

Electronic Supplementary Information

High Surface Area Ordered Mesoporous BiFeO₃ Semiconductor with Efficient Water Oxidation Activity

Ioannis Papadas,^a Joseph A. Christodoulides,^b George Kioseoglou^a and Gerasimos S. Armatas^{a,*}

^a *Department of Materials Science and Technology, University of Crete, Heraklion GR-71003, Crete, Greece.*

^b *Naval Research Laboratory, 4555 Overlook Ave SW, Washington, DC 20375, USA.*

*E-mail: garmatas@materials.uoc.gr.

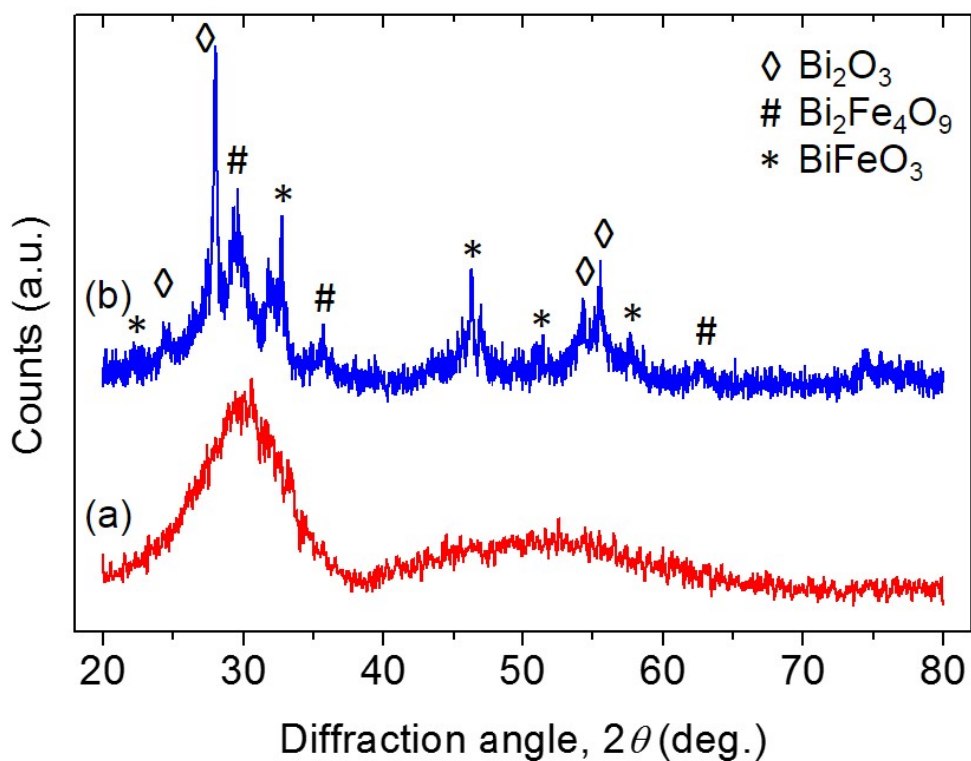


Fig. S1 XRD pattern of mesostructured frameworks casted from mesoporous CMK-3 carbon, (a) without using tartaric acid along with the $\text{Bi}(\text{NO}_3)_3$ and $\text{Fe}(\text{NO}_3)_3$ compounds and (b) using tartaric acid at a 0.5:1 molar ratio with respect to metal ions. The product in (b) is composed of crystalline Bi_2O_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$ and BiFeO_3 .

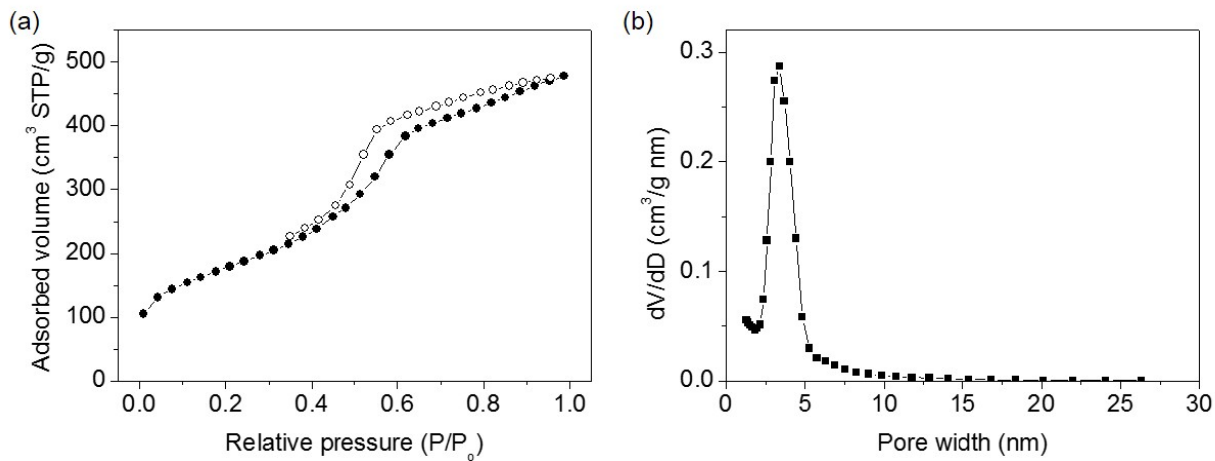


Fig. S2 (a) Nitrogen adsorption and desorption isotherms at 77 K and (b) the corresponding NLDFT pore size distribution for mesoporous CMK-3 carbon, indicating a mesopore size of 3.2 nm. Analysis of the adsorption data with the BET method gives surface area of $632 \text{ m}^2\text{g}^{-1}$ and total pore volume of $0.73 \text{ cm}^3\text{g}^{-1}$. Given an estimation of the mesopore diameter (D_p) at 3.2 nm and the unit cell size (a_0) at 9.8 nm, the pore wall thickness (WT) is about 6.6 nm, according to the equation $WT = a_0 - D_p$.

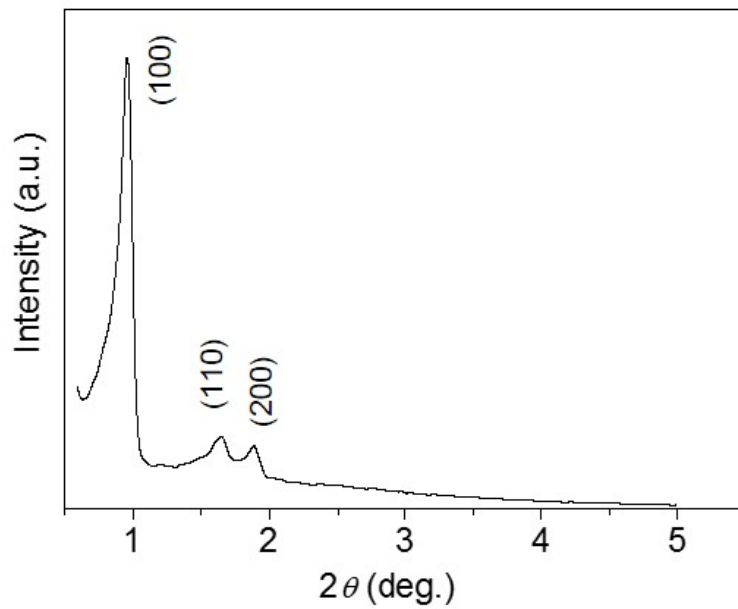


Fig. S3 Low-angle XRD pattern of mesoporous SBA-15 silica. The indexing of the Bragg diffractions is consisted with a hexagonal $p6mm$ unit cell with lattice parameter $a_0=10.7$ nm.

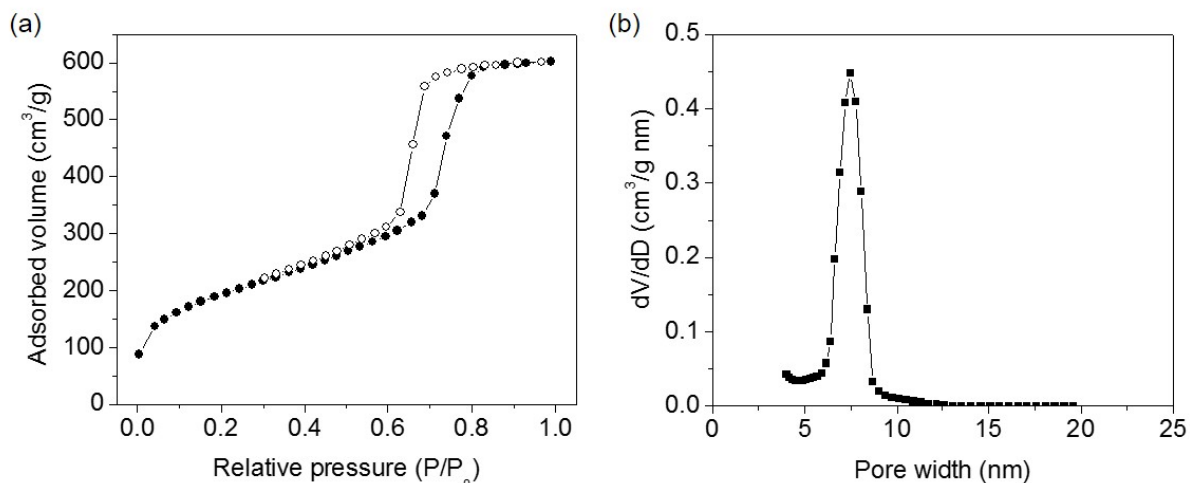


Fig. S4 (a) Nitrogen adsorption and desorption isotherms at 77 K and (b) the corresponding NLDFT pore size distribution for mesoporous SBA-15 silica, indicating a mesopore size of 7.8 nm. Analysis of the adsorption data with the BET method gives surface area of $650 \text{ m}^2\text{g}^{-1}$ and total pore volume of $0.88 \text{ cm}^3\text{g}^{-1}$. Given an estimation of the mesopore diameter (D_p) at 7.4 nm and the unit cell size (a_0) at 10.7 nm (see Fig. S3), the pore wall thickness (WT) is about 3.3 nm, according to the equation $WT = a_0 - D_p$.

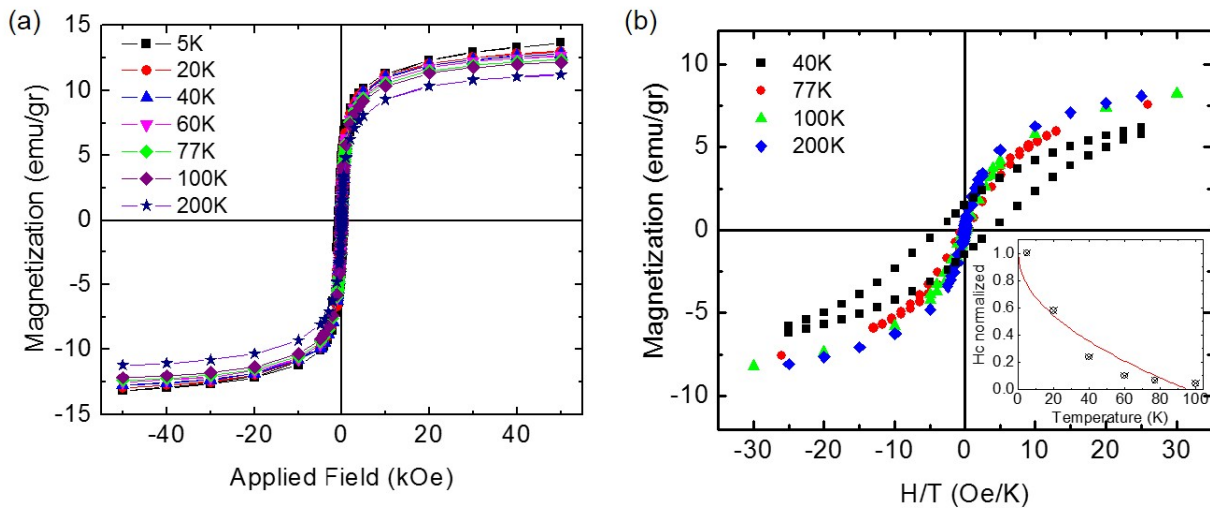


Fig. S5 (a) M-H loops at different temperatures for mesostructured BiFeO₃ in the -50 to +50 kOe range. Fast saturation of the magnetization is observed. (b) Magnetization plotted as function of H/T in the very narrow range of -35 to +35 Oe for 40, 77, 100 and 200 K. The inset shows the temperature dependence of the coercivity normalized to the value at 5 K. Black points are the experimental data and red line is root square dependence of the coercivity ($H_c = 1 - (T/T_B)^{1/2}$) assuming blocking temperature T_B = 95 K.

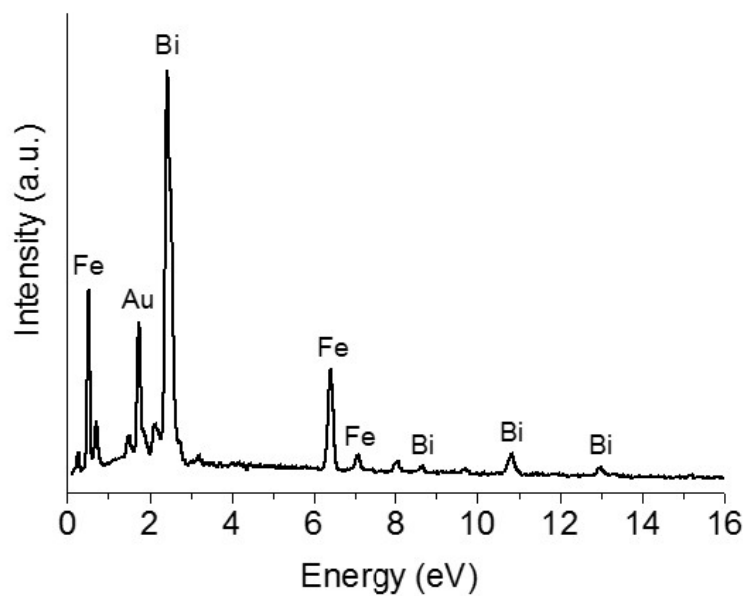


Fig. S6 Typical EDS spectrum for mesoporous Au/BiFeO₃ photocatalyst. The EDS analysis indicates an average atomic ratio of Au/Bi/Fe ~0.8:49.7:49.5 that corresponds to a ~1 wt % Au loading.

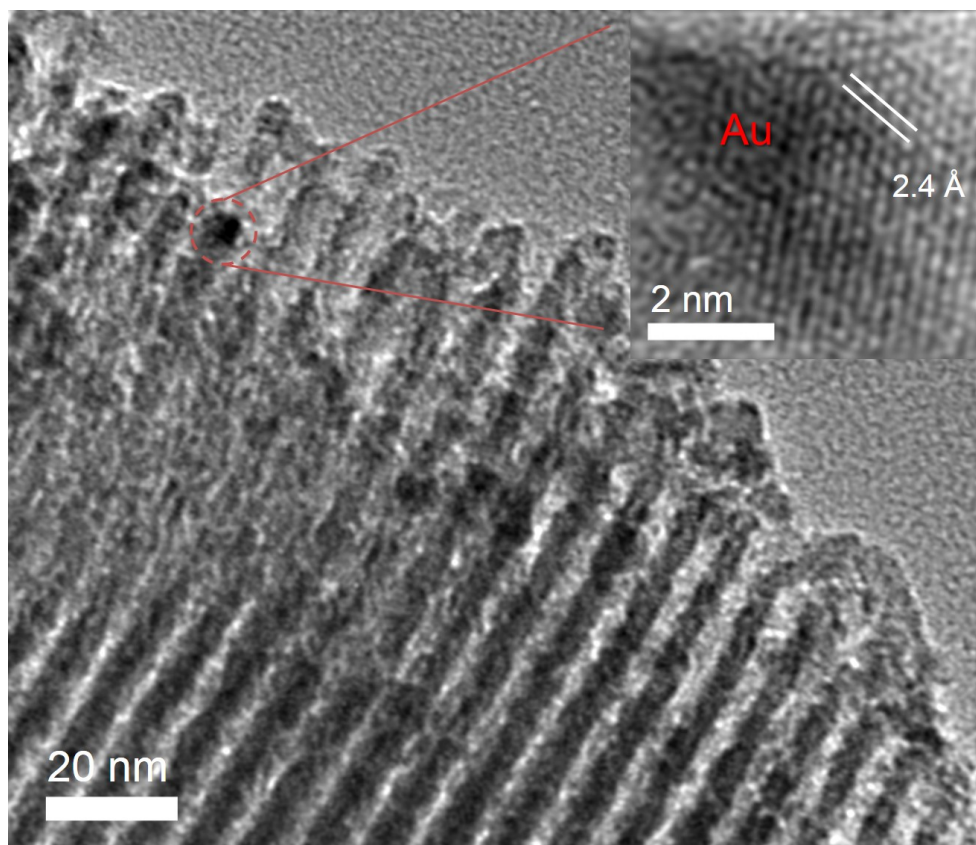


Fig. S7 Typical TEM image of mesoporous Au/BiFeO₃ sample. The inset shows the HRTEM image of an individual Au nanoparticle. The measured d -spacing is around 2.4 Å which is in consistent with the Au (111) crystal plane.

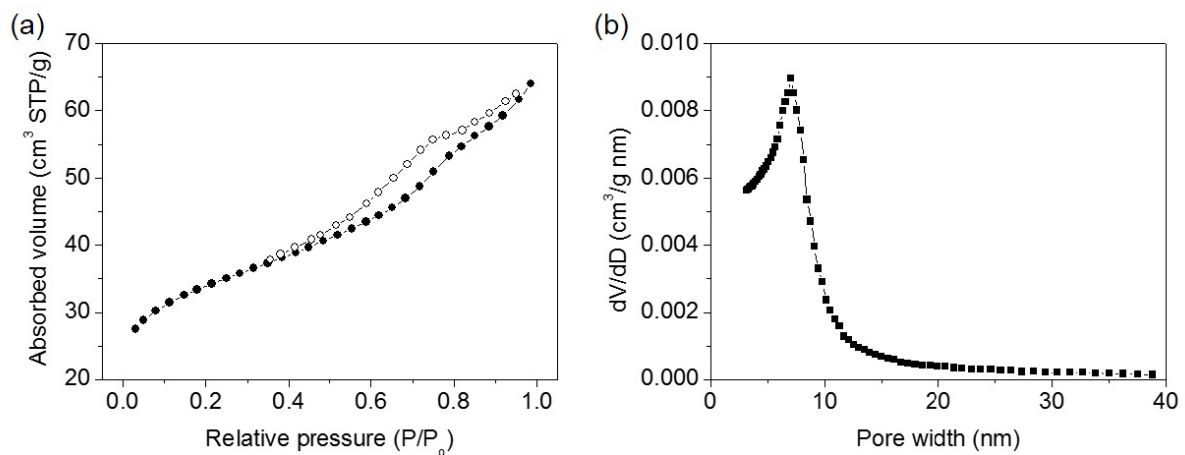


Fig. S8 (a) Nitrogen adsorption and desorption isotherms at 77 K and (b) the corresponding NLDFT pore size distribution for mesoporous Au/BiFeO₃ photocatalyst. Analysis of the adsorption data with the BET method gives surface area of 116 m²g⁻¹ and total pore volume of 0.10 cm³g⁻¹. The NLDFT analysis of the adsorption data indicates a mesopore size of 7.0 nm.

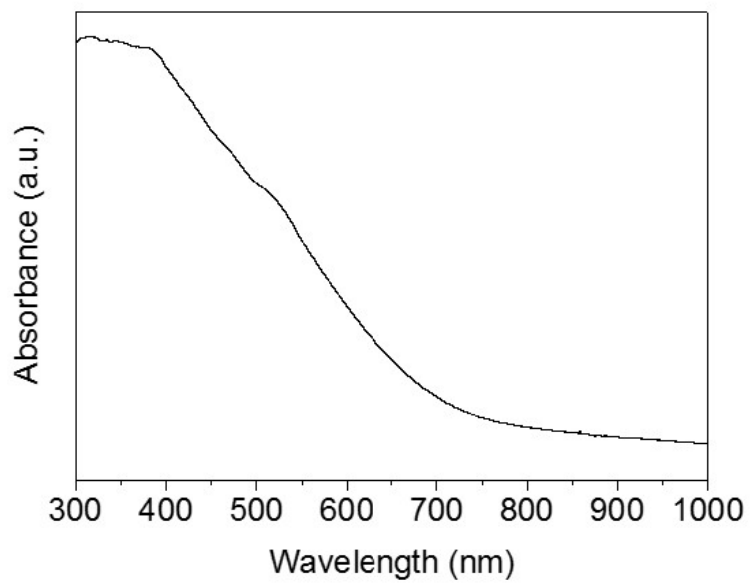


Fig. S9 UV-Vis/NIR absorption spectrum of mesoporous Au/BiFeO₃ heterostructure.

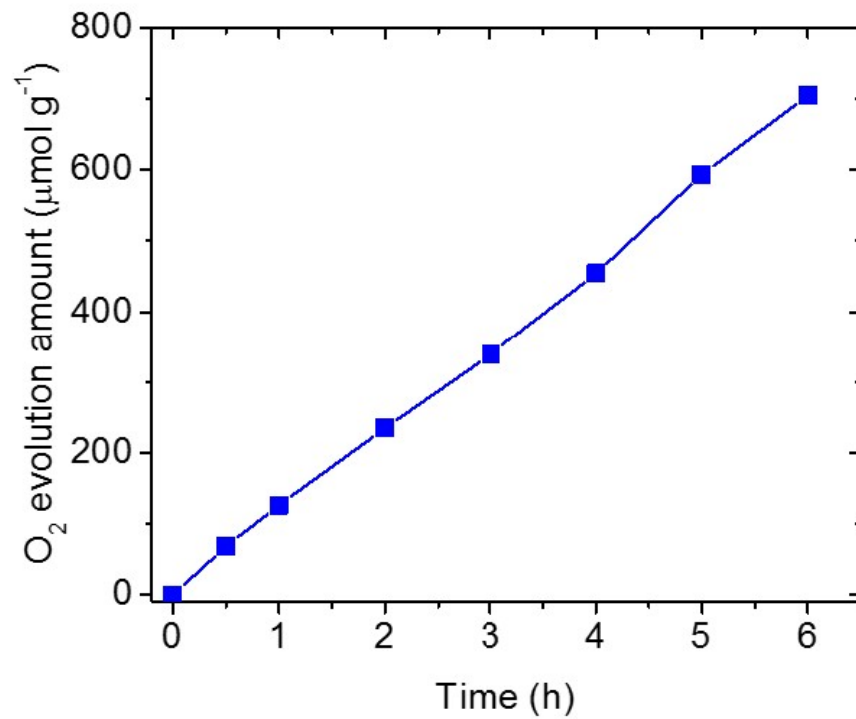


Fig. S10 Oxygen evolution profile for mesoporous Au/BiFeO₃ under visible light irradiation, showing a O₂ evolution rate of ~120 μmol h⁻¹ g⁻¹.