## Supporting information for

## A Continuous Etching Process for Highly-Active Pd Nanoclusters and Their *in-situ* Stabilization

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**Fig S1**. Pd samples collected at different reaction time after the introduction of NaBH<sub>4</sub>. a) 0 min, b) 10 h. The product originally exist as large particles, and then it is gradually etched into tiny water soluble nanoclusters.



**Fig. S2.** UV/Vis spectra of the Pd samples collected at different etching time after the addition of NaBH<sub>4</sub>. The characteristic Plasmonic band of large particles at 302 nm will gradually dissappear during their transformation into small nanoclusters.



Fig. S3. TEM images of Pd-SiO<sub>2</sub> samples prepared with different amounts of L-methionine. a) 0 mM, b) 2.5 mM. The etching time for Pd species are both 20 h after the introduction of NaBH<sub>4</sub>, and then a sol-gel process is introduced for the formation of a silica matrix.



Fig. S4. The N2 adsorption–desorption isotherms of the Pd nanoclusters sample. The curve shows an typical hysteresis loop at high partial pressures, indicating the formation of a mesoporous structure.