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Supporting Information

Microwave-Plasma Induced Reconstruction of Silver Catalysts for Highly Efficient Oxygen Reduction

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Experimental

BSCF was synthesized by a combined EDTA-citrate complexing process. $Ba(NO_3)_2$ (99.99+%, Sigma-Aldrich), $Sr(NO_3)_2$ (99.99+%, Sigma-Aldrich), $Fe(NO_3)_3 \cdot 9H_2O$ (99.9+%, Sigma-Aldrich) and $Co(NO_3)_2 \cdot 6H_2O$ (99+%, Sigma-Aldrich) were used as the raw materials for metal sources. Stoichiometric amounts of these metal nitrates were mixed in deionized water and heated at 80°C. EDTA (99.9%, Sigma-Aldrich) and anhydrous citric acid (99.5%, Sigma-Aldrich) were then added as the complexing agents. The molar ratio of total metal nitrates, EDTA and citric acid in the solution was 1:1:2. To ensure complete complexation, solution pH was adjusted to 8 by adding NH_3 aqueous solution (28%). After evaporation of water at 150°C, a dark purple gel was recovered. The gel was pre-treated on the furnace at 250°C for 8 hours to form a

solid precursor. The solid precursor was then calcined at 900^{o}C for 5 hours in air to obtain BSCF powders.

The BSCF powders were mixed with ethyl cellulose and terpinol to form slurry. The BSCF scaffold (porous BSCF layer) was prepared by tape casting the slurry onto both sides of a $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) disc followed by heating at 1000^{o}C for 2h. The average diameter of pores in BSCF scaffold is larger than 5 μm, which facilitates the infiltration process. Infiltration was used to introduce 1 M $AgNO_3$ solution into BSCF scaffold followed by thermal decomposition of $AgNO_3$ at 500 ^{o}C for 2 h. The Ag particles were obtained by treating the infiltrated samples under microwave plasma for different time.

The electrochemical impedance spectra (EIS) of the symmetric cells were obtained using an Autolab, PGSTAT30 electrochemical workstation. The frequency range was 0.01 Hz to 100 kHz and the signal amplitude was 10 mV under open cell voltage conditions.

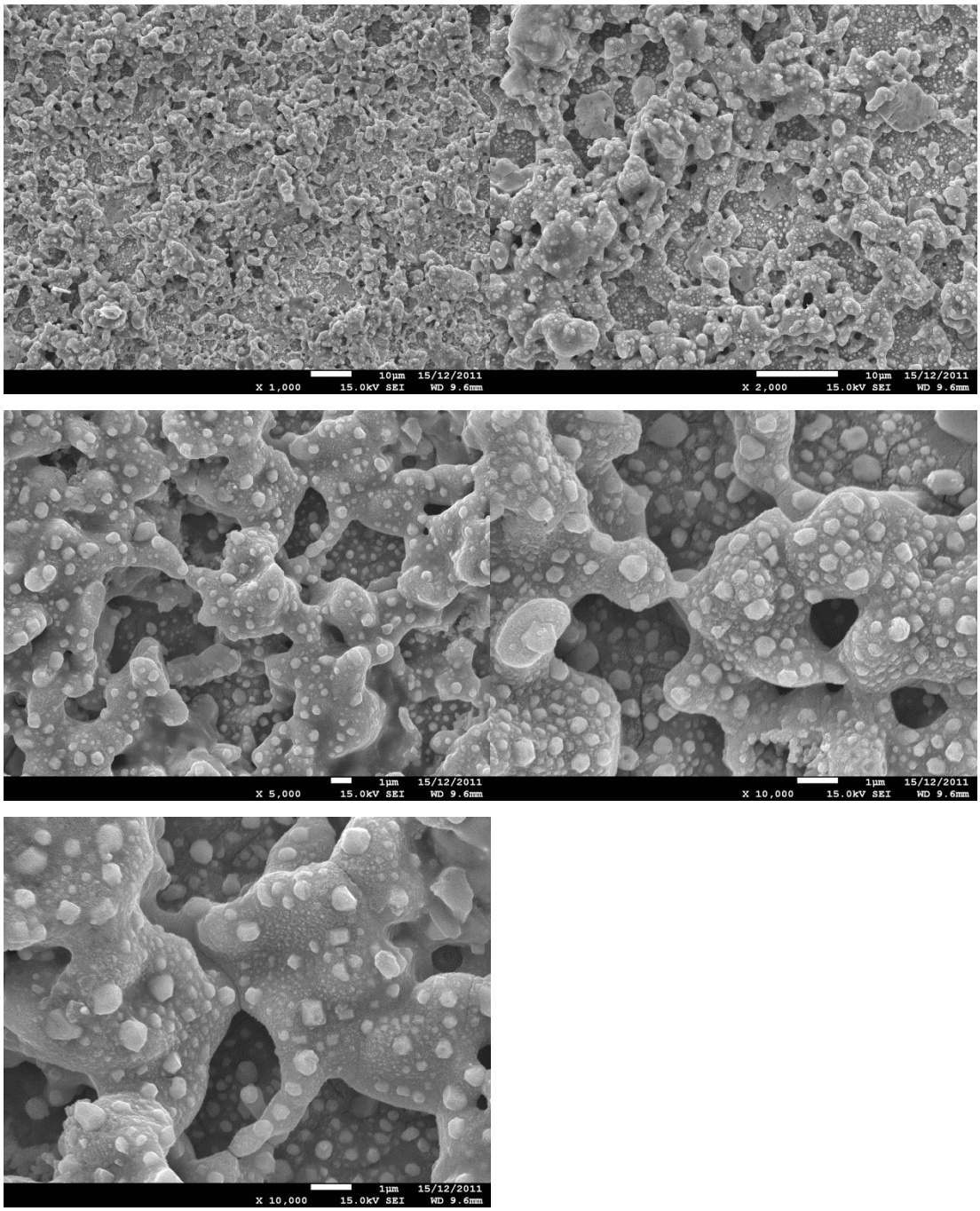
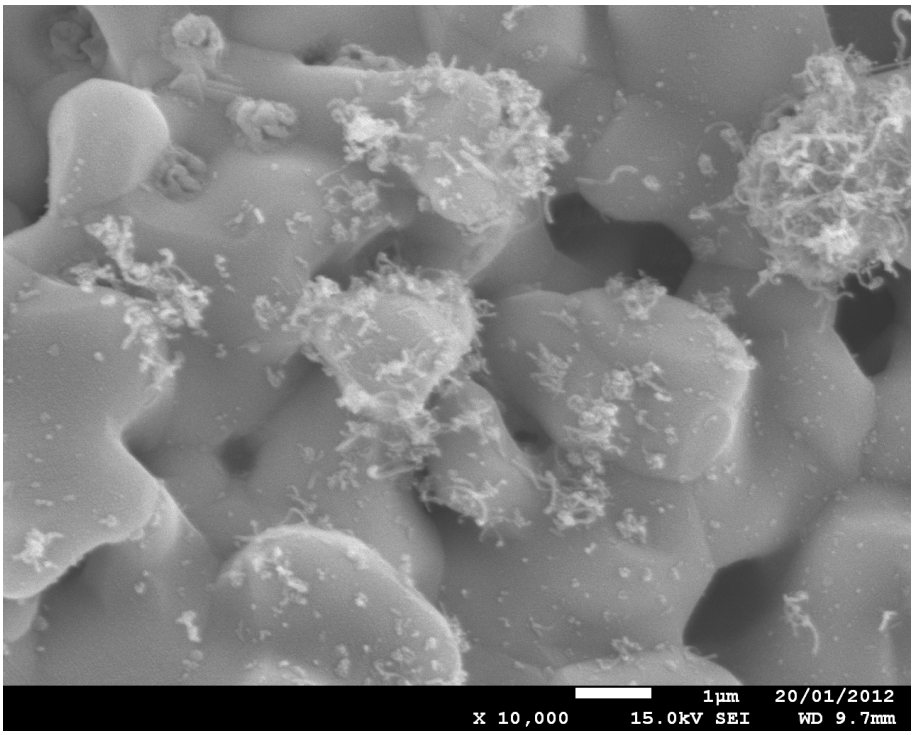


Figure S1 Random selected SEM images of Ag-BSCF-40min at different magnifcations.



FigureS2 SEM image of Ag-BSCF-80min. The fuzz-like silver wires are formed due to over heating of silver at high temperature and vacuum condtions.

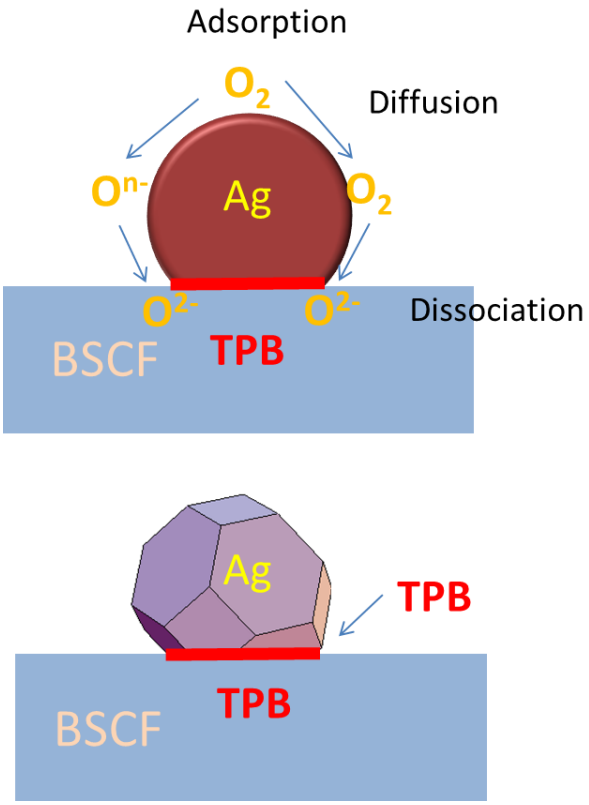


Figure S3 The correlation between the crystallographic structure changes of Ag nanoparticles and the three phase boundary (TPB). The oxygen reduction reaction (ORR) on Ag contains three steps including adsorption, diffusion and dissociation. The barriers of adsorption, diffusion and dissociation are higher on the silver-oxygen two-phase boundary (2PB), while the oxygen reduction process is easier to occur on silver-BSCF-oxygen TPB because of the large number of defects on the connected BSCF surface which can lower the barrier for ORR. In our study, the TPB lengths of Ag-BSCF-20min and Ag-BSCF-40min are similar because of similar particle size of silver. Therefore, the pronouncedly increased oxygen reduction reactivity is related to the abundance of {111} and {100} facets of silver particles in Ag-BSCF-40min. These low-index planes are more favourable for oxygen adsorption, diffusion and dissociation sites leading to the lowered barriers for ORR.