

Supporting information for

Development of an automated SILAR method for the sustainable fabrication of BiOI/TiO₂ photoanodes

Roberto Altieri^{a,b}, Fabian Schmitz^{a,b}, Manuel Schenker^{a,b}, Felix Boll^{a,b}, Matteo Crisci^{a,b}, Luca Rebecchi^c, Pascal Schweitzer^{a,d}, Ilka Kriegel^c, Bernd Smarsly^{a,b}, Derck Schlettwein^{a,d}, Francesco Lamberti^e, Teresa Gatti^{a,f*} and Mengjiao Wang^{f*}

^aCenter for Materials Research, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

^bDepartment of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.

^cFunctional Nanosystems, Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy

^dInstitute of Applied Physics, Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

^eDepartment of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova, Italy

Table of Contents

- Top-view SEM images of FTO, mesoporous TiO₂ and compact TiO₂ (Figure S1)
- Comparison between the BiOI/TiO₂ heterojunction prepared by Autodrop and the one prepared by manual spin-SILAR (Figure S2)
- Relationships between Autodrop parameters and considerations (Figure S3)
- GIXRD patterns of T/BiOI 1.2 at different orientations with respect to the incident beam (Figure S4)
- XPS spectra of T/BiOI heterojunctions at different BiOI thickness (Figure S5)
- Chronoamperometric trend for the the T/BiOI 1.2 photoanode covered with ALD Al₂O₃ (Figure S6)
- IPCE characterization of relevant T/BiOI photoanodes (Figure S7)

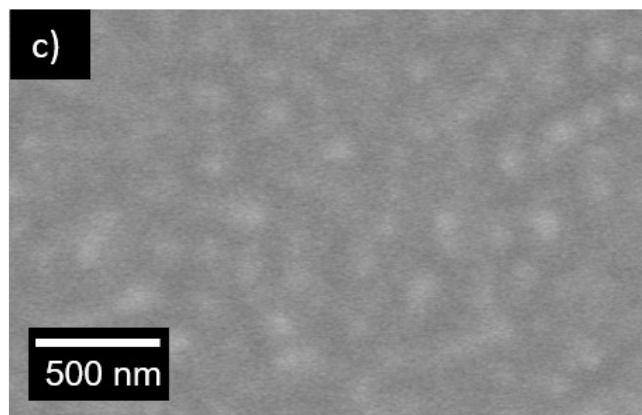
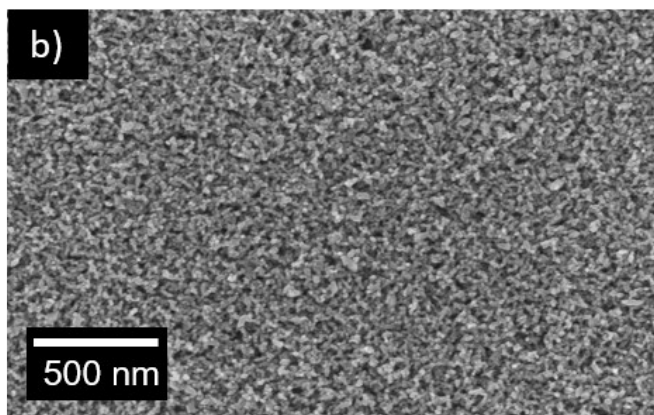
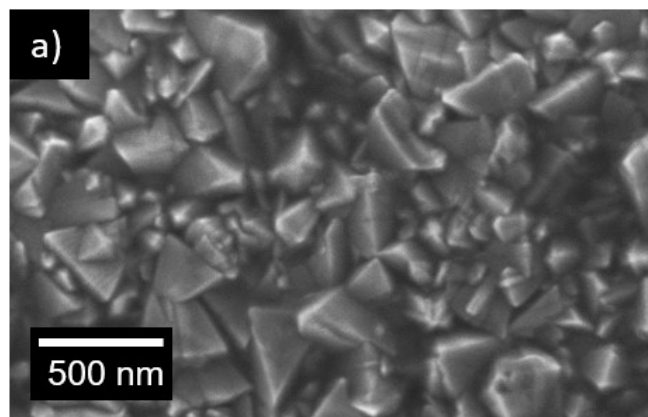


Figure S1. SEM images of a) bare FTO substrate, b) mesoporous TiO₂ and c) TiO₂ compact layer on top of FTO glass.

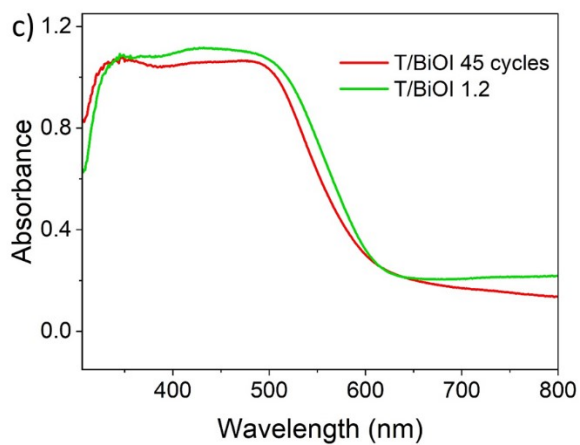


Figure S2. Optical images of a) T/BiOI 45 cycles and b) T/BiOI 1.2. c) UV-Vis spectra converted in absorbance from DRS.

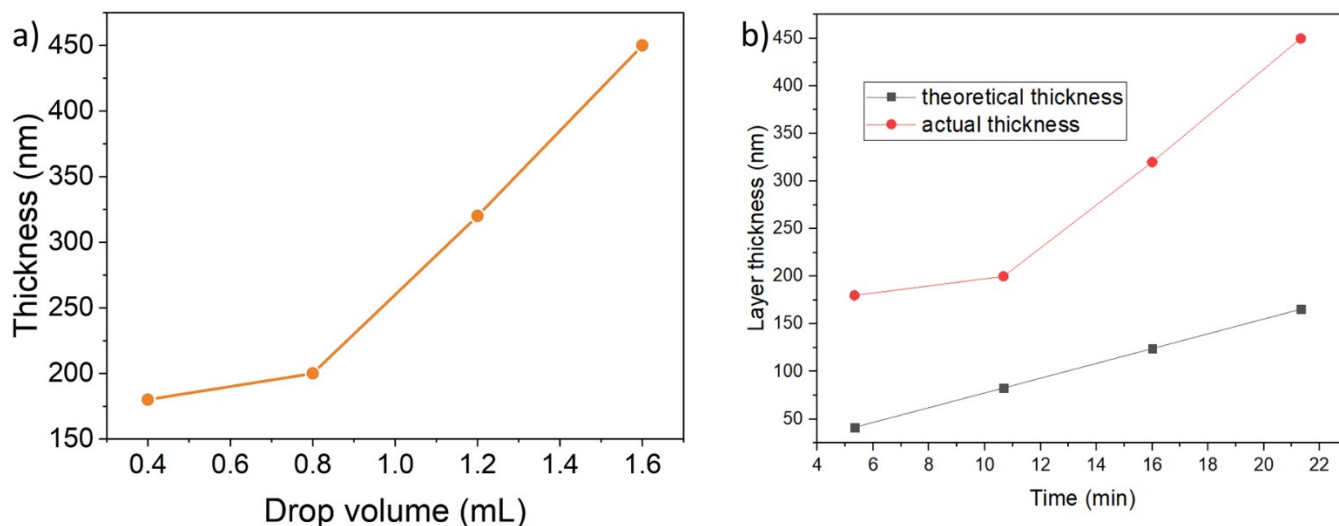


Figure S3. a) Relationship between the BiOI film thickness and the drop volume of the precursor solutions. b) Relationship between the BiOI film thickness and the coating time.

The theoretical thickness of the BiOI layer is calculated as follows:

It is known that the drop rate of the precursors is $75 \mu\text{L}/\text{min}$, the concentration of the precursors is 5 mM , the atomic mass of BiOI is $351.88 \text{ g}/\text{mol}$.

We assume that 95% of the precursor is wasted during the spin-coating process, then the remained BiOI should be $6.6 \mu\text{g}/\text{min}$.

The density of BiOI is $8.5 \text{ g}/\text{cm}^3$ and the thickness of one layer of BiOI is 0.94 nm . We assume that all the above BiOI is perfectly aligned on the 1 cm^2 substrate, then, in 1 min, there should be at least 8.26 layers of BiOI grown on the substrate.

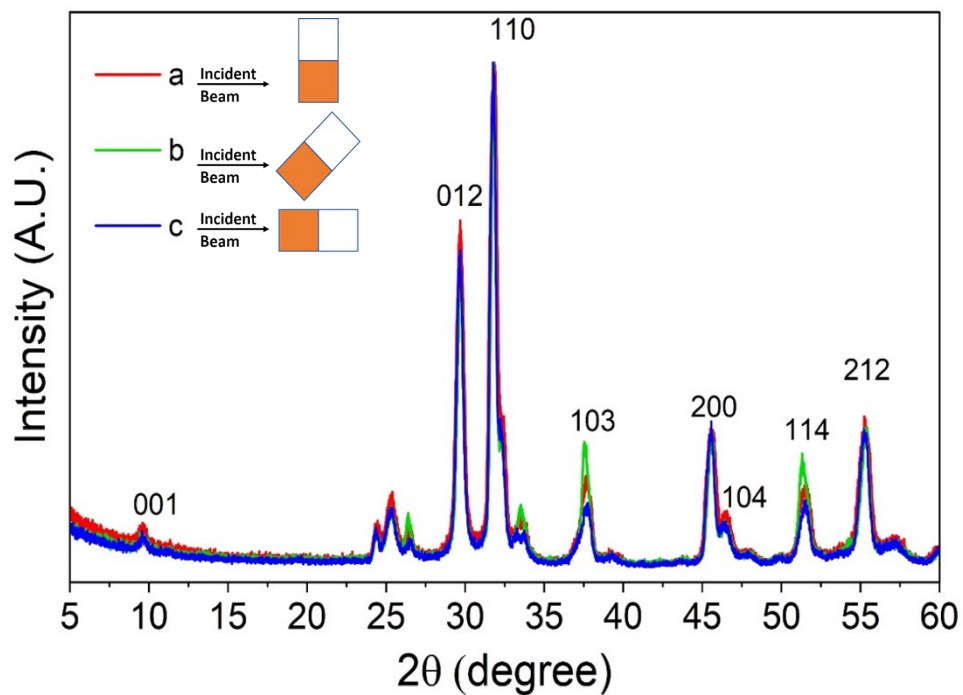


Figure S4. XRD patterns of T/BiOI 1.2 obtained by changing the relative position of the incident beam by 45° between the different diffractograms in the figures. The 2 main reflection peaks maintain the same relative intensity for the same sample regardless of the relative position of the film, rotated at 45° and 90° from the initial position in the XRD sample holder. It is thus possible to assume that the growing BiOI on the surface forms from the 012 plane.

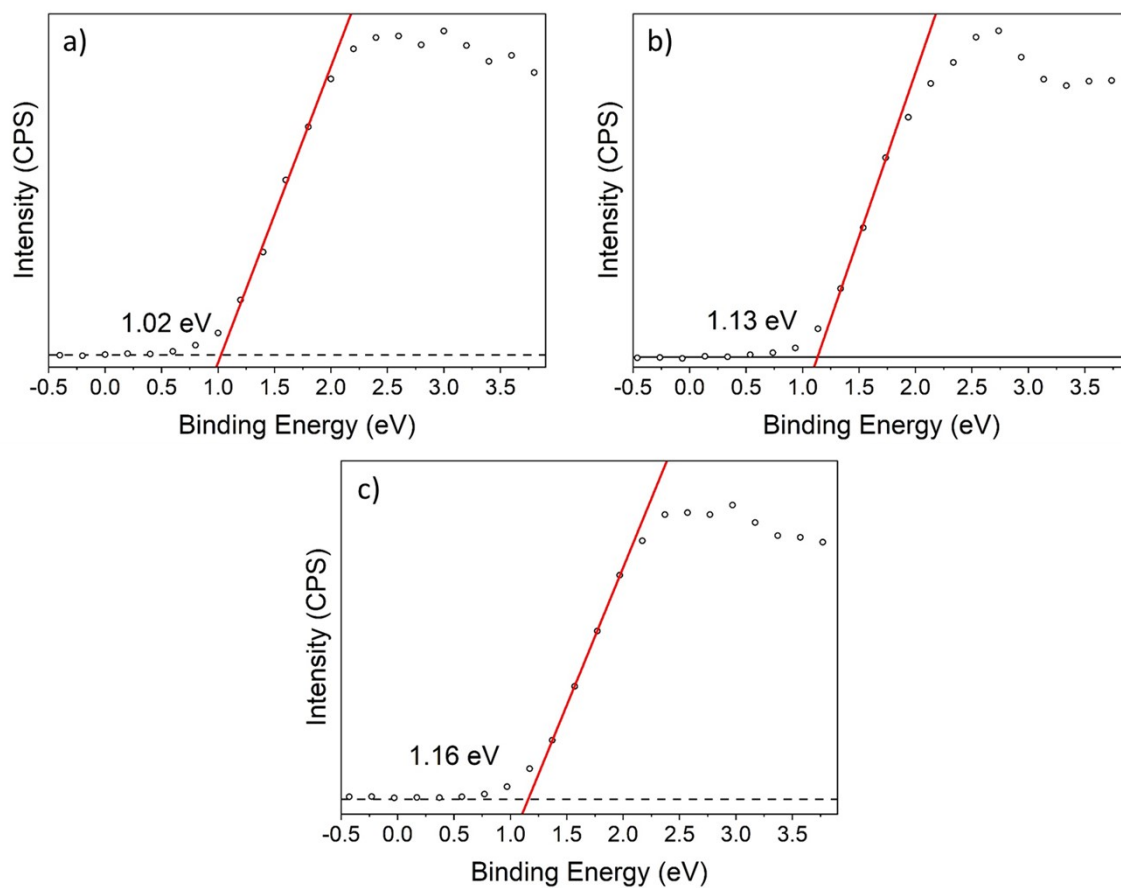


Figure S5. XPS spectra of a) T/BiOI 0.4, b) T/BiOI 0.8 and c) T/BiOI 1.6 in the region of the VBM. The binding energy scale is reported with respect to E_F . The VBM occurs at the intersection of a line fit to the linear portion of the leading edge and the extended background line between the VBM and E_F .

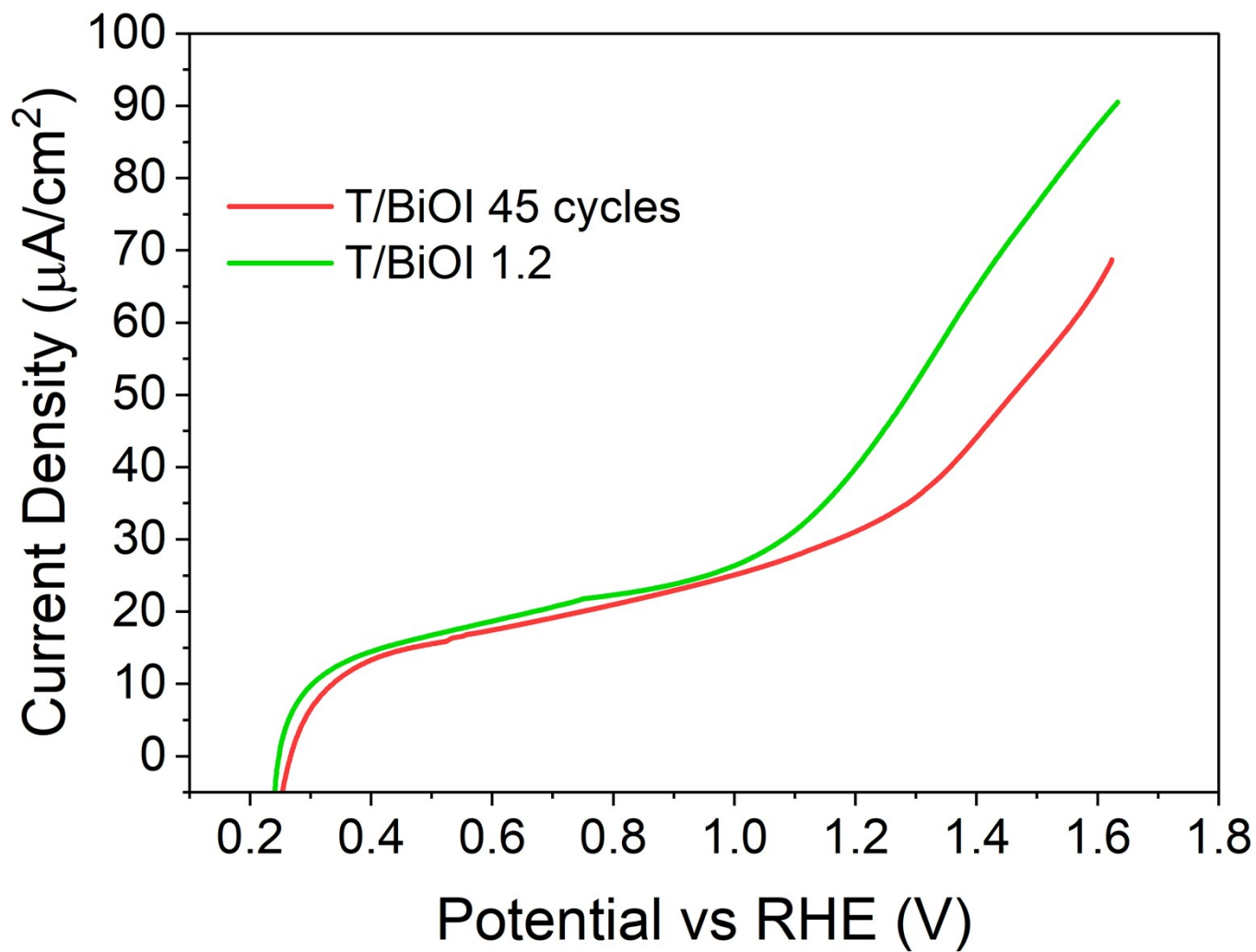


Figure S6. LSV of T/BiOI 45 and T/BiOI 1.2.

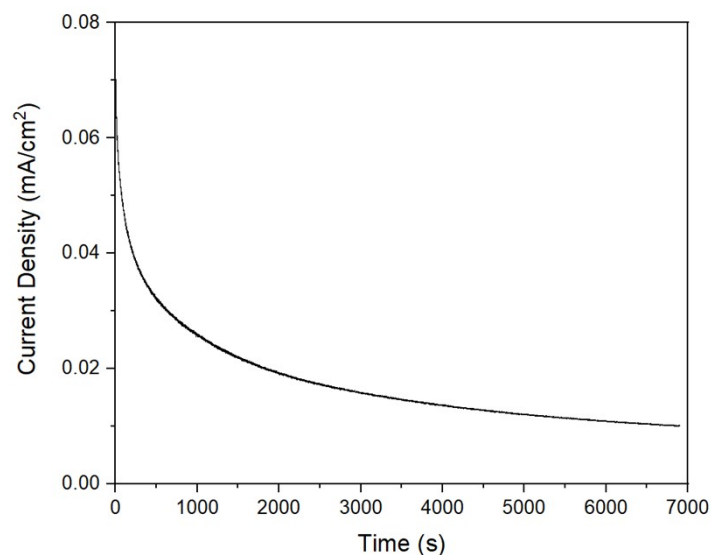


Figure S7. Chronoamperometry at 1.23 V vs RHE of the T/BiOI 1.2 film with a 20 nm ALD Al₂O₃ protection layer. The chronoamperometry was measured under Xenon arc lamp with an LSZ189 AM 1.5G filter with an intensity set to 100 mW cm⁻².

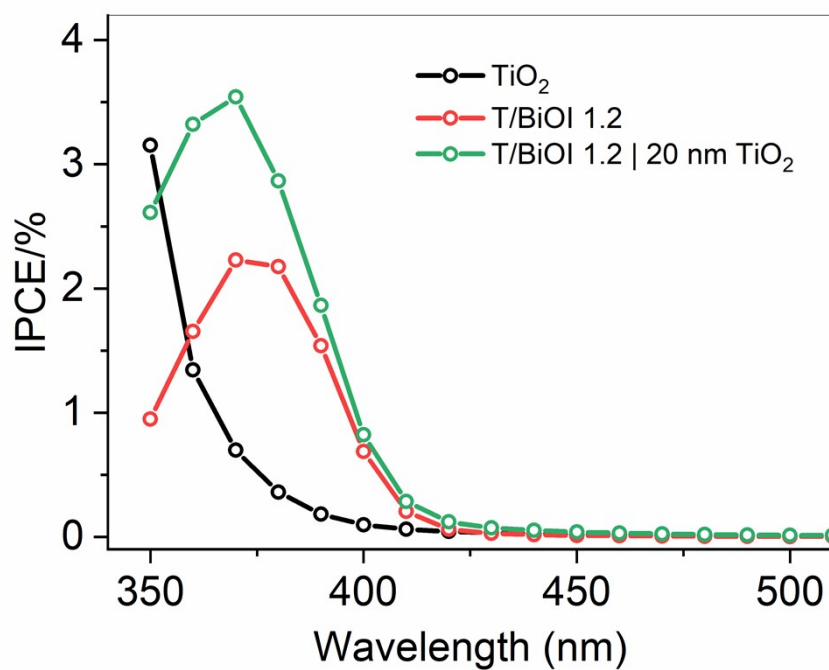


Figure S8. IPCE spectra of T/BiOI 1.2 with and without the TiO₂ protective layer deposited via ALD.