Supporting Information

1. Typical procedure for the preparation of silica nanoparticles

1 mmol Igepal CO-520 was dispersed in 10 ml of cyclohexane by sonication for 40 min. Then 80 µl of ammonia solution was added into the prepared solution. Finally, 60 µl of tetraethyl orthosilicate was added and the mixture was stirring for 48 h in order to complete the hydrolysis and condensation reactions of the precursors to silica.

2. Pd electrode preparation and electrochemical measurements

A polished glass-carbon disk electrode was used as the substrate (d = 5 mm). 10 µl of suspension containing 3DOM Pd networks or ultrafine Pd black (0.5 mg/ml) after ultrasonication was pipetted onto the electrode and dried in air at room temperature. Then, 2 µl of Nafion solution (5 wt.%) was pipetted on it and the Pd working electrode was obtained. A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as the reference electrode, a platinum wire as the counter electrode and the as-prepared Pd electrodes as the working electrode. The Pd loading was 25 µg cm^{-2}. Cyclic voltammeter (CV) with a scanning rate of 50 mV S^{-1} and chronoamperometry (CA) experiments at 0.23 V were performed in a 0.5 M H_2SO_4 + 0.5 M HCOOH solution at room temperature.

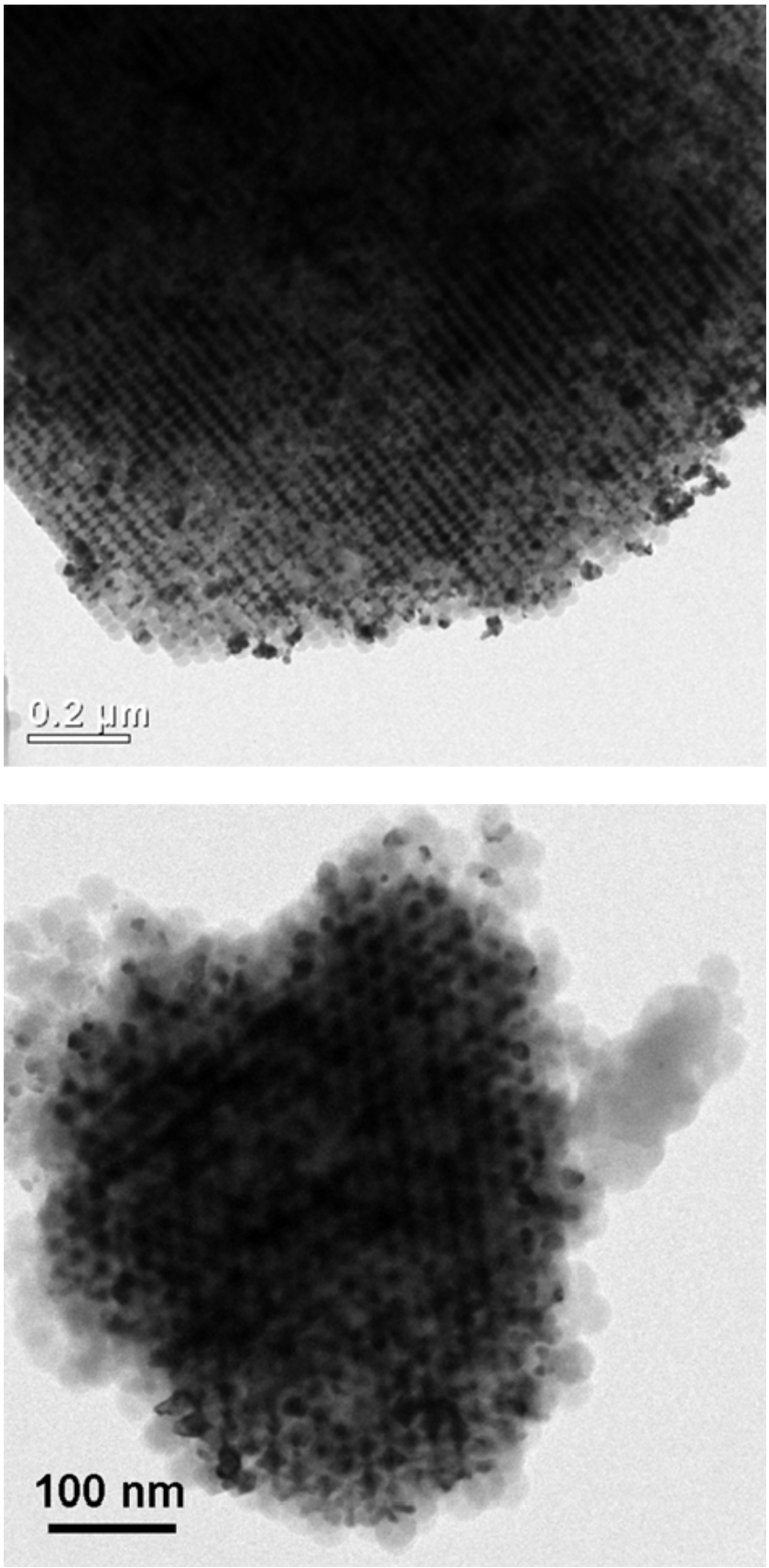

Fig. S1 TEM images of Pd-infiltrated silica super crystal

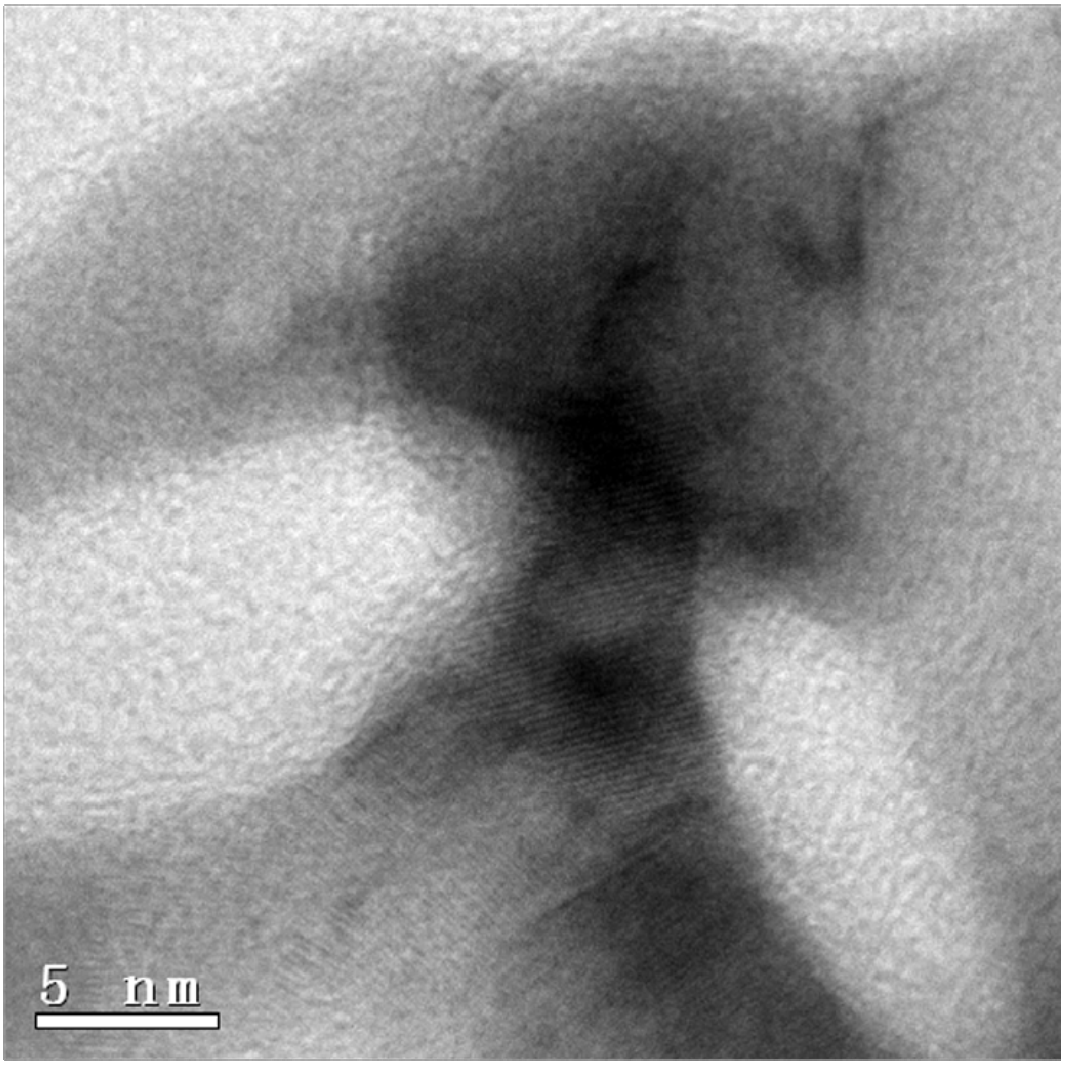

Fig. S2 HRTEM image of silica-free 3DOM Pd networks

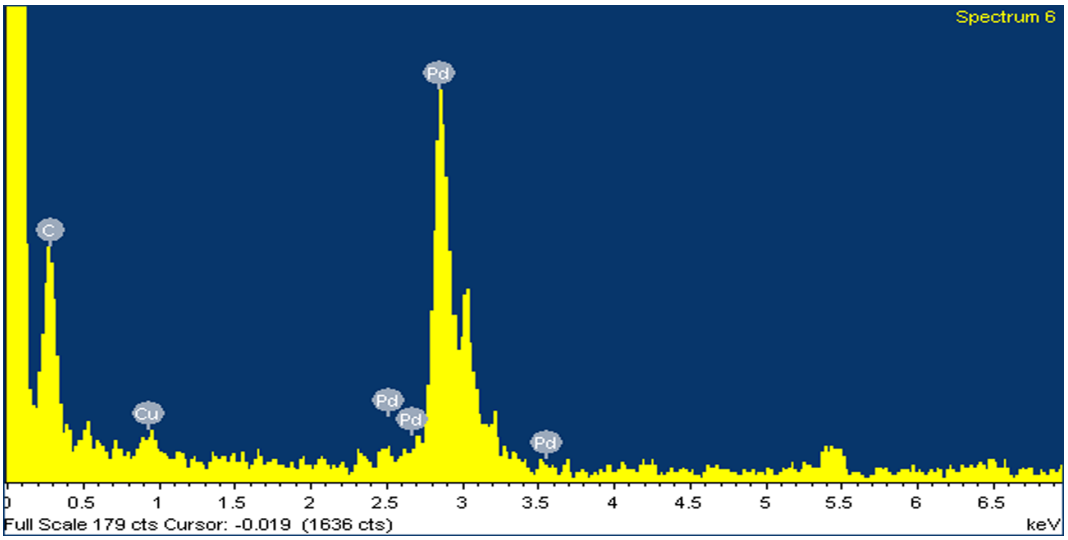

Fig. S3 EDX of silica-free 3DOM Pd networks

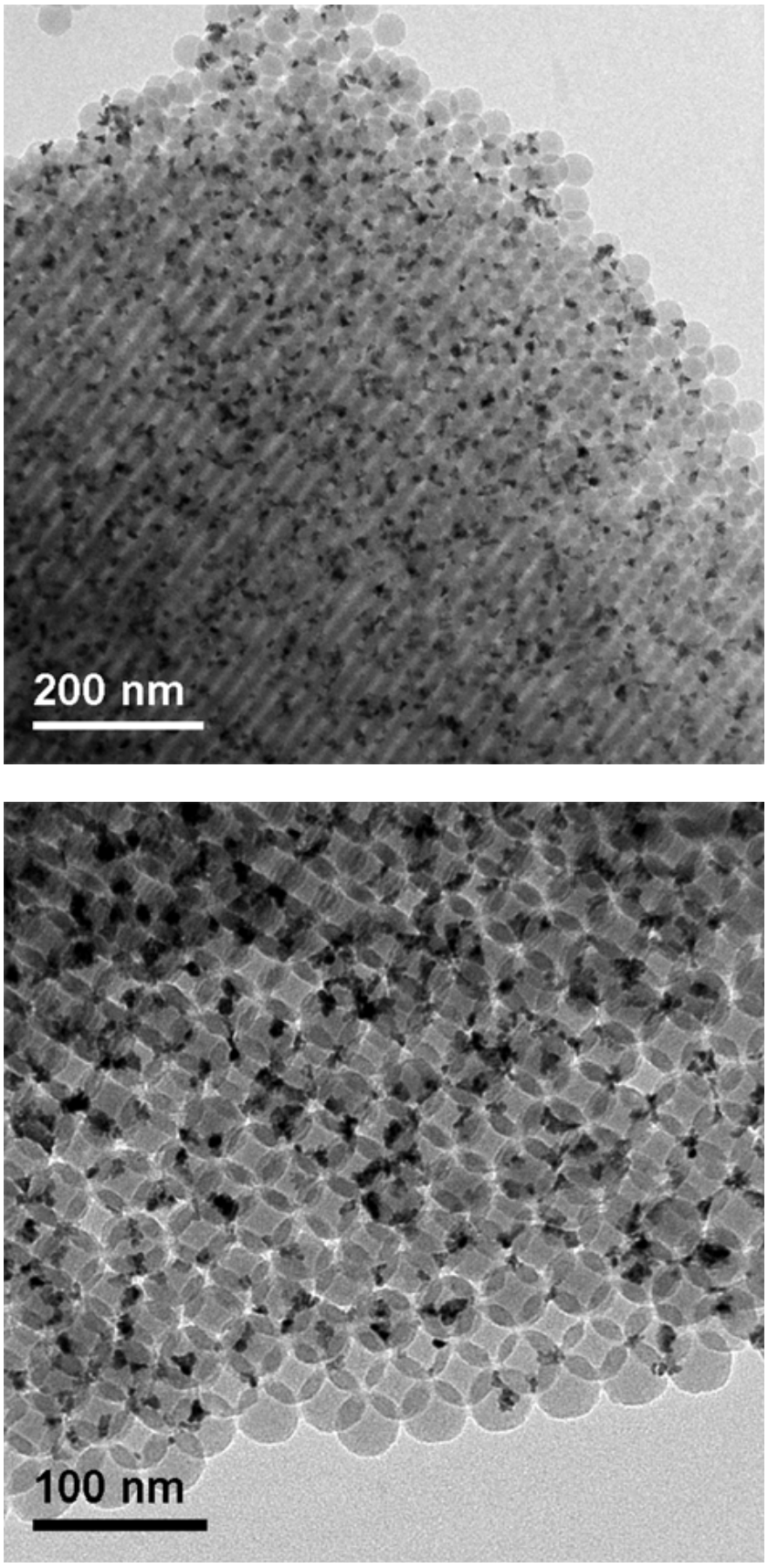

Fig. S4 TEM images of Pt infiltrated silica super crystal