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Supporting information



Figure S1 SEM (a) image of large scale of hierarchically porous Pd nanospheres. The

bar is 1 μm.



Figure S2 XRD pattern of hierarchically porous Pd nanospheres.

In the XRD diffraction pattern (Figure S2) of hierarchically porous Pd nanospheres, several sharp diffraction peaks are observed at 16.7°, 29.8°, 39.0°, 67.1°, which can be assigned to diffraction from the 111, 220, 222, and 531 planes of Pd crystal, respectively.



Figure S3 The exterior size distribution of hierarchically porous Pd nanospheres

Figure S3 shows wide size distribution of hierarchically porous Pd nanospheres, and the average size is about 223 nm from DLS data (Figure S3).



Figure S4 The chemical structure of acridine orange base (a), TEM (b) and SEM (c) images of Pd product synthesized in the presence of acridine orange base.



Figure S5 The chemical structure of 5-carboxy-x-rhodamine N-succinimidyl ester (a), and TEM (b) image of Pd product synthesized in the presence of 5-carboxy-xrhodamine N-succinimidyl ester



Figure S6 Time-dependent TEM observations during the growth of hierarchically porous Pd nanospheres sample. (a) 1min; (b) 2 min; (a) 3 min; (b) 4 min.



Figure S7 The CV curves of porously chess box-like Pd nanostructure towards formic acid oxidation in the solution of $0.1 \text{ M H}_2\text{SO}_4$ and 0.1 M HCOOH. Scan rate: 50 mV/s.



Figure S8 SEM images of hierarchically porous Pd nanospheres after 300 cycles of catalyzing formic acid electrooxidation in the solution of 0.1M H₂SO₄ and 0.1M HCOOH. The bars in the (a) and (b) are 100 nm and 50 nm, respectively.



Figure S9 The CV curves of hierarchically porous Pd nanospheres towards ethanol oxidation in the solution of 1 M KOH and 1 M ethanol. Scan rate: 50 mV/s.

	Main elements			
Sample	Pd (wt%)	N (wt%)	C (wt%)	O (wt%)
Pd nanospheres	99.36	0.09	0.44	0.11

Table S1 Quantitative analysis of main elements in hierarchically porous Pd nanosphere sample

Table S2 The comparison of catalytic activity among hierarchically porous Pd nanosphere and other Pd nanostructures

The type of Pd nanostructure	Mass activity	References
Hierarchically porous Pd nanosphere	305 mA/mg	This work
Chess box-like Pd nanostructure	281.2 mA/mg	This work
Dentritic Pd nanostructures	187.2 mA/mg	Ref.23
Pd polyhedron networks	27.5 mA/mg	Ref.24
Pd nanocrystals	139 mA/mg	Ref.25
Flower-like Pd nanostructures	139.5 mA/mg	Ref.26