Supporting information

Ordered indium-palladium nanoparticles: synthesis and the role of indium boosting superior electrocatalytic activity for ethanol oxidation reaction

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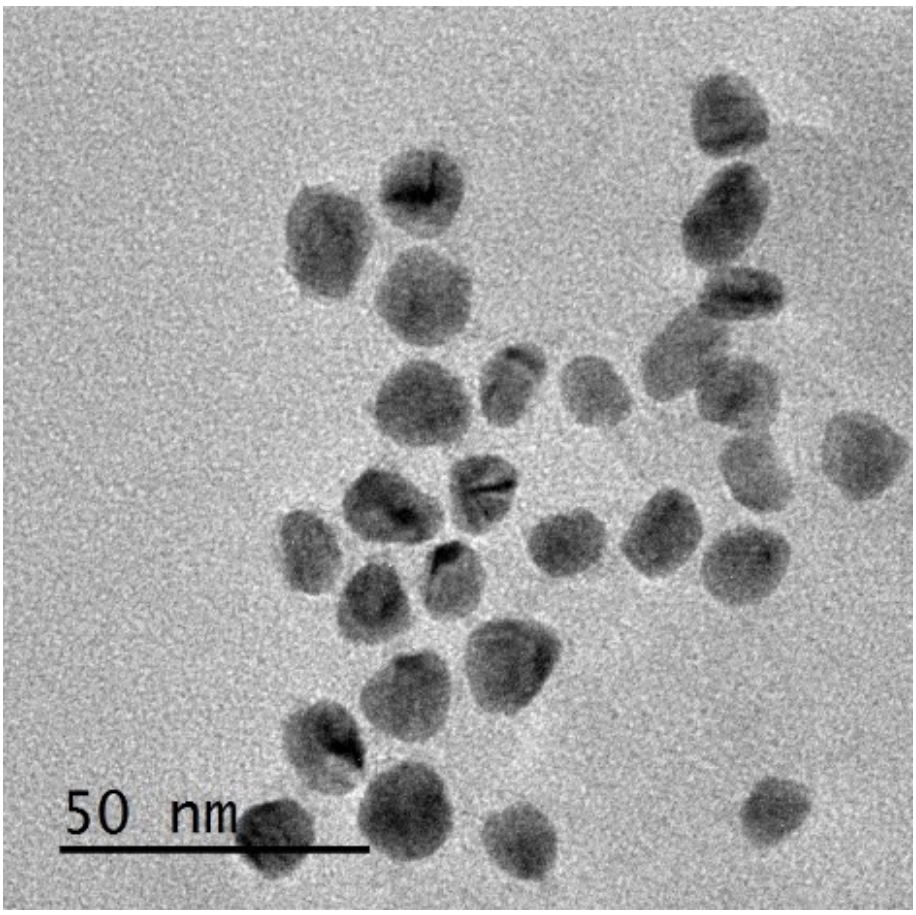

Figure S1. TEM image of In_3Pd_5 compound prepared without TOP.

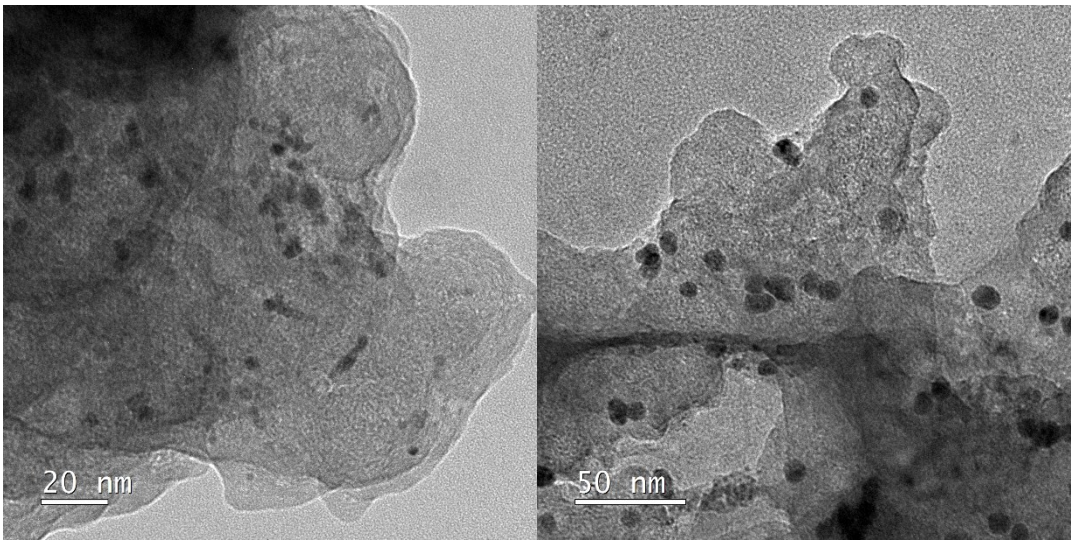

Figure S2. TEM images of nanocatalysts before and after EOR.

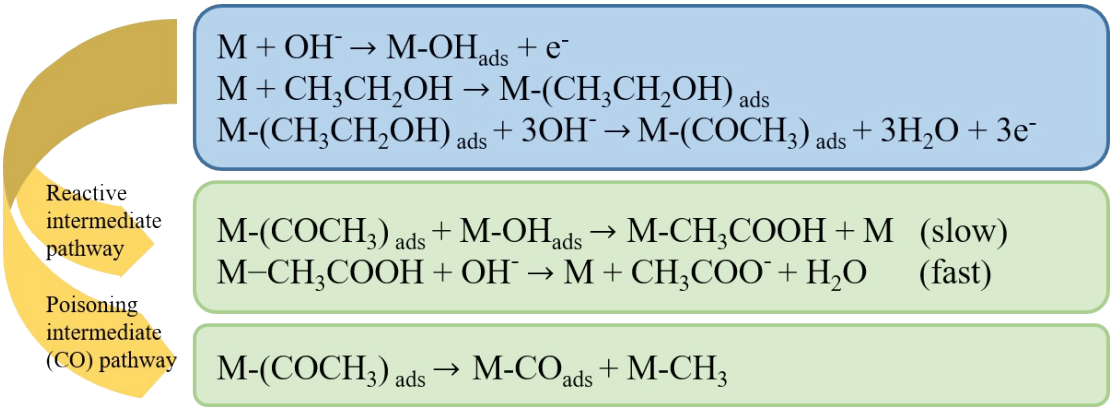

Figure S3. Scheme of possible pathway for EOR in alkaline media on In-Pd compound surface.

Table S1. Comparison of the activity and durability of various Pd-containing nanomaterials for EOR in alkaline media

Catalyst	electrolyte	Improvement compare to Pd/C	Ref.
In_3Pd_2 NP/C	**1M KOH 1M ethanol**	**5.8 times**	**This work**
In_3Pd_5 NP/C	**1M KOH 1M ethanol**	**4.0 times**	**This work**
PdCo NTAs/CFC	1M KOH 1M ethanol	4.0 times	*Angew. Chem. Int. Ed. 2015 , 54 , 3669*
Pd7/Ru1 bimetallic nanodendrites	1M KOH 1M ethanol	3.0 times	*Nanoscale. 2015, 7, 12445*
Pd-PEDOT/graphene nanocomposites	1M KOH 1M ethanol	2.78 times	*J. Mater. Chem. A. 2015, 3 (3), 1077*
Au-Pd core-shell	0.27M EtOH 0.5 M KOH	3.07 times	*Nano Lett. 2016, 16, 5514−5520*
Porous bimetallic PdNi	1M KOH 1M ethanol	3.53 times	*Journal of Colloid and Interface Science 493 (2017) 190–197*
$Pd_{40}Ag_{60}/C$	1M NaOH 1M ethanol	3.5 times	*Journal of Alloys and Compounds 688 (2016) 447e453*
Pd_3Pb nanocrystals	0.5 KOH 1M ethanol	1.4 times	*Journal of Power Sources 301 (2016) 160e169*

Table S2. OH · adsorption energy on metal surface.

	OH radical reacted with	Before adsorption energy (eV)	Chemical adsorption energy (eV)	Chemical reaction energy (eV)
Case1	Pd (Pd)	-83763.921	-84215.021	4.410
Case2	In (In_3Pd_5)	-45415.682	-45868.600	2.592
Case3	In (In_3Pd_2)	-48944.769	-49398.620	1.659
Case4	In (In)	-21019.070	-21473.828	0.752
Case5	Ge (Pd_2Ge)	-57119.648	-57571.342	3.816
Case6	Cu (PdCu)	-41367.140	-41820.531	2.119
Case7	Pb (Pd_3Pb)	-127213.185	-127662.365	6.331
Case8	Co/Pd mixing (PdCo)	-75533.962	-75986.518	2.954
Case9	Ag/Pd mixing (PdAg)	-119715.021	-120165.211	5.320
Case10	Sn (Pd_2Sn)	-72336.716	-72786.781	5.445

Chemical reaction energy (eV)= Chemical adsorption energy (eV) - OH · energy - Before adsorption (eV), which OH radical energy is -455.510 eV.

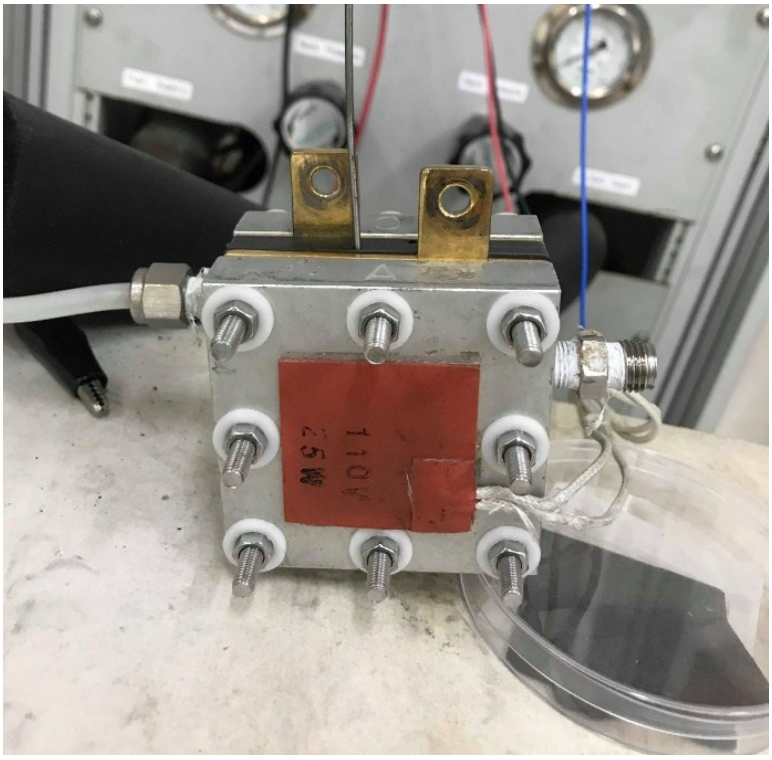

Figure S4. Scheme for assembly of DMFC full stack.

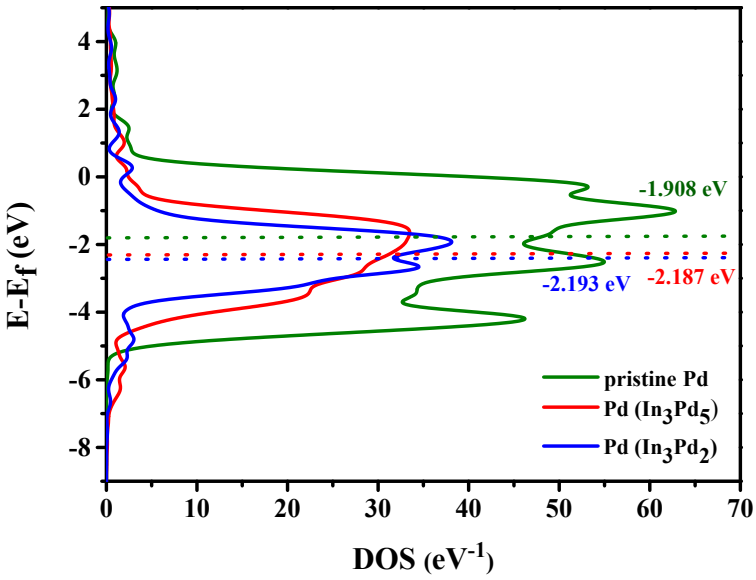

Figure S5. Projected density of states (PDOS) of Pd 3d orbitals for a 24-atom nanocluster of InPd compound and Pd

Supplementary method 1

Discrete Fourier transform calculations were performed by CASTEP[1, 2] a program that uses Kohn-Sham density functional theory[3-5] and a plane-wave pseudopotential method[6, 7]. An ultrasoft pseudopotential, which provides a lower cut-off energy compared with a norm-conserving pseudopotential, was used along the generalized gradient approximation[7, 8] based on the Perdew-Burke-Ernzerh of exchange-correlation functional[9]. For all the compounds which was assumed to extend infinitely, a *k*-point (7,7,1) grid was used to describe a supercell and calculate the energy. By contrast, a gamma point grid was used to describe the molecular system of all compound. The cut-off energy was set to be 500 eV and the standard quasi-Newtonian BFGS optimization method[10] was employed to relax the structure to its minimum energy configuration. The convergence criteria for the total energy, maximum ionic force, maximum ionic displacement, maximum stress and self-consistent field tolerance were 1×10^5 eV/atom, 3×10^{-2} eV/Å, 1×10^{-3} Å, 5×10^2 GPa and 2×10^{-7} eV/atom, respectively. The cell lengths for *x*, *y* and *z* are 60, 60 and 10 Å, respectively.

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