrows in panels a-c indicate positive and negative scan directions, respectively.

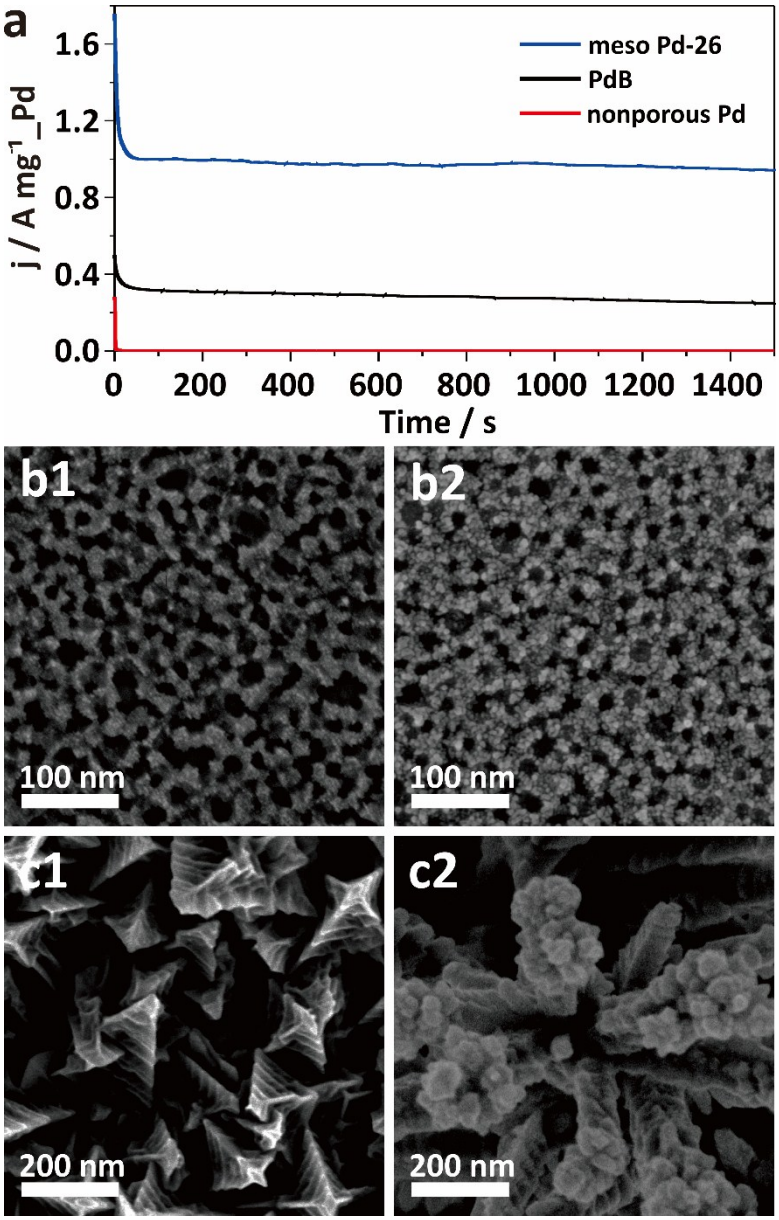

Fig. S6. (a) Amperometric *i-t* curves of non-porous Pd film, commercial PdB, and meso Pd-26 film at a constant potential of –0.1 V (*vs*. SCE) for 1500 s in 1.0 M KOH containing 1.0 M C_2H_5OH. SEM images of the (b) meso Pd-26 and (c) non-porous Pd film obtained in the absence of the block copolymer PS-*b*-PEO (b1, c1) before and (b2, c2) after the stability test.

References

[S1] M. Sasidharan, D. Liu, N. Gunawardhana, M. Yoshio and K. Nakashima, *J. Mater. Chem.*, 2011, **21**, 13881