Supporting information for

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

Ai-Zhi Zhong, a,b Wei Zou b Wen-Xin Mao, a,b Rong-Wen Lu* b, An-Min Cao* a and Li-Jun Wan*

a Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China. Email: anmin_cao@iccas.ac.cn

b State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China. E-mail: lurw@dlut.edu.cn

Fig S1. Pd samples collected at different reaction time after the introduction of NaBH₄. 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 NaBH₄. The characteristic Plasmonic band of large particles at 302 nm will gradually disappear during their transformation into small nanoclusters.

![Fig. S2](image1.png)

Fig. S3. TEM images of Pd-SiO₂ 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 NaBH₄, and then a sol-gel process is introduced for the formation of a silica matrix.

![Fig. S3](image2.png)
Fig. S4. The N2 adsorption–desorption isotherms of the Pd nanoclusters sample. The curve shows a typical hysteresis loop at high partial pressures, indicating the formation of a mesoporous structure.