Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

## Porous Octahedral PdCu Nanocages as High Efficient Electrocatalysts for Methanol Oxidation Reaction

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Figure S1 SEM image of PdCu-5 nanocages without PVP



Figure S2 a-c) SEM images and d-f) TEM images of Cu<sub>2</sub>O octahedral precursors



Figure S3 TEM images of Cu<sub>2</sub>O@PdCu structures



Figure S4 TEM image of the shell structures of PdCu-5 nanocages.

Method	Pd : Cu mass ratio				
	$Pd_1Cu_1$	Pd <sub>1</sub> Cu <sub>3</sub>	Pd <sub>1</sub> Cu <sub>5</sub>	Pd <sub>1</sub> Cu <sub>7</sub>	Pd <sub>1</sub> Cu <sub>9</sub>
ICP	89:11	82:18	80:20	79:21	73:27
EDS	85:15	82:18	81:19	79:21	69:21

 Table S1 Compositions of as-prepared nanocages determined by ICP, EDS.



**Figure S5** a) SEM and b-c) TEM images of PdCu-1 nanocages. d) SEM and e-f) TEM images of PdCu-3 nanocages



**Figure S6** SEM images of a) PdCu-7 nanocages and b) PdCu-9 nanocages. c) Corresponding TEM image of PdCu-7 nanocages.



Figure S7 The ECSA normalized CVs of as-prepared nanocages and commercial Pd/C modified GCE in  $N_2$ -saturated 1.0 M KOH + 1.0 M CH<sub>3</sub>OH solution at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S8** a) HRTEM images of a) the shell structures of PdCu-5 nanocages and b) the shell structures of PdCu-1 nanocages.

As shown in Figure S8, it can be found that the PdCu-5 nanocages show more obvious voids in the shell structure than the PdCu-1 nanocages, indicating that the PdCu-5 nanocages possess higher porosity than the PdCu-1 nanocages.



**Figure S9** TEM images of etched PdCu-5 nanocages (denoted as PdCu-5-E) with different magnifications.



**Figure S10** Comparison CV curves of the PdCu-5 nanocages and PdCu-5-E nanocages in N<sub>2</sub>-saturated 1.0 M KOH solution at a scan rate of 50 mV s<sup>-1</sup>. b) Pd mass and c) the ECSA normalized CVs of PdCu-5 nanocages and PdCu-5-E nanocages modified GCEs in N<sub>2</sub>-saturated 1 M KOH+ 1 M CH<sub>3</sub>OH solution at a scan rate of 50 mV s<sup>-1</sup>.



Figure S11 ECSA normalized i–t curves of the PdCu-5 nanocages, and commercial Pd/C in  $N_2$ -saturated 1.0 M KOH + 1.0 M CH<sub>3</sub>OH solution.



Figure S12 a) TEM images of PdCu-5 nanocages after CV test of 200 cycles