

## Supporting Information

### Shedding light on light-driven lithium ion de-insertion reaction: towards the design of a photo-rechargeable battery

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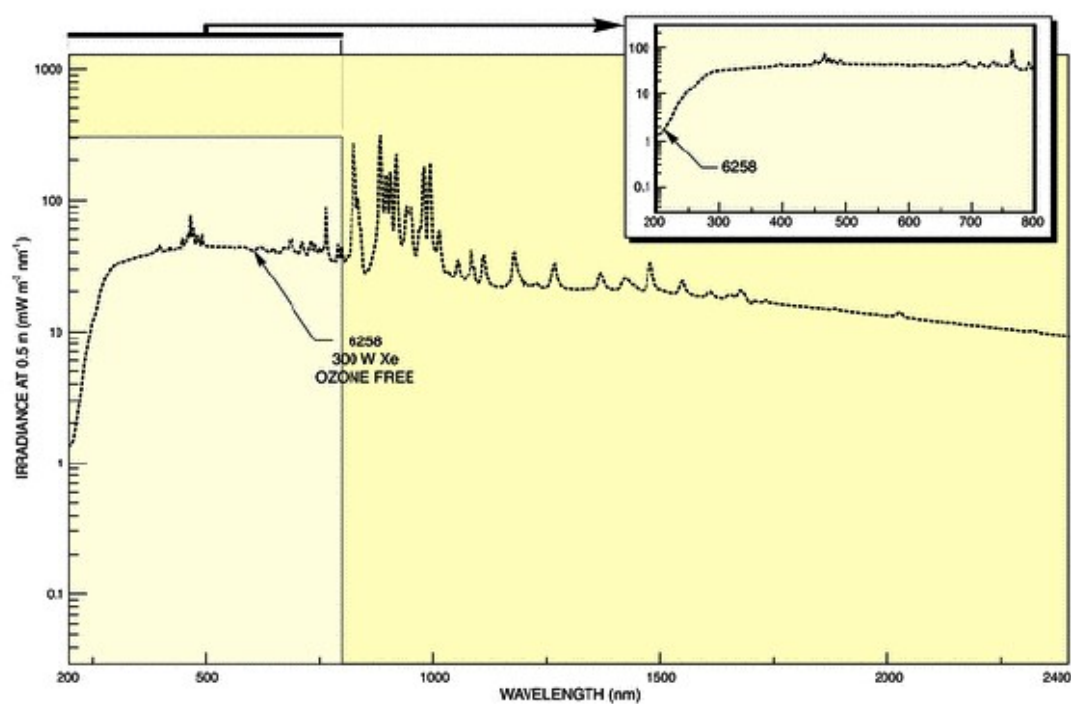


Fig. SI 1. Newport 300W Xe arc lamp sans ozone spectrum (model 6258).

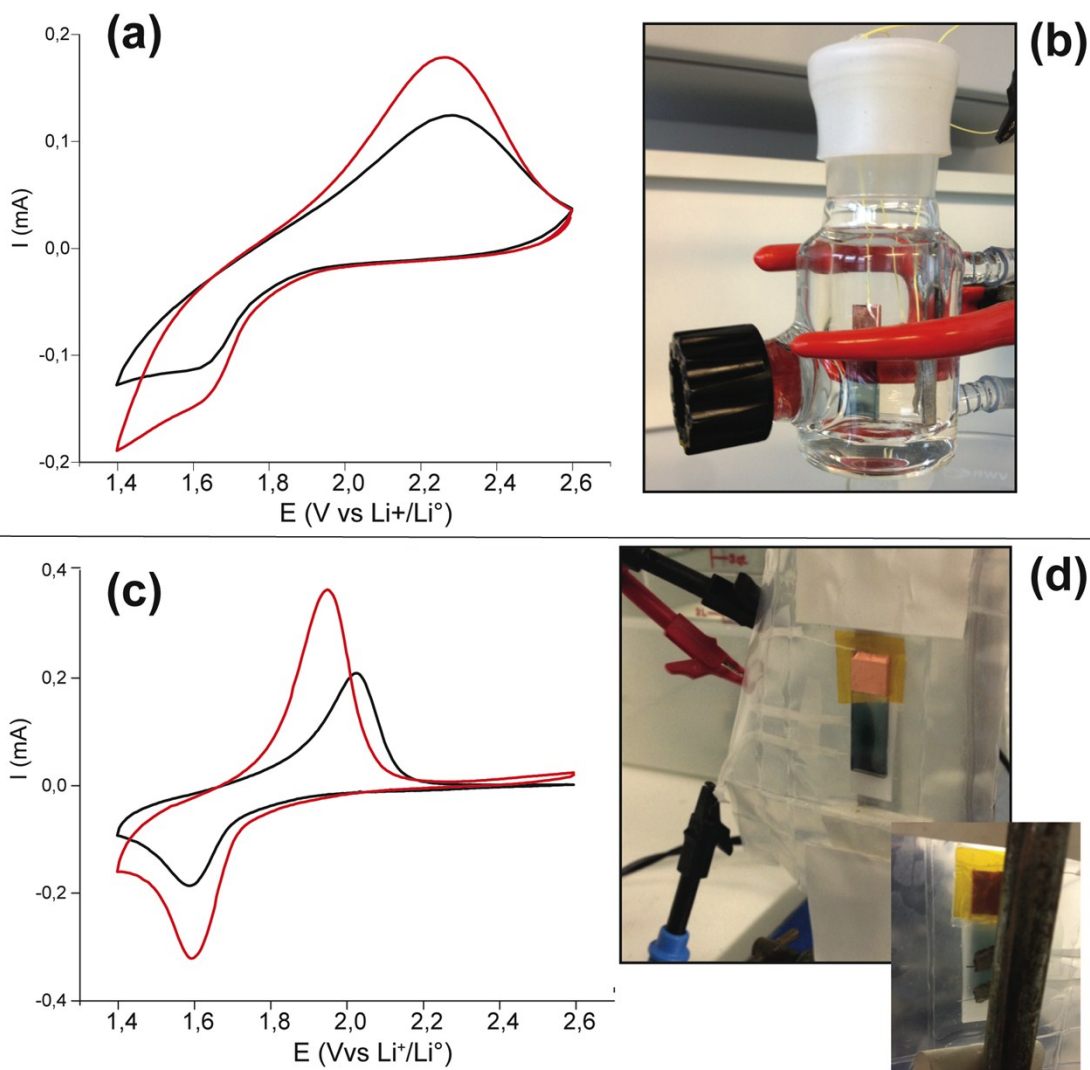


Fig. SI 2. (a, c) Cyclic voltammograms at scan rate  $0.5 \text{ mV}\cdot\text{s}^{-1}$  of mesoporous anatase  $\text{TiO}_2$  film on FTO /glass substrate in **dark** (black curves) and **light** (red curves) conditions. The voltammograms were performed in a water-cooled cell with a quartz window, shown in (a). Please note that the temperature of the water-cooled cell after 5.5 h of constant illumination only suffers for an increase of  $1.3^\circ\text{C}$  (b) Same experiment performed in a pouch cell-like configuration, using Whatman glass microfibers filters as separator, as shown in (c) and (d). In the case of the water-cooled cell (b), the electrolyte was a solution  $\text{LiPF}_6$  1M in EC:DMC (1:1 in vol). In the case of the pouch cell (d), the electrolyte used was solution  $\text{LiTFSI}$  (Bis(trifluoromethane)sulfonimide lithium salt) 0.2 M in EMIM TFSI (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). In both case, the  $\text{TiO}_2$  was synthesized from the dip-coating of a solution whose concentration in inorganic salts was 1M.

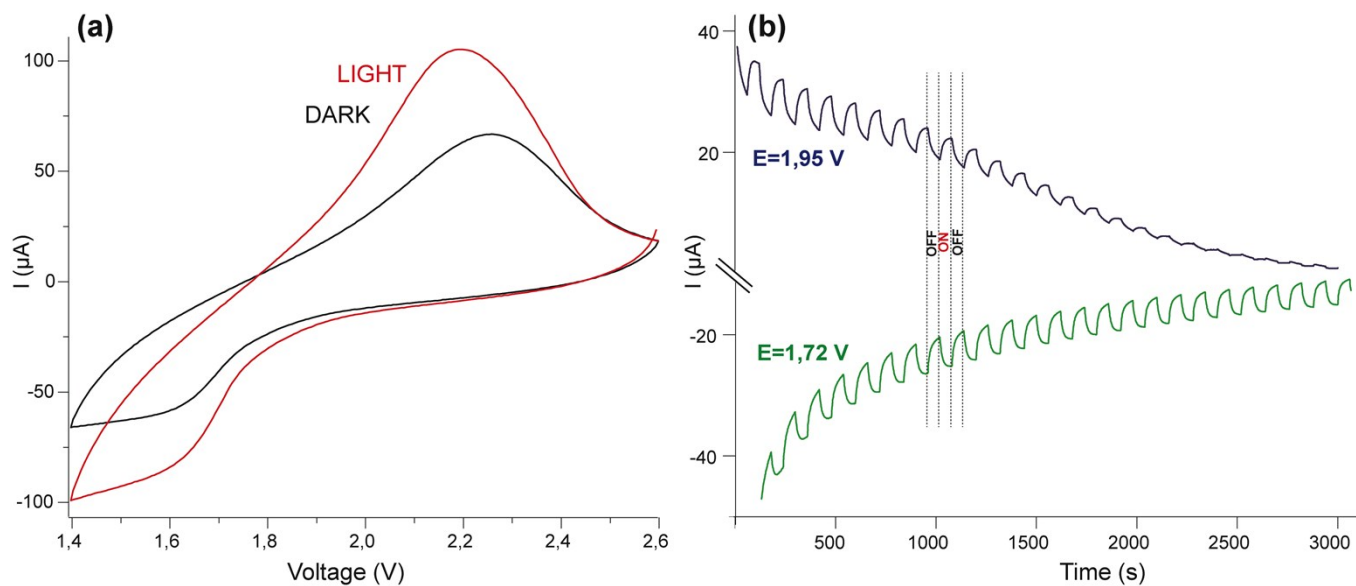


Fig. SI 3. Three electrodes sealed glass cell configuration: glass/FTO/ $\text{Li}_x\text{TiO}_2$ // $\text{LiPF}_6$  1M in EC:DMC (1:1 in vol)//graphite C, ref.  $\text{Li}^\circ$ . (a) Cyclic voltammograms at scan rate  $0.5 \text{ mV}\cdot\text{s}^{-1}$  in **dark** (black curves) and **light** (red curves) conditions. (b) Potentiostatic experiments, light ON/OFF every 1 min for  $E$  set at 1.95 V and 1.72 V. In this case, directly after the cell assembly, mesoporous  $\text{TiO}_2$ /FTO was pre-lithiated using  $\text{Li}^\circ$  as both reference and counter electrode, using a linear sweep voltammetry from 2.6 V to 1.4 V at  $0.5 \text{ mVs}^{-1}$ .

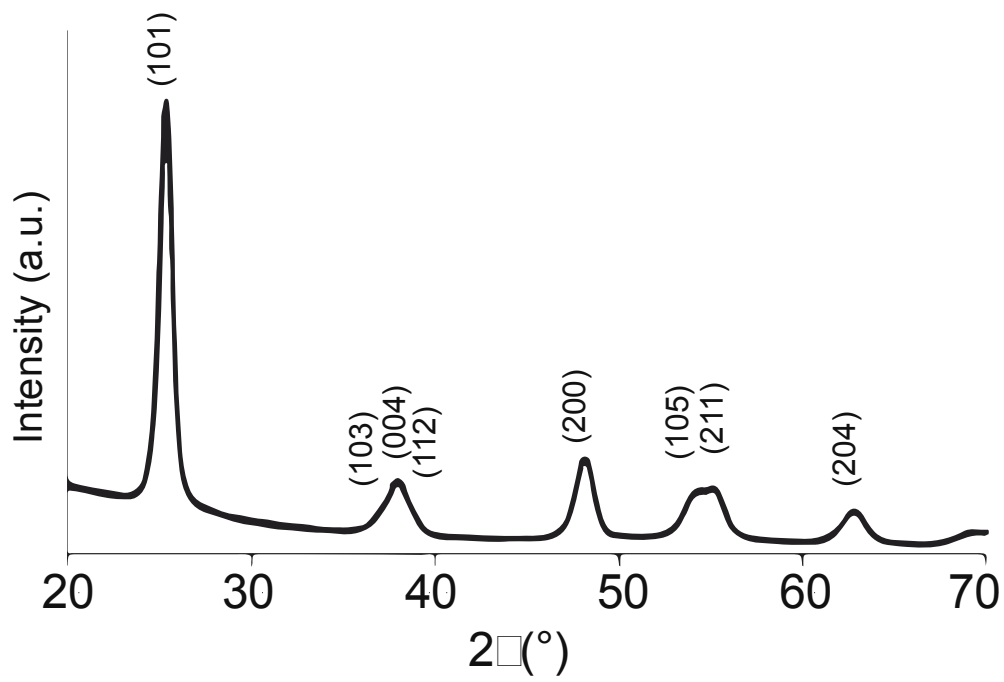


Fig. S1 4. X-ray diffractogram of mesoporous anatase TiO<sub>2</sub> thin film.

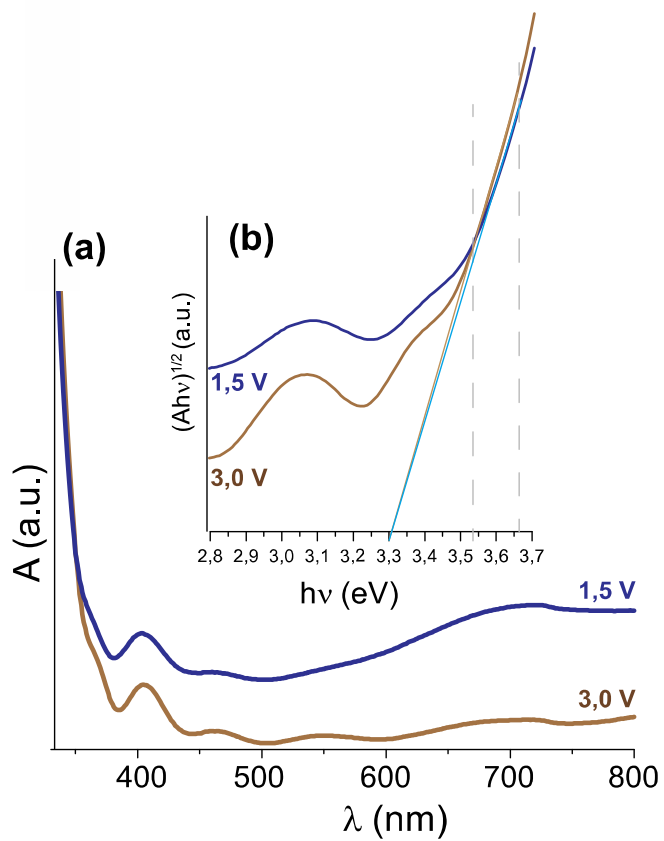


Fig. SI 5. (a) UV-VIS spectra of anatase  $\text{TiO}_2$ -based mesoporous thin film at 3V vs  $\text{Li}^+/\text{Li}^0$  (transparent state) and at 1.5V vs  $\text{Li}^+/\text{Li}^0$  (blue state). (b) Corresponding Tauc plot for  $\text{TiO}_2$ 's indirect band gap.

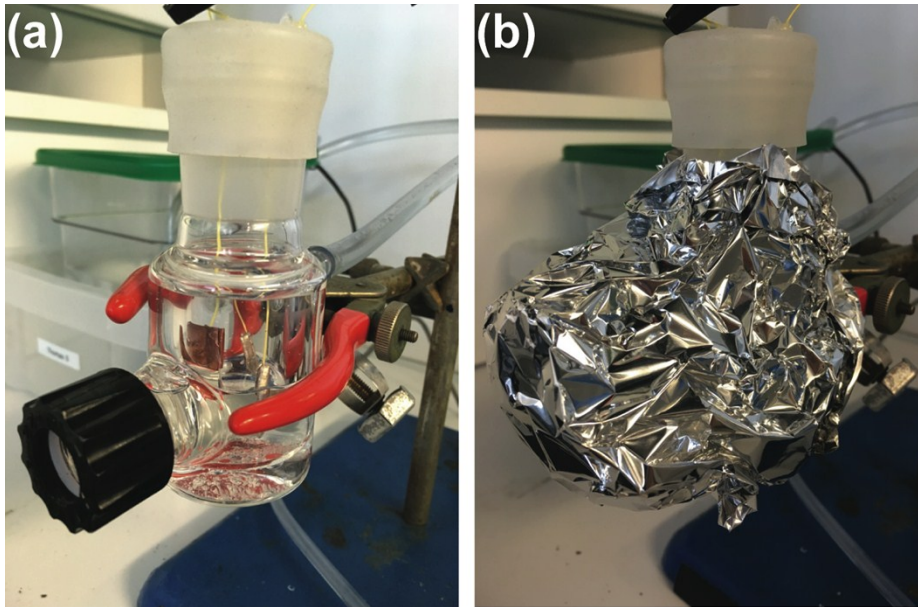


Fig. SI 6. (a) Water-cooled cell without Aluminum, as used for “light condition” or light chopped potentiostatic experiments. (b) The same cell wrapped in Al foil for experiments in “dark condition”.

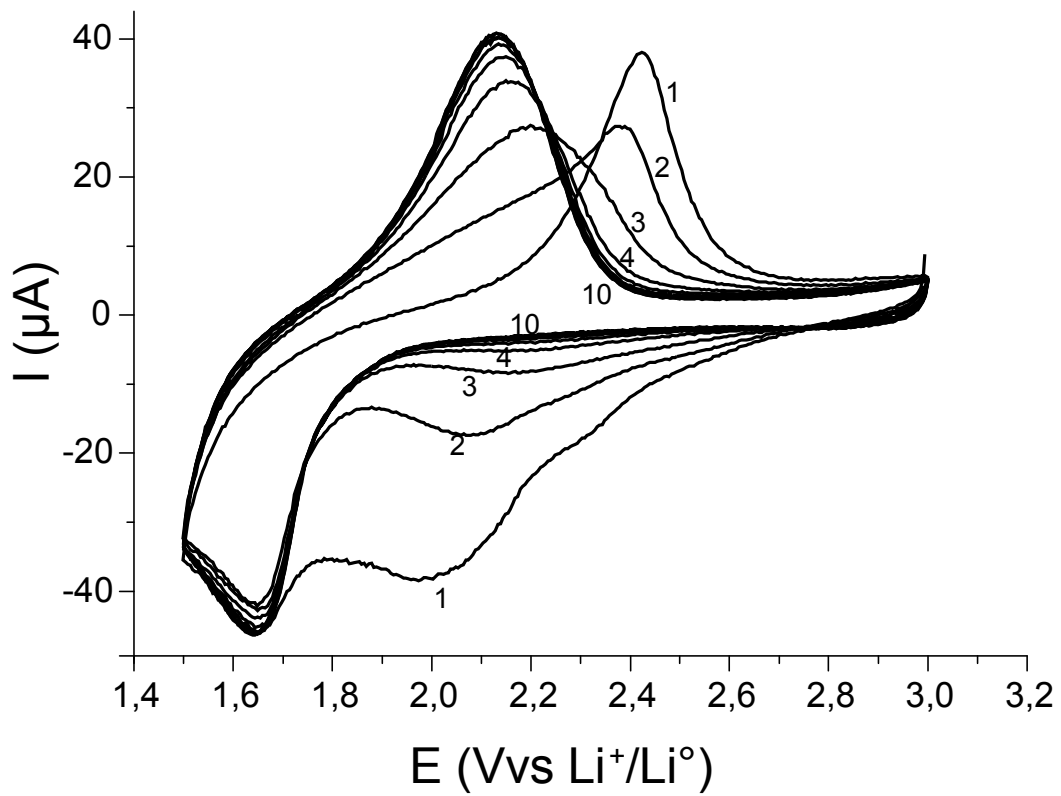


Fig. SI 7. First ten cyclic voltammograms at scan rate  $0.5\text{mV}\cdot\text{s}^{-1}$  of mesoporous anatase  $\text{TiO}_2$  thin film (stabilization treatment). The number of the cycle is indicated in the graph as reference.

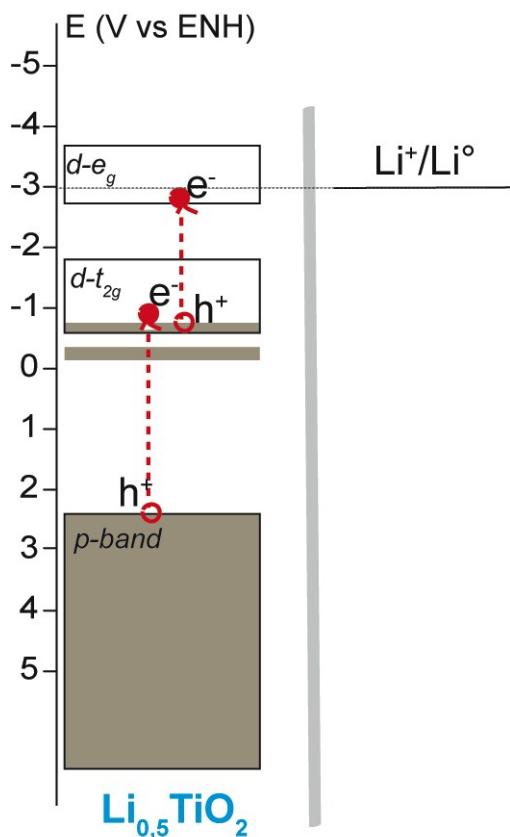


Fig. SI 8. Scheme of a suggested mechanism to explain photoinduced lithium-ion extraction,  $\text{Li}_{0.5}\text{TiO}_2$  electronic structure is based on Wagemaker et al.<sup>1</sup> Two potential electronic transitions are identified within the Li-rich phase that could give rise to an exciton: (i) a transition from the valence to the conduction band, as commonly expected from a semiconductor and (ii) from a transition from the Fermi level to the empty d-eg band.<sup>2</sup> The latter could succeed in raising the electron up to the  $\text{Li}^+/\text{Li}^0$  level allowing Li reduction at the counter electrode. In the case of the first transition, an extra light absorption would be necessary in order to drive the electrons to reduce lithium at the negative electrode. In order to support these mechanisms, further investigations are currently ongoing.



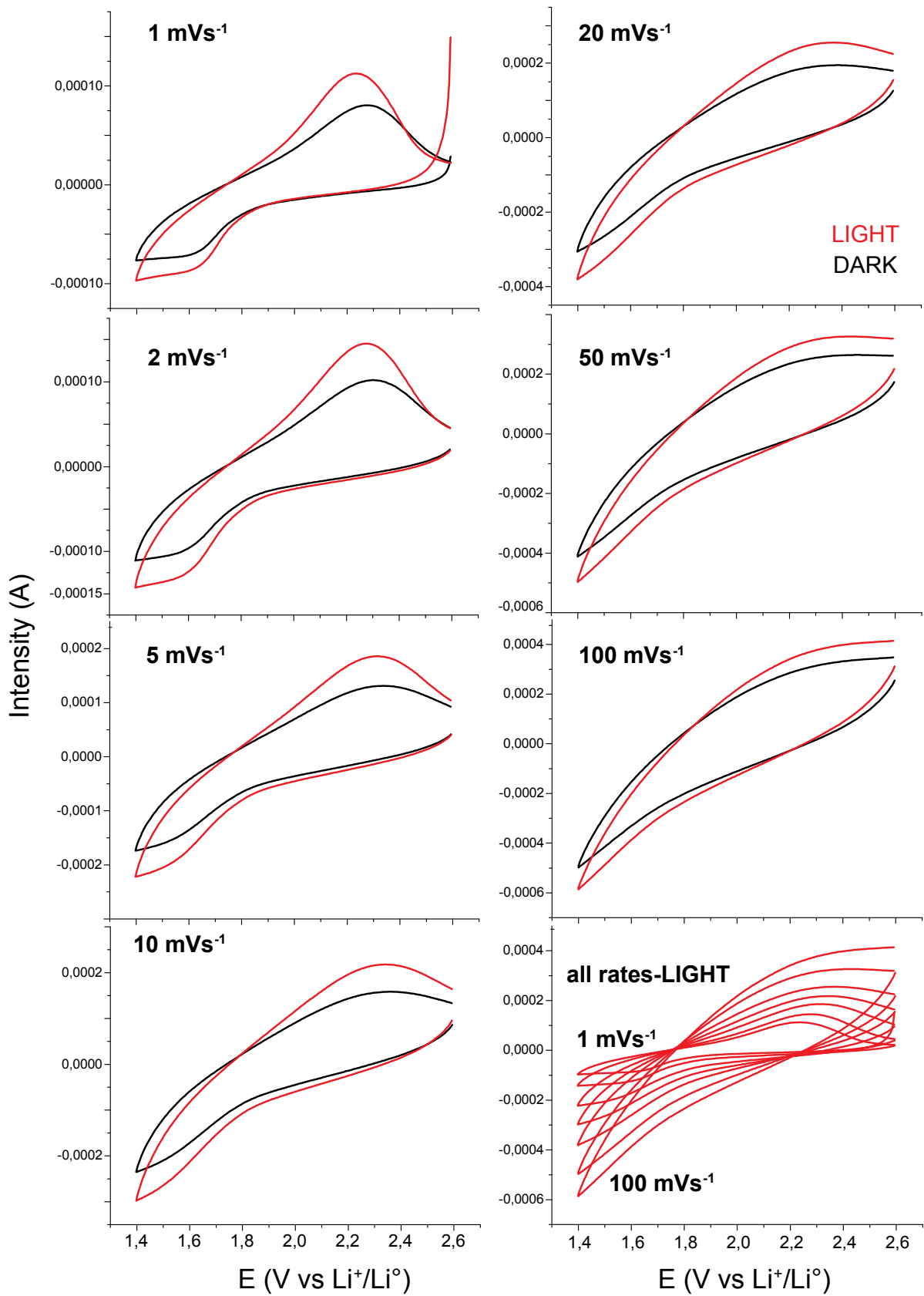


Fig. SI 9. Cyclic voltammograms at different scan rates (1-1005mV.s<sup>-1</sup>) under DARK and LIGHT conditions of mesoporous anatase TiO<sub>2</sub> thin film.

## References

1. M. Wagemaker, A. Van Der Ven, D. Morgan, G. Ceder, F. M. Mulder and G. J. Kearley, *Chem Phys*, 2005, **317**, 130-136.
2. V. M. Khomenko, K. Langer, H. Rager and A. Fett, *Phys Chem Miner*, 1998, **25**, 338-346.