

Electronic Supplementary Information

## **Unconventional Pd Nanoparticles' Growth Induced by Competitive Effect between Temperature-dependent Coordination and Reduction of Grafted Amino Ligands for Heck Reaction**

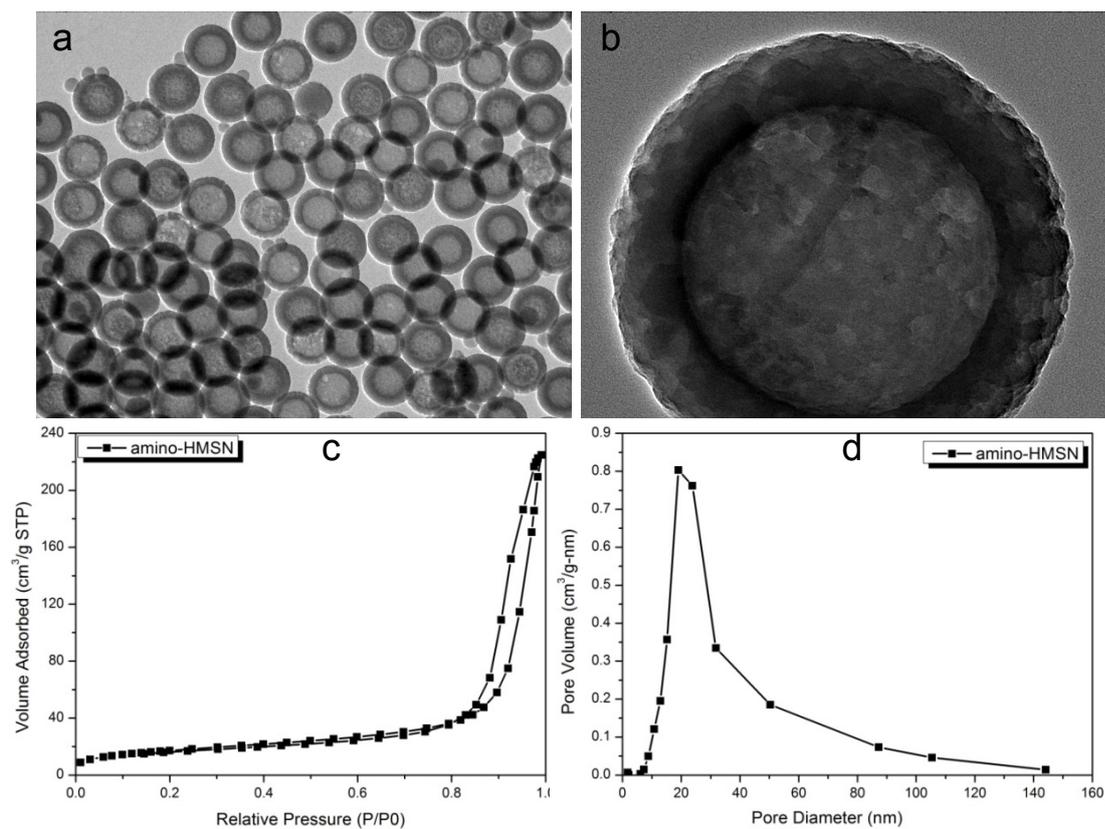
By Kun Zhang,<sup>a</sup> Hangrong Chen,<sup>\*a</sup> Xiaoxia Zhou,<sup>a</sup> Yun Gong,<sup>a</sup> Guobin Zhang,<sup>a</sup> Xia Wang,<sup>a</sup> Yu Chen<sup>a</sup> and Jianlin Shi<sup>\*a</sup>

<sup>a</sup> State Key Laboratory of High Performance Ceramics and Superfine Microstructure; Shanghai Institute of Ceramics, Chinese Academy of Sciences; No.1295 Ding-xi Road, Shanghai; 200050 (P.R.China).

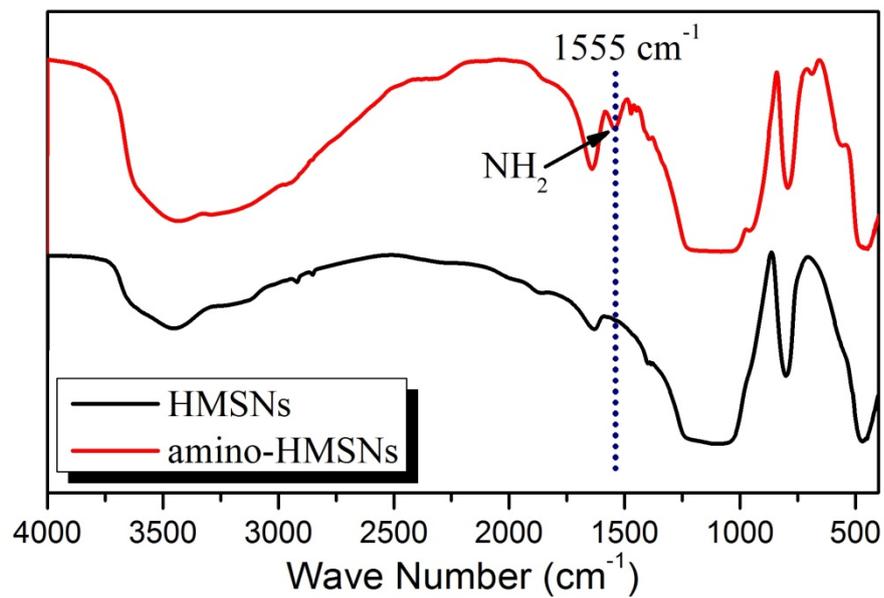
\* Email address: [hrchen@mail.sic.ac.cn](mailto:hrchen@mail.sic.ac.cn), and [jlshi@sunm.shcnc.ac.cn](mailto:jlshi@sunm.shcnc.ac.cn)

Tel: (+86)021-5241-2706. Fax: (+86)21-5241-3122

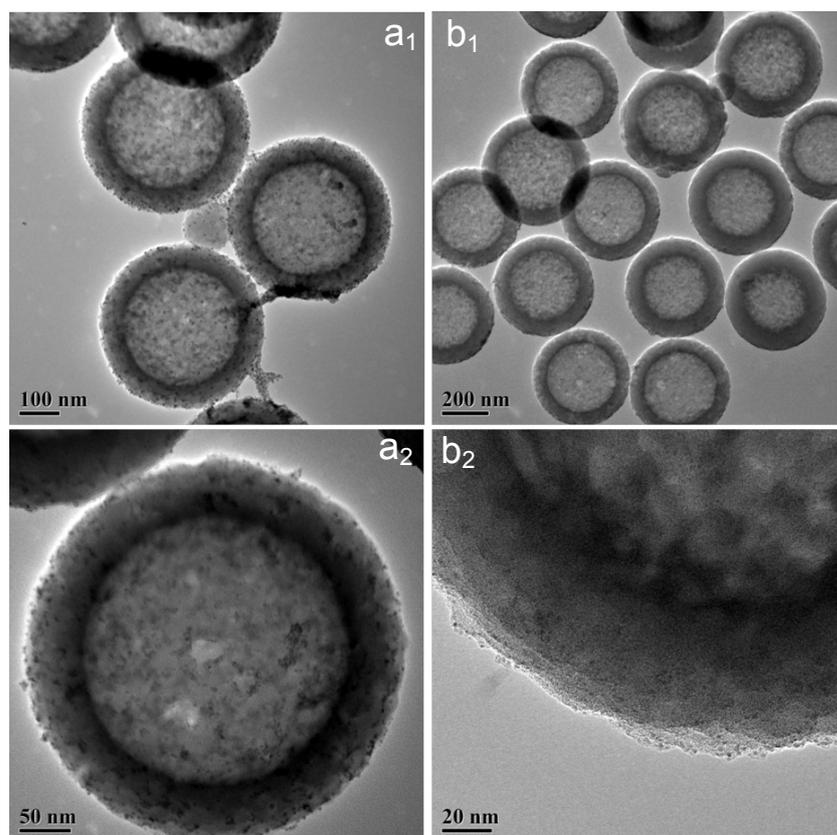
## Figures and tables



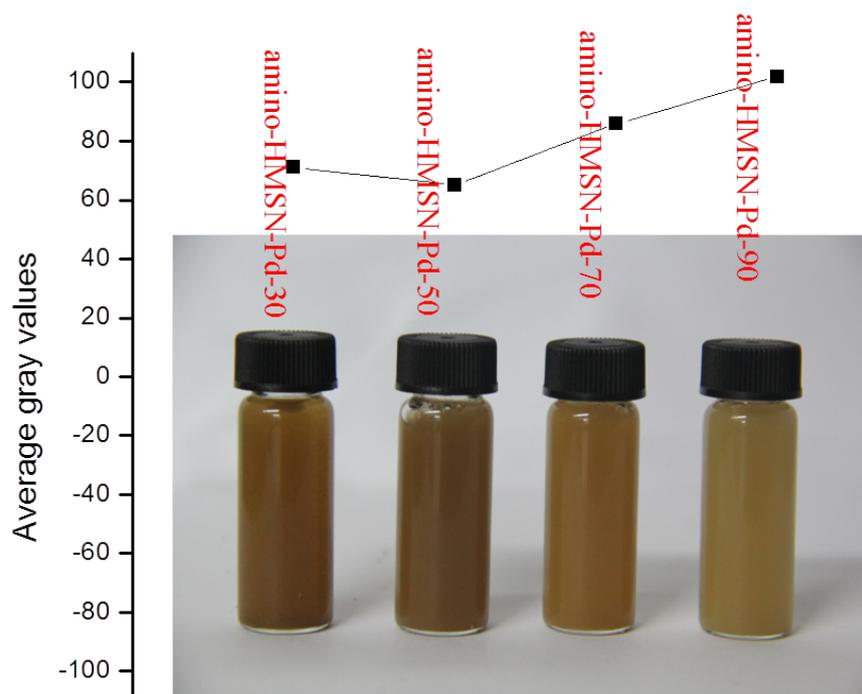
**Figure S1.** TEM images (a,b),  $N_2$  adsorption and desorption isotherms (c) and pore diameter distributions (d) of amino-HMSNs.



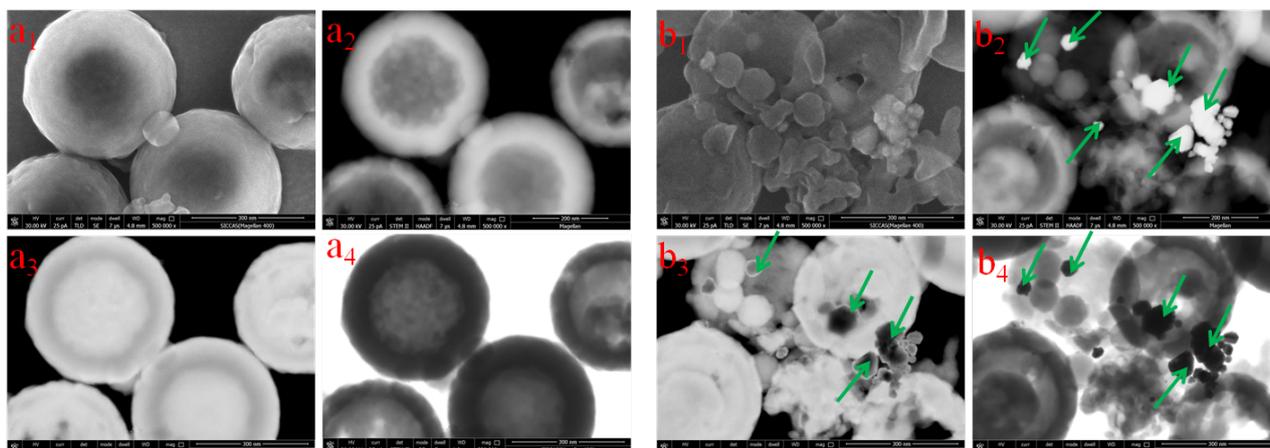
**Figure S2.** FTIR spectra of HMSNs and amino-HMSNs, and at  $1543 \text{ cm}^{-1}$ , the characteristic peak of N-H was observed in amino-HMSNs, indicating the existence of amino groups.



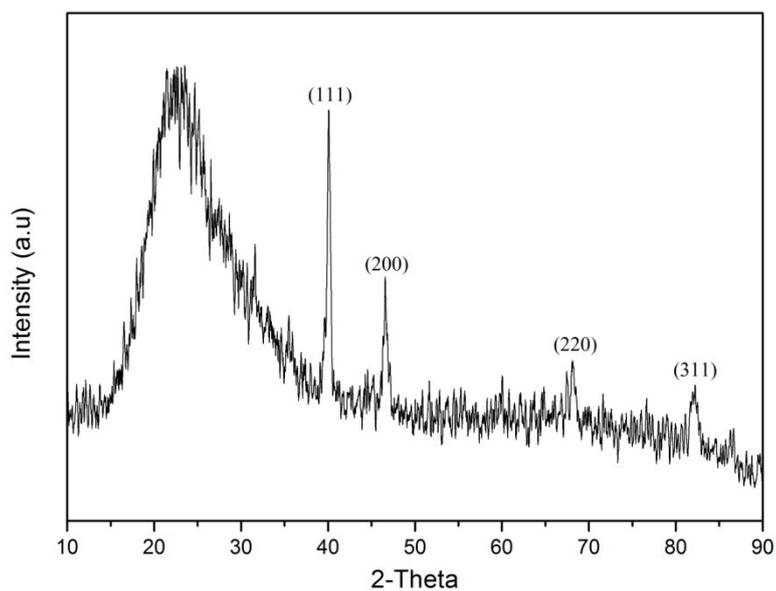
**Figure S3.** TEM images of amino-HMSN-Pd-30 (a<sub>1</sub>, a<sub>2</sub>) and amino-HMSN-Pd-90 (b<sub>1</sub>, b<sub>2</sub>).



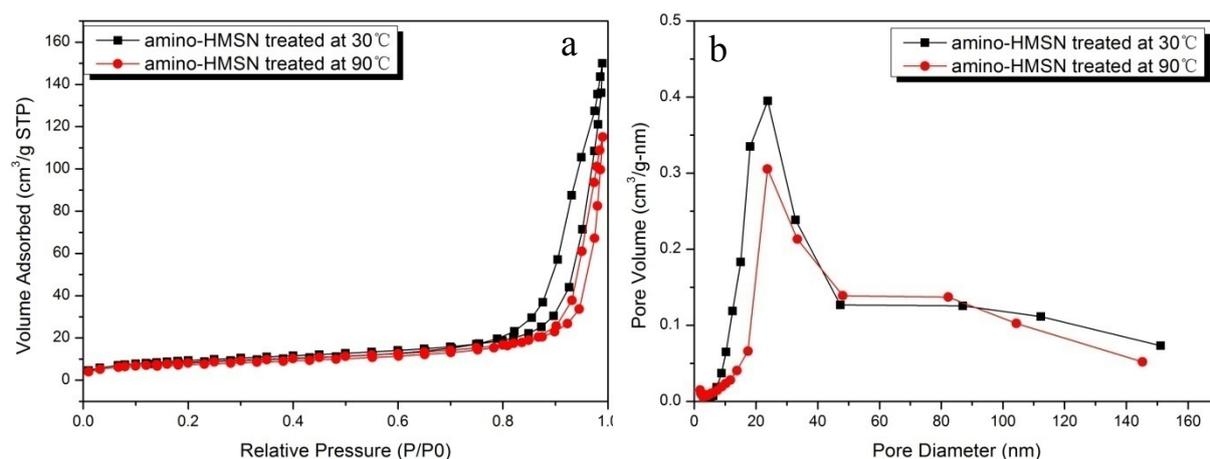
**Figure S4.** Digital photos and average gray values of amino-HMSN-Pd-30, amino-HMSN-Pd-50, amino-HMSN-Pd-70 and amino-HMSN-Pd-90. The average gray values can be measured *via* the software, SONOMATH developed by Chongqing AMBITION T.C.



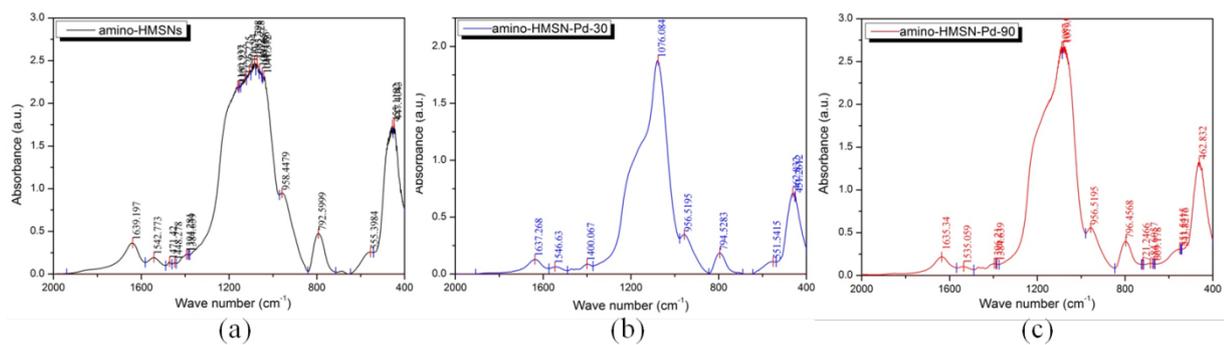
**Figure S5.** SEM, high angle annular dark field (HAADF), dark field (DF) and bright field (BF) images of cal-HMSNs after reacting with Pd precursors at 30 °C (a<sub>1</sub>-a<sub>4</sub>) and 90 °C (b<sub>1</sub>-b<sub>4</sub>).



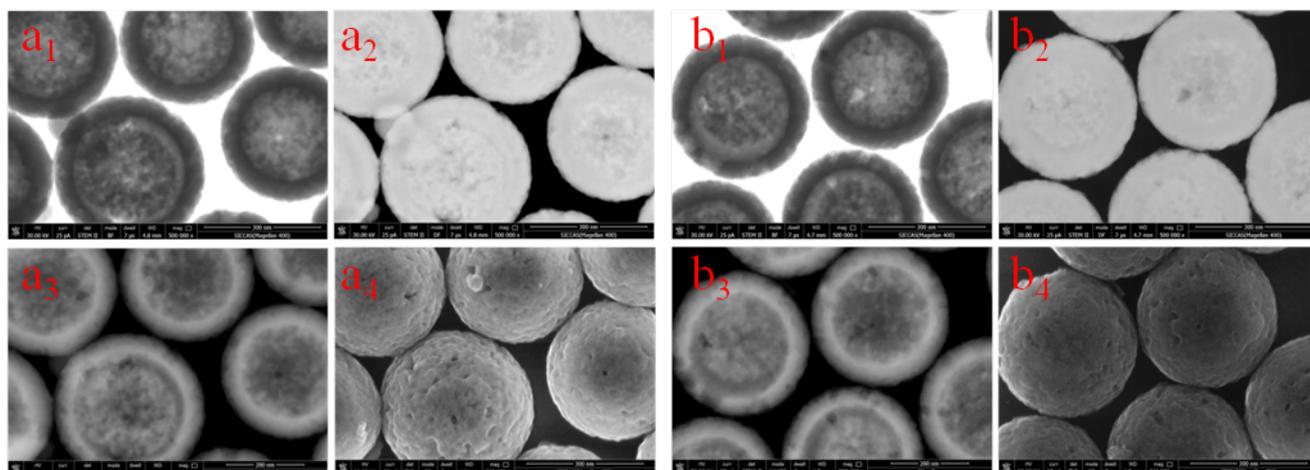
**Figure S6.** Powder X-ray diffraction of cal-HMSNs treated with Pd precursors at 90 °C.



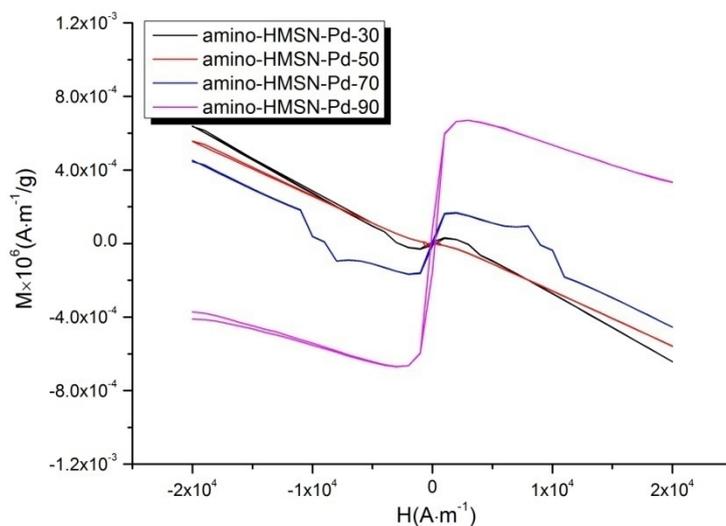
**Figure S7.** N<sub>2</sub> isotherms (a) and pore diameter distribution (b) of amino-HMSN after hydrothermal treatment at 30 °C and 90 °C for 4h; BET Surface Area: 34 m<sup>2</sup>/g, Pore volume: 0.23 cm<sup>3</sup>/g and Pore diameter : 14.5 nm for amino-HMSN treated at 30 °C, but for amino-HMSN treated at 90 °C, BET Surface Area: 35 m<sup>2</sup>/g, Pore volume: 0.21 cm<sup>3</sup>/g and pore diameter: 13.9 nm. So no prominent variations of BET surface area, pore diameter, and pore volume between amino-HMSNs treated at 30 °C and 90 °C emerged.



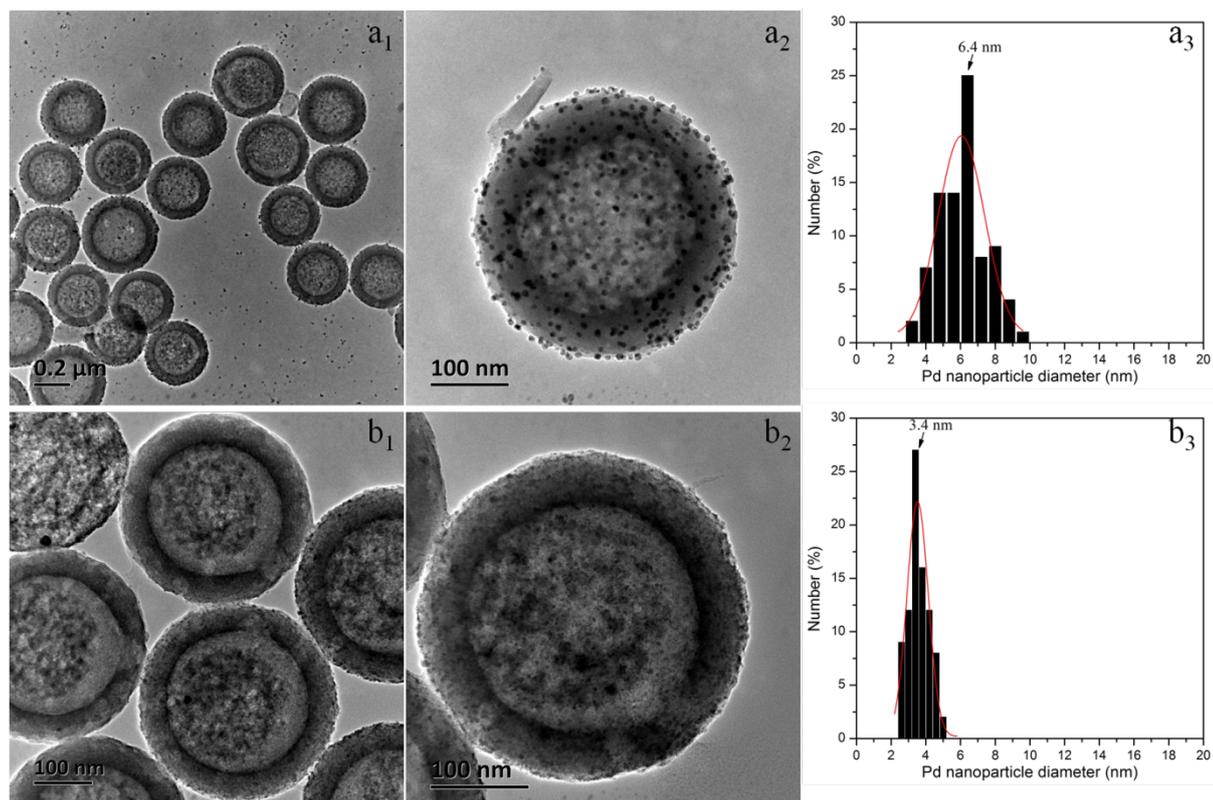
**Figure S8.** (a-c) FTIR absorbance spectra of amino-HMSNs (a), amino-HMSN-Pd-30 (b) and amino-HMSN-Pd-90 (c).



**Figure S9.** SEM and STEM images after amino-HMSNs after reacting with Pt precursors at 30 °C (a<sub>1</sub>-a<sub>4</sub>) and 90 °C (b<sub>1</sub>-b<sub>4</sub>).



**Figure S10.** The magnetizing curves of amino-HMSN-Pd-30, amino-HMSN-Pd-50, amino-HMSN-Pd-70 and amino-HMSN-Pd-90 at different measurement temperatures (30 °C for amino-HMSN-Pd-30, 50 °C for amino-HMSN-Pd-50, 70 °C for amino-HMSN-Pd-70 and 90 °C for amino-HMSN-Pd-90).



**Figure S11.** TEM images of amino-HMSN-Pd-30 (a<sub>1</sub>,a<sub>2</sub>) and amino-HMSN-Pd-90 (b<sub>1</sub>,b<sub>2</sub>) dispersed in deionized water after 2 months at room temperature; (a<sub>3</sub>,b<sub>3</sub>) Corresponding Pd size distributions in amino-HMSN-Pd-30 (a<sub>3</sub>) and amino-HMSN-Pd-90 (b<sub>3</sub>)

**Table S1.** Peak area ratios of different samples between at 795 cm<sup>-1</sup> and 1555 cm<sup>-1</sup>.

Samples	Peak area ratio between at around 795 cm <sup>-1</sup> and 1555 cm <sup>-1</sup>
Amino-HMSN	2.037
Amino-HMSN-Pd-30	2.525
Amino-HMSN-Pd-50	3.143
Amino-HMSN-Pd-70	3.104
Amino-HMSN-Pd-90	2.362

**Table S2.** Pt atom mass percentages coordinated with amino-HMSNs at 30 °C, 50 °C, 70 °C and 90 °C.

Temperature (°C)	Pt content (%)
30	0.194
50	0.552
70	1.974
90	4.572