Supporting Information.

Stable hybrid organic/inorganic photocathodes for hydrogen evolution with amorphous WO_3 hole selective contact.

Alessandro Mezzetti,[1,2] Fumagalli Francesco,[1] Antonio Alfano,[1,3] Daniele Iadicicco,[1,4] Maria Rosa Antognazza[1] and Fabio di Fonzo.[1,*]

[1] Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy.
[2] Politecnico di Milano, Dipartimento di Fisica, P.zza L. da Vinci 32, 20133 Milano, Italy.
[3] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta",Piazza Leonardo da Vinci, 32, 20133 Milano, Italy
[4] Politecnico di Milano, Dipartimento di Energia, Via Ponzio 34/3, 20133 Milano, Italy.
[*] Corresponding author, e-mail: fabio.difonzo@iit.it

To convert from the measured reference electrode potential (versus Ag/AgCl in saturated KCl) to the reversible hydrogen electrode (RHE) potential, the following equation is used:

$$E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + E^{0}_{Ag/AgCl} \quad \left[E^{0}_{Ag/AgCl} = +\,0.1976\,V\right]$$

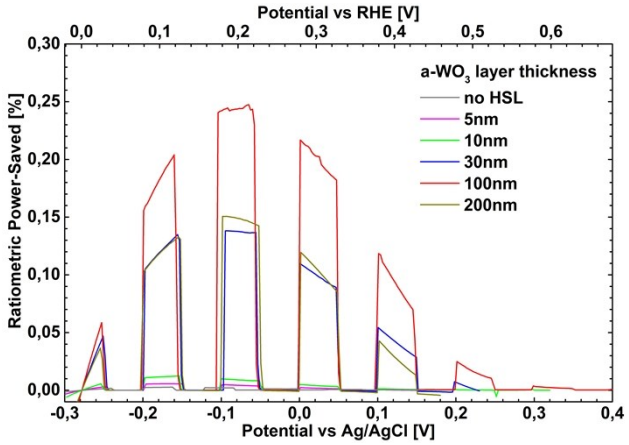

Figure S1. Ratiometric power saved curves as a function of the applied bias for a series of hybrid organic photocathodes with varying thickness of the amorphous WO_3 layer. The peak of the curve is the maximum power point in the corresponding linear sweep voltammetry curve.

The depletion layer with x_d is calculated with the following equation, derived from Poisson's equations under the full depletion approximation for a metal/semiconductor junction:

$$x_d = \sqrt{\frac{2\varepsilon_s(\varphi_m - \varphi_s)}{qN_d}} \qquad \text{[Eq. S1]}$$

where ε_s is the relative dielectric permittivity of the semiconductor, $\varphi_{m/s}$ is the work function of the metal and of the semiconductor, q is the electron charge and N_d is the donor density of the semiconductor.

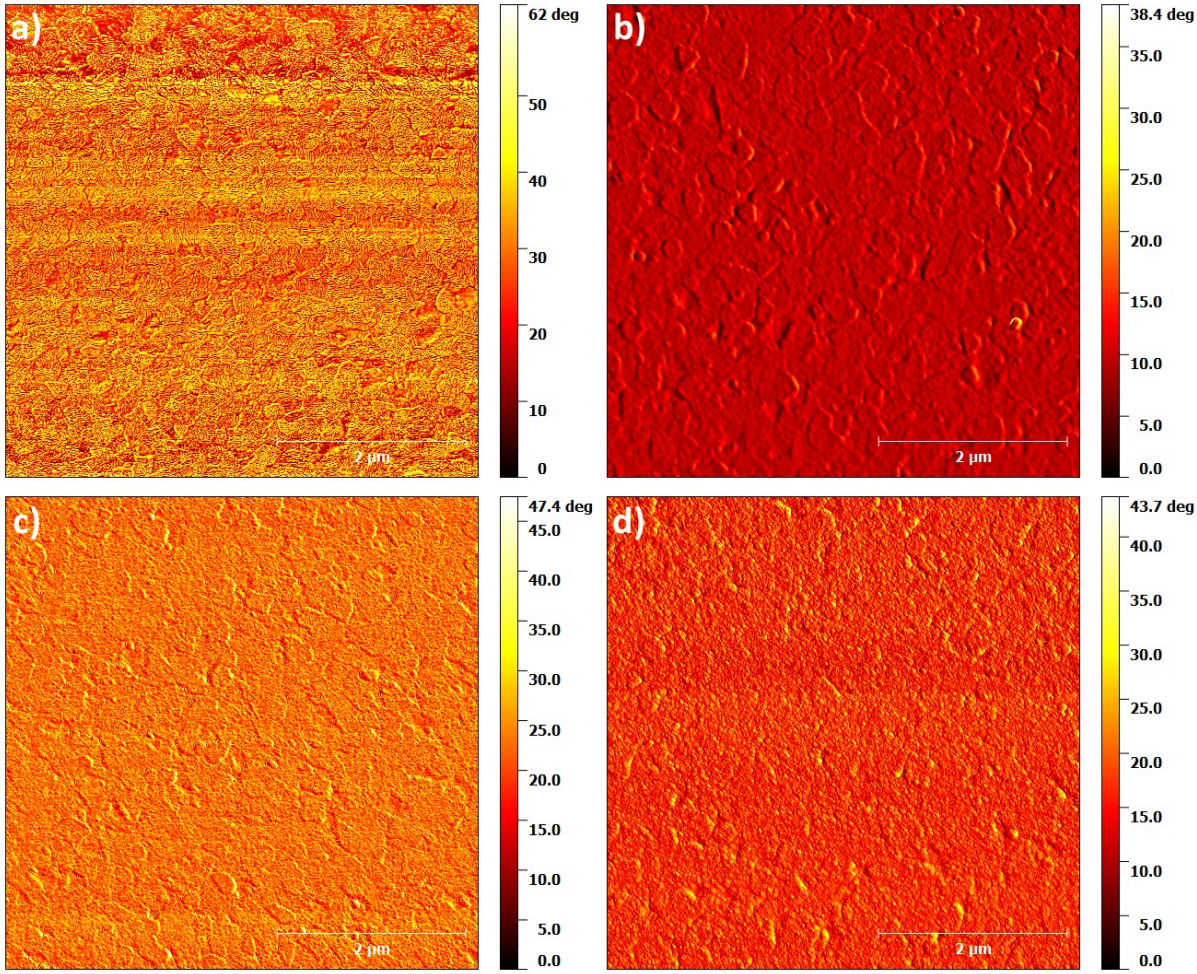

Figure S2. Atomic force microscopy phase images showing surface morphology of (a) bare ITO and (b-d) ITO/WO_3 with different WO_3 HSL thickness (5 nm, 30 nm and 100 nm respectively).

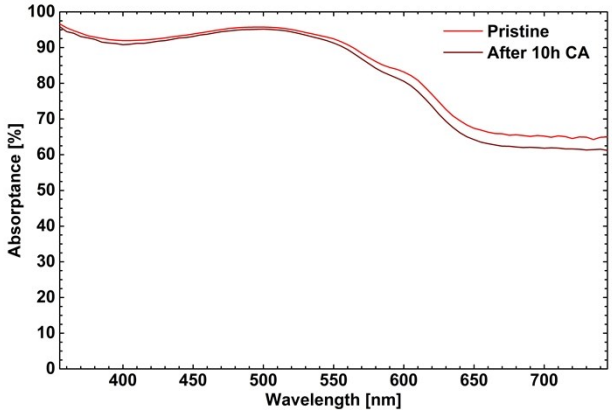

Figure S3. Spectroscopic analysis of complete photocathode architecture showing the UV-Vis-nIR absorptance spectra of a pristine device and of a device that has undergone a 10-hour chronoamperometry.