January 28, 2020

Supplementary Material

Materials Synthesis, Characterization and DFT Calculations. The Visible-Light-Active Perovskite-like Barium Bismuthate ($Ba_{1.264(4)}Bi_{1.971(4)}O_4$) Photocatalyst.

D.S. Shtarev,[1,2] A.V. Shtareva,[1,2] R. Kevorkyants[3], A.V. Rudakova,[3] M.S. Molokeev,[2,4,5] T.V. Bakiev[3], K.M. Bulanin,[3,6] V.K. Ryabchuk,[3,6] and N. Serpone [7,*]

1 *Yu. A. Kosygin Institute of Tectonics and Geophysics, Far Eastern branch of the Russian Academy of Sciences, 65 Kim Yu Chen Street, Khabarovsk, 680063 Russian Federation; emails:* shtarev@mail.ru and avshtareva@mail.ru

2 *Far Eastern State Transport University, 47 Seryshev Street, Khabarovsk, 680021 Russian Federation; email:* msmolokeev@mail.ru

3 *Saint-Petersburg State University, Laboratory "Photoactive Nanocomposite Materials", Ul'yanovskaya 1, Petergof, Saint-Petersburg, 198904, Russian Federation; emails:* ruslan.kevorkyants@gmail.com, aida.rudakova@spbu.ru, tairbakiev@gmail.com

4 *Kirensky Institute of Physics, Akademgorodok 50, bld. 38, Krasnoyarsk, 660036 Russian Federation*

5 *Siberian Federal University, 79 Svobodny pr., 660041 Krasnoyarsk, Russian Federation*

6 *Saint-Petersburg State University, Department of Photonics, Ul'yanovskaya 1, Petergof, Saint-Petersburg, 198904 Russian Federation*; *email*: v.ryabchuk@spbu.ru and k.bulanin@spbu.ru

7 *PhotoGreen Laboratory, Dipartimento di Chimica, Universita di Pavia, via Taramelli 12, Pavia 27100, Italia; email:* nick.serpone@unipv.it

* Corresponding author: nick.serpone@unipv.it

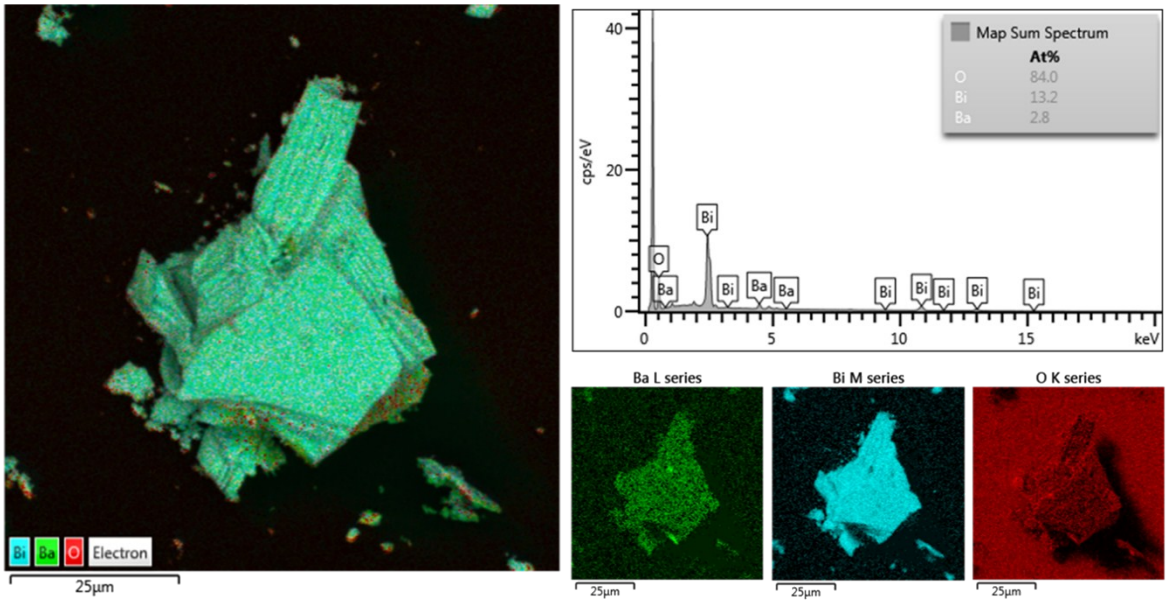


Figure S1. EDX spectrum and mapping of the elements of the barium bismuthate particle.

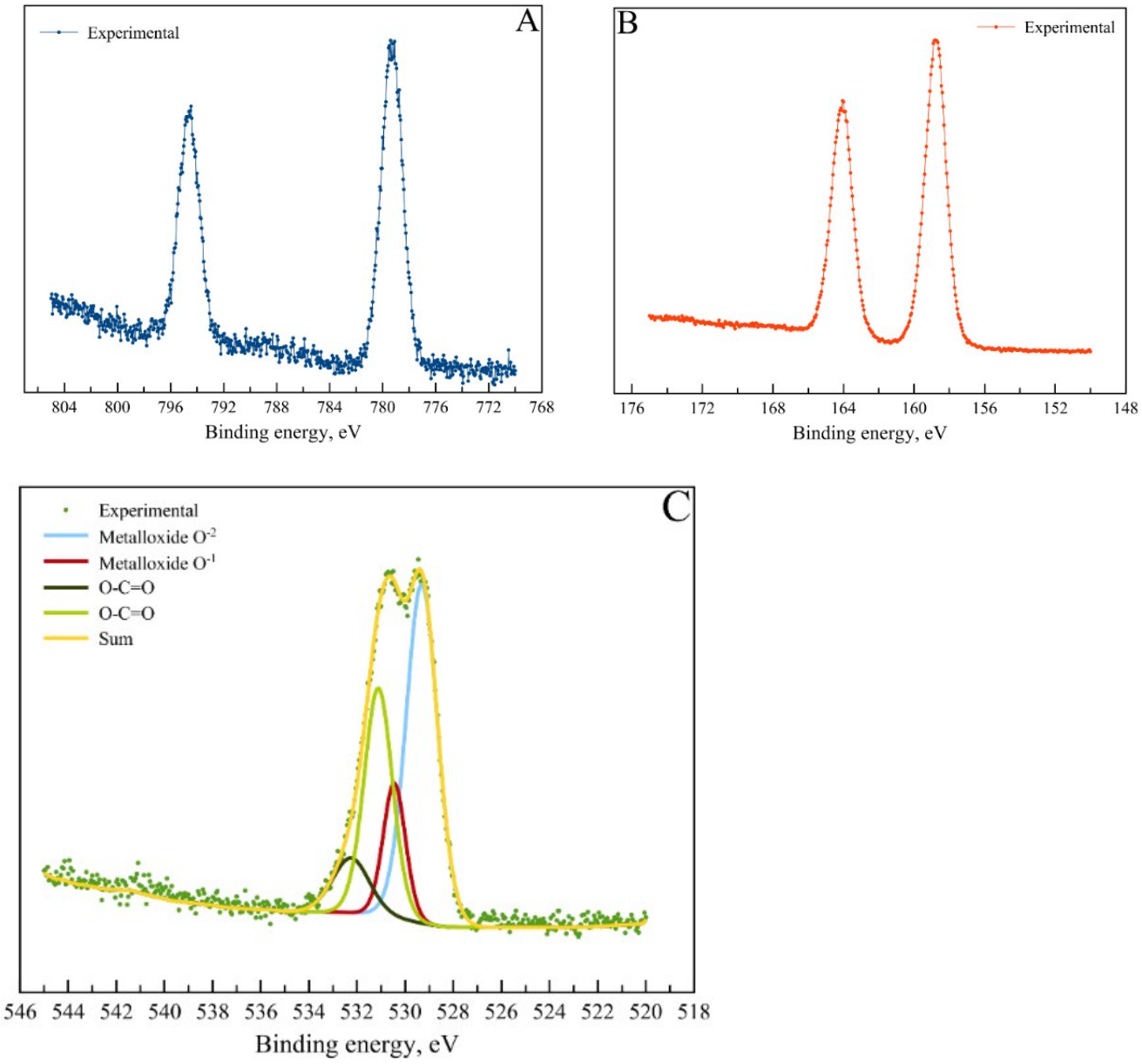


Figure S2. XPS spectra and deconvolution results of the synthesized barium bismuthate $Ba_{1.264(4)}Bi_{1.971(4)}O_4$ sample in the Ba*3d* (A), Bi*4f* (B), and O*1s* (C) regions.

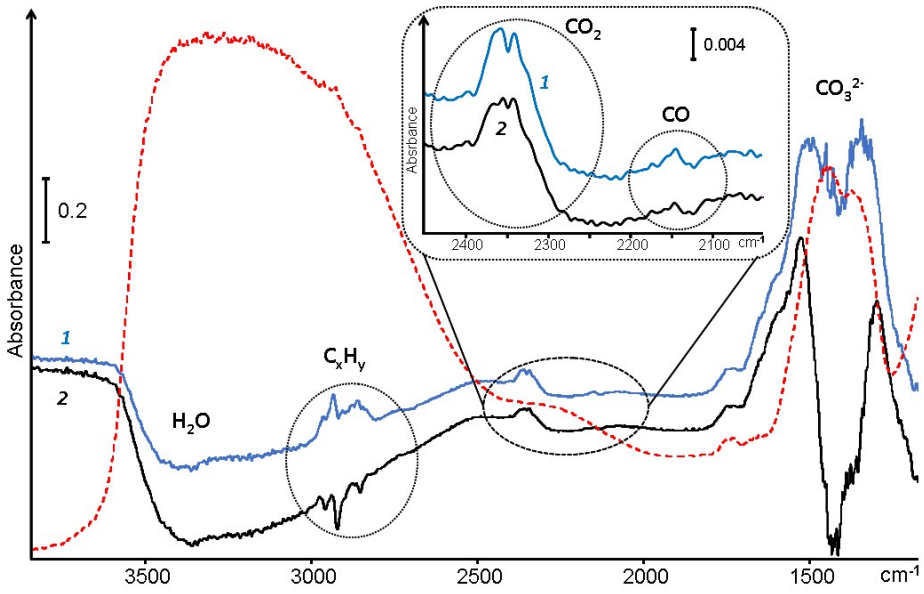
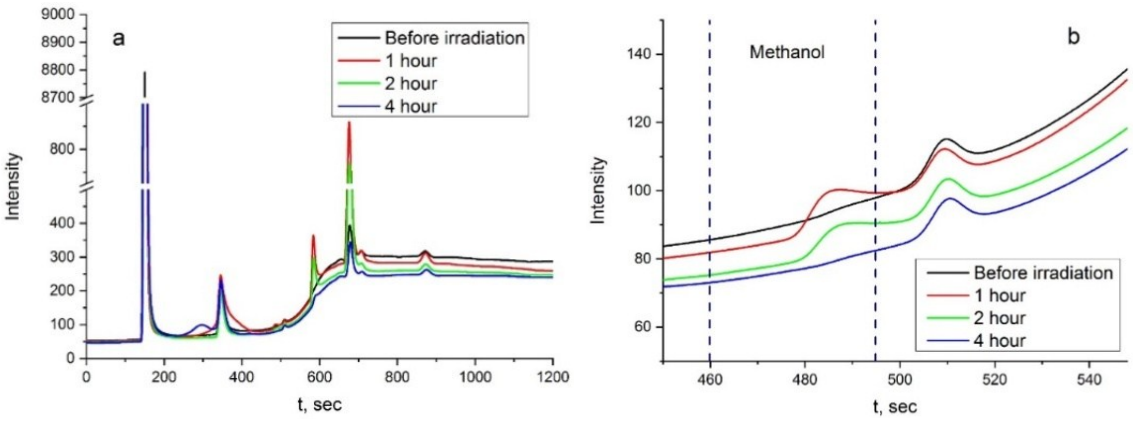


Figure S3. FTIR spectroscopic results of the photocatalytic reduction of CO_2 on the $Ba_{1.264(4)}Bi_{1.971(4)}O_4$ bismuthate particle surface in the gas/solid system: ***1*** (blue line) – difference spectrum of the sample irradiated for 30 min; **2** (black line) – difference spectrum of the sample irradiated for 100 min; ***3*** (red dotted line) – original spectrum of the barium bismuthate sample before the photo-experiment, as a reference. Difference spectra were obtained by subtraction of the spectrum of the sample after introduction of CO_2 from the current spectrum. The inset shows an enlarged view of difference spectra ***1*** and ***2*** in the 2450–2050 cm^{-1} spectral regions.



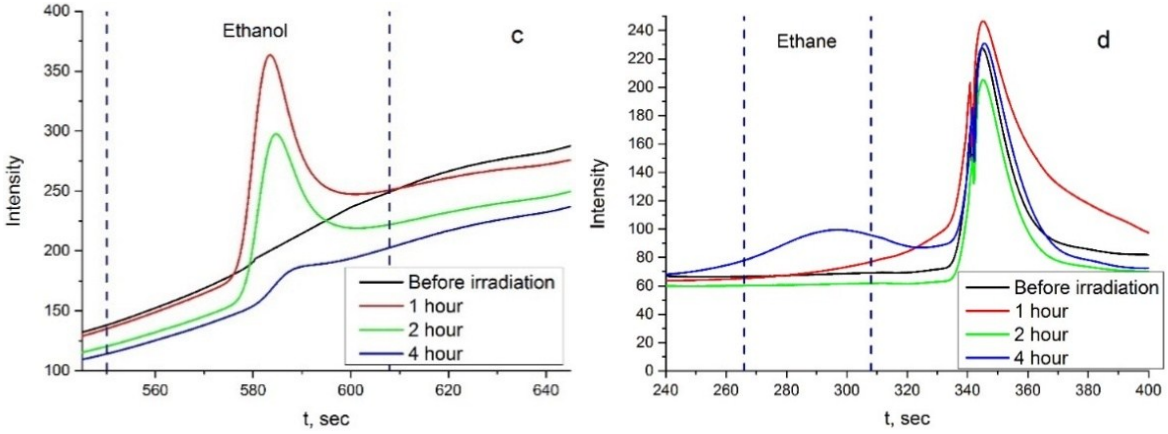


Figure S4. Results of chromatographic analyses from liquid aliquots taken from the photocathode compartment of the PEC cell before and during the photoelectrochemical reaction. (a) Overall view of the chromatograms of the liquid samples from the photocathode compartment of the PEC cell before irradiation (black) and after irradiation for 1 (red), 2 (green), and 4 (blue) hrs; (b)-(d) enlarged chromatograms in the retention areas of methanol (460–495 sec), ethanol (550–608 sec) and ethane (266–308 sec).

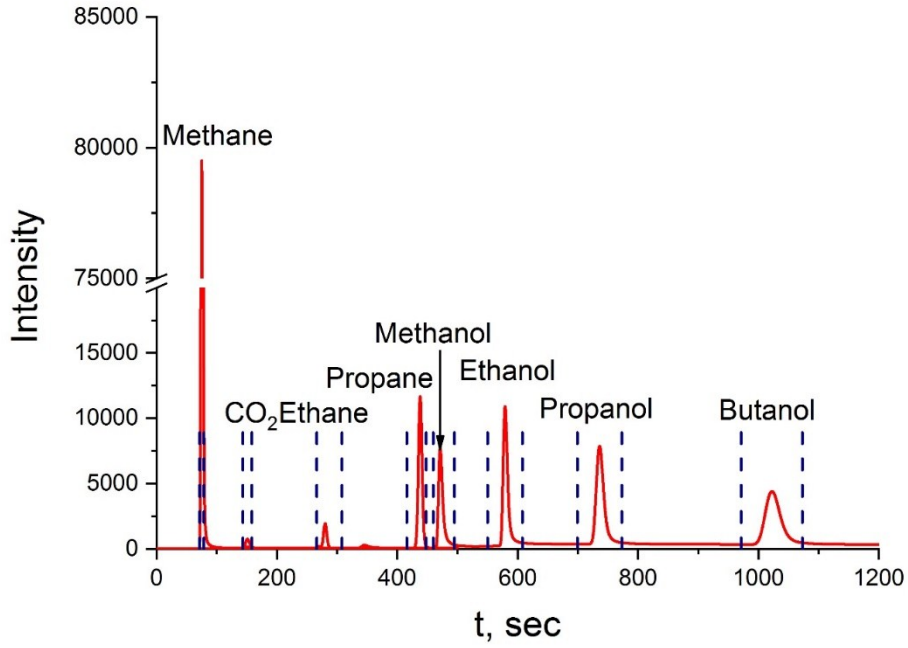


Figure S5. Chromatograms of possible products from the photoreduction of CO_2 (red solid line); vertical blue dashed lines define the confidence intervals used for product identification within ±5 % of the retention time required for maximum product generation.

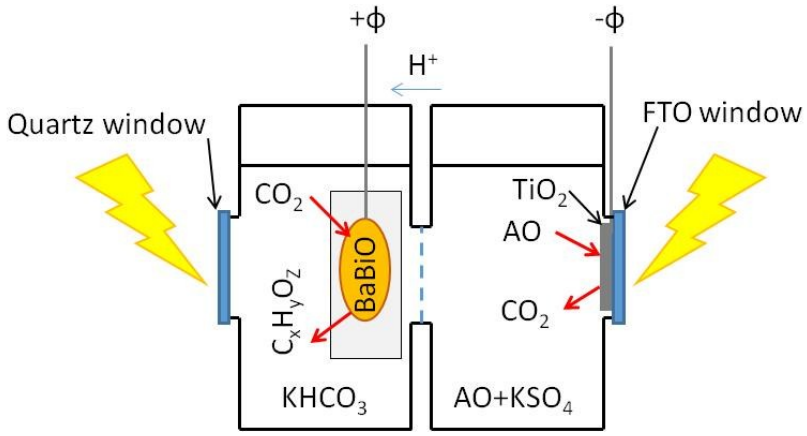


Figure S6. Scheme of the PEC cell for the photoelectrochemical reduction of CO_2; AO is ammonium oxalate, and $C_xH_yO_Z$ denotes various products of the CO_2 reduction.

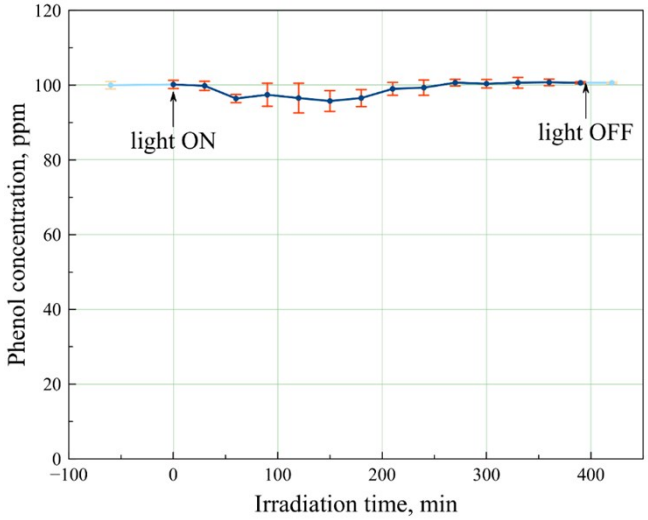


Figure S7. Time course of the concentration of phenol in aqueous media in the presence of $Ba_{1.264(4)}Bi_{1.971(4)}O_4$ as a function of irradiation time.