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$_2$H$_5$OH 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$_2$H$_5$OH. 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**