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Electronic Supplementary Information

Oxygen Evolution Catalysts on Supports with 3-D Ordered Array Structure and Intrinsic Proton Conductvity for Proton Exchange Membrane Steam Electrolysis

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In order to investigate the decomposition behavior and to obtain the calcination temperature of ITO precursors, TG-DTA curves of precipitates containing 10 mol% Sn were examined and the results are shown in Fig. S1 (solid lines). According to the TG-DTA curves, the decomposition was a three main stage process. The first weight loss below 240 °C was assigned to physical dehydration and the decomposition of citric and oxalic acid whereas the second weight loss in the range 250-300 °C was connected to the formation of tin doped indium oxide. The strongest exothermic peak indicated that the formation of tin doped indium oxide powders occurred in this temperature range. A very weak exothermic peak at 500 °C in the DTA curves can be ascribed to the crystallization of tin doped indium powders. Complete removal of the template is very important for the preparation of a uniform macrostructure. Structural templates can be removed either by calcination[1] or by HF treatment.[2] In general the PS template is removed by calcination, which not only opens up the macroporous structure but also induces a high-temperature solid phase reaction. As also shown in Fig. S1 (dotted lines) complete decomposition of the PS template occurred in the temperature range of 300-420 °C.

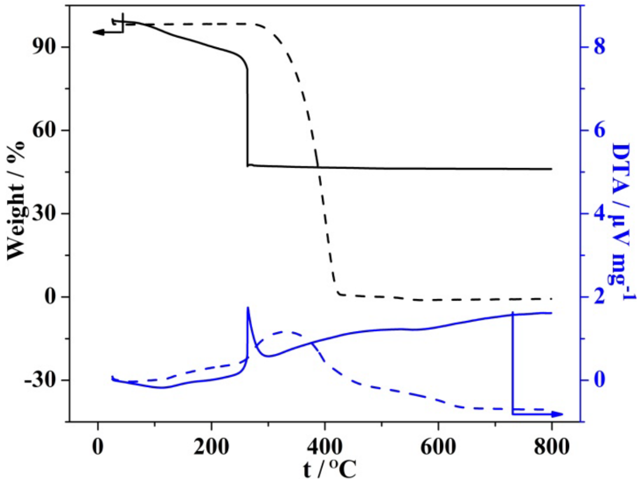

Fig. S1 TG-DTA curves of the ITO precursors (solid lines) and of the PS template (dotted lines)

In the following preparation of 3-DOM ITO, the PS structural template and the tin doped indium oxide precursor was first heated to 270 °C and kept at that temperature for 1 h to form the tin doped indium oxide. In this calcination process, the excess heat produced by the oxidative decomposition of the precursors should be removed in order to obtain a uniform structure. Therefore, a low heating rate of 1 °C min^{-1} was used to prevent the PS template from collapsing.

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[1] a) Y. C. Wei, J. Liu, Z. Zhao, A. J. Duan, G. Y. Jiang, C. M. Xu, J. S. Gao, H. He, X. P. Wang, *Energy Environ. Sci.* **2011**, *4*, 2959-2970; b) B. Z. Fang, J. H. Kim, M. Kim, J. S. Yu, *Chem. Mater.* **2009**, *21*, 789-796.

[2] a) G. S. Chai, I. S. Shin, J. S. Yu, *Adv. Mater.* **2004**, *16*, 2057-2061; b) W. Hu, Y. Q. Wang, X. H. Hu, Y. Q. Zhou, S. L. Chen, *J. Mater. Chem.* **2012**, *22*, 6010-6016.

The temperature was subsequently slowly increased to 400 °C in order to completely decompose the PS template and to obtain the macroporous framework of tin doped indium oxide. Finally the temperature was increased to 500 °C and held at that temperature for 1 h to crystallize the material.

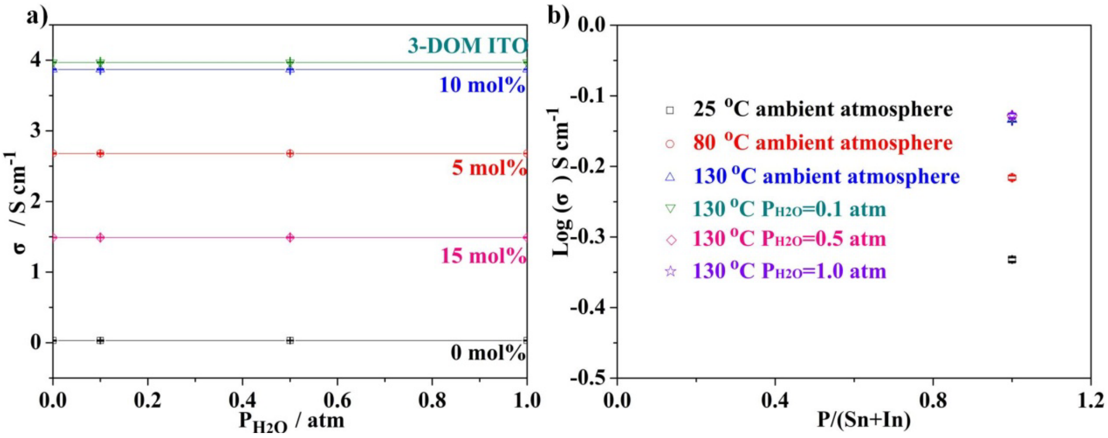

Fig. S2 (a) The electronic conductivity independence of the water vapor partial pressure for 3-DOM ITO and tin doped indium oxides with different tin molar content. (b) The conductivities of 3-DOM TIP-ITO at different temperatures and partial pressures of water vapor.

To illustrate the contribution of of proton conductivity measurements were made under varying water partial pressures, which is expected to enhance the proton conductivity but not the electronic conductivity. As shown in Fig. S2, the oxide based supports showed independence of the conductivity of the water partial pressure whereas the phosphate containing composite exhibited a significant increase in the conductivity as the water partial pressure was increased.

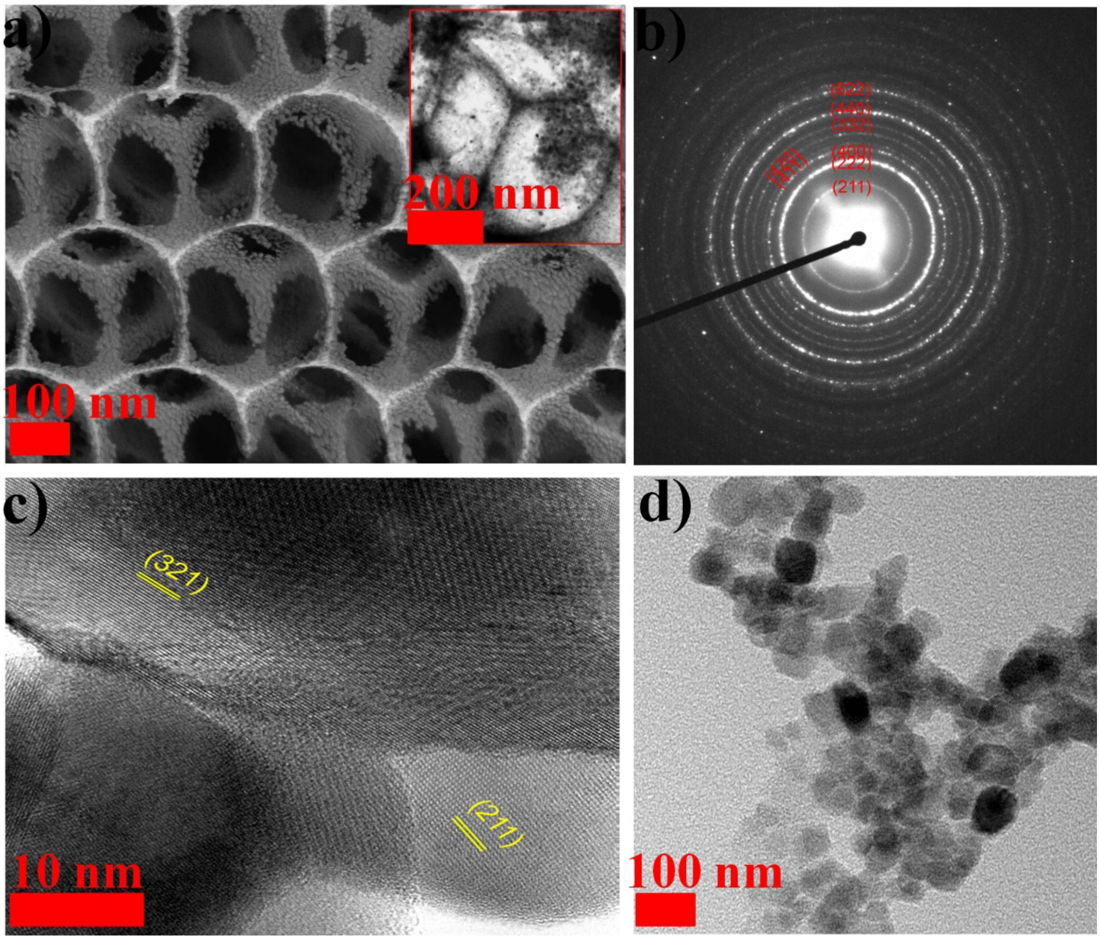

Fig. S3 SEM (a), TEM (inset of a), selected area electron diffraction (b) and HRTEM images (c) of 3-DOM ITO, TEM image of ITO (d).

Fig. S3a showed the SEM image of the prepared 3-DOM ITO. Similarly with the 3-DOM TIP-ITO, the ordered hexagonal array of macropores was clearly visible. Meanwhile, TEM image (inset of Fig. S3a) also showed the same pore structure. The selected area electron diffraction (Fig. S3b) and HRTEM image (Fig. S3c) were indexed as the same crystal structure with the result of XRD characterization. From the electron diffraction pattern, all the main crystal planes (211), (222), (400), (411), (420), (332), (440) and (622) were found. By the measurement of lattice spacings of crystal planes in HRTEM image, (211) and (321) can be accurately identified.

Fig. S3d showed the TEM image of the ITO. As can be seen, the ITO powders were in the form of nanospheres within a narrow range of around 60 nm.

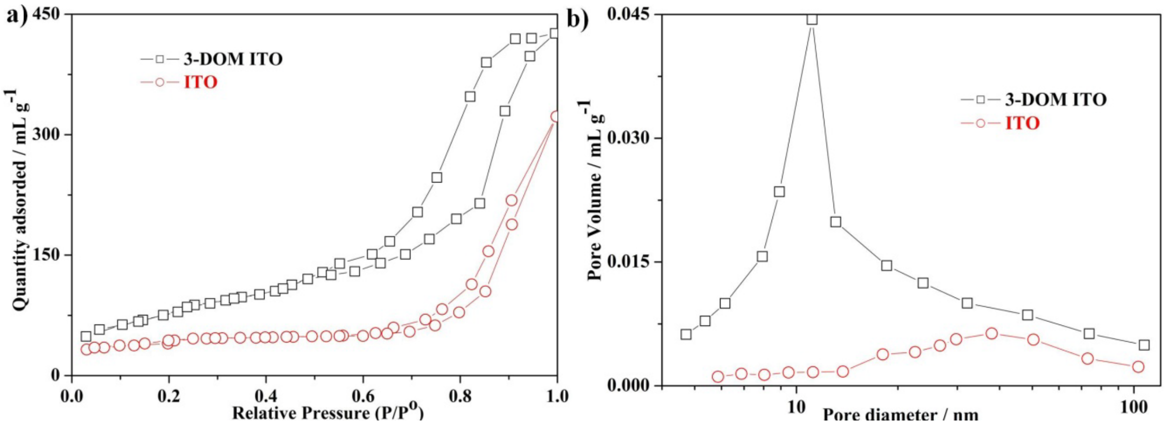

Fig. S4 N_2 adsorption/desorption isotherms (a) and BJH pore-size distribution curves (b) analyzed from the desorption branch of 3-DOM ITO and ITO.

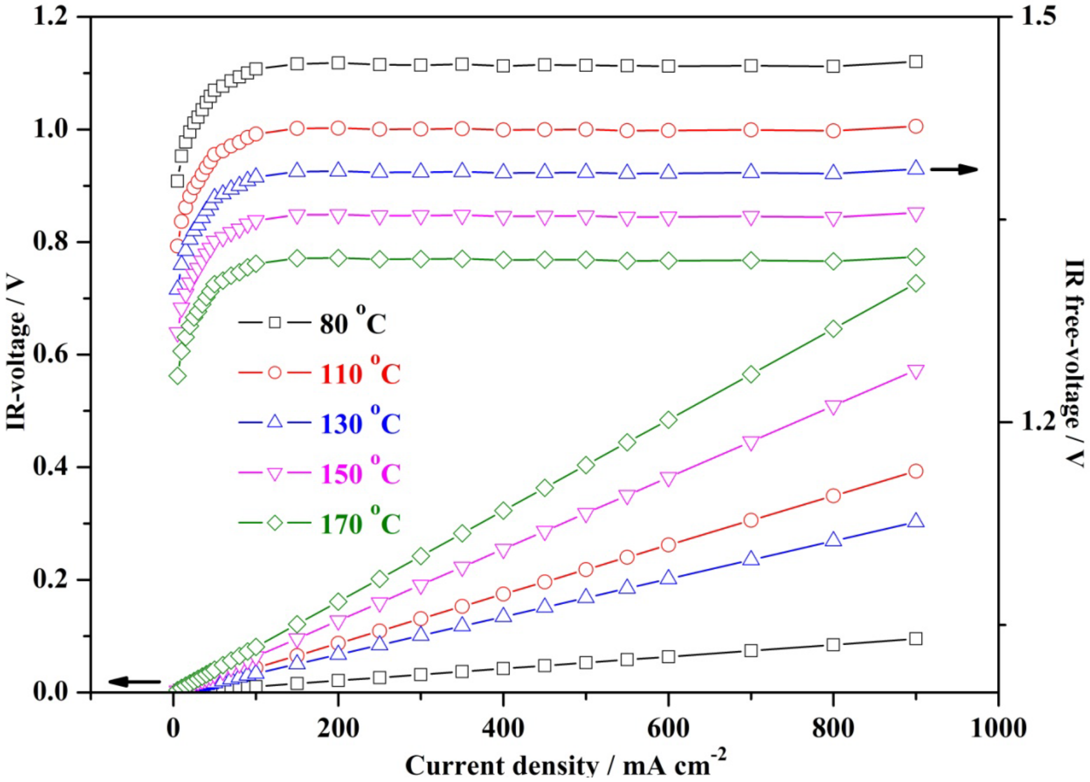

Fig. S5 Regression results of polarization curves of PEM liquid water fed electrolysis cell using IrO_2/3-DOM TIP-ITO operating at 80 °C with Aquivion^{TM} E79-05S membrane and for steam fed electrolysis cells operating at temperature ranging from 110-170 °C with H_3PO_4 doped Aquivion^{TM} E79-05S membrane.