Supporting Information

An experimental and theoretical study on the electronic and structural properties of CdSe@TiO$_2$ nanotubes arrays

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Electrodeposition of CdSe into TiO$_2$NT

All chemicals used were of analytical grade and underwent no further purification: selenium oxide (SeO$_2$, Sigma-Aldrich 99.9%), cadmium sulphate (CdSO$_4$, Sigma-Aldrich 99.9%) and sulphuric acid (H$_2$SO$_4$, Alfa-Aesar 98%).Electrochemical experiments were carried out in a potentiostat/galvanostat (Autolab PGSTAT 302N, Metrohm-Eco Chemie) controlled by GPES® and FRA® software.

Firstly, the electrodeposition processes of the CdSe were evaluated by cyclic voltammetry onTiO$_2$NT.At a concentrationof 1mmol L^{-1},the elementswereanalysedseparately and, after that, the Cd^{2+} ionswere studiedin the presence ofSe. After studies of the electrochemical deposition potential, the electrodeposition of all films was performed in a stationary bath at 25 ºC using the pulsed deposition method and an electrolytic bath containing 5mmol L^{-1} Cd^{2+}, 1 mmol L^{-1} SeO$_2$, and 0.5mol L^{-1}H$_2$SO$_4$ (as supporting electrolyte). The ration Cd/Se of 5/1 was selected in order to favour a stoichiometric obtaining of CdSe by an excess of Cd^{2+} ions [1]. Prior to deposition, the TiO$_2$NTworking electrode was immersed in the electrolytic bath and ultrasonicated during5 min for diffusingof the solution intro the nanotubes.

The electrochemical behaviour of the individual Cd^{2+}and H$_2$SeO$_3$ species, as well as, of the binary system on the TiO$_2$NT surface were analysed, the cyclic voltammograms (CV) can be seen in Figure 1. The CV curves were recorded at 50 mV s^{-1} from 0 V to 0.9 V vs. Ag/AgCl/Cl$^-$$_{(sat.\ KCl)}$ and the electrochemical profile of the working electrode was taken in SE at the same condition.
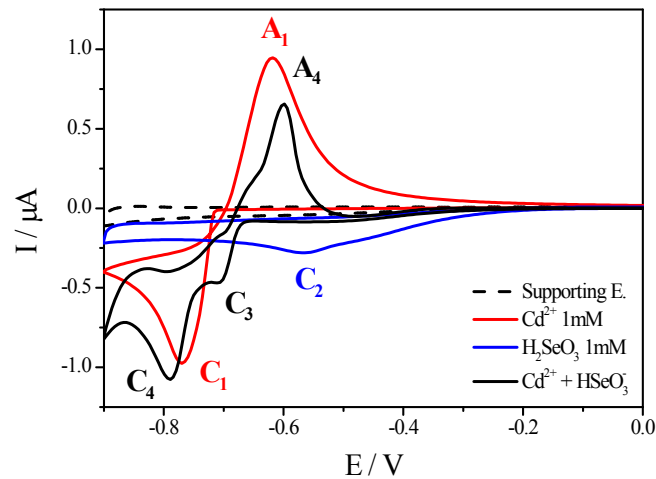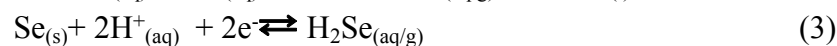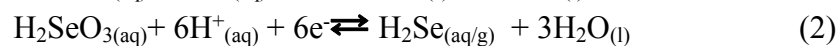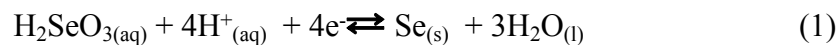
Figure S1 -Cyclic voltammograms on Ti_2ONT and at a scan rate of 50 mV s^{-1} for H_2SO_4 0.5 mol L^{-1}(black dashed line),as supporting electrolyte (SE), andSE + 1 mmol L^{-1}solutions of Cd^{2+} (red line), H_2SeO_4(blue line) and Cd^{2+} + H_2SeO_4 (black solid line).

For the CV in the presence of Cd^{2+}in SE (red line),one cathodic peak at about -0.77 V (C_1)during the forward scan and one anodic peak at about -0.62 V (A_1) during the reverse scan can be seen. These peaks can be attributed to Cd reduction and dissolution, respectively. For the system containing only Se species in SE (blue line), any anodic peak was evidently observed and, because of this, we believe that the broad cathodic peak (C_2) observed during the forward scan can be associated to these reactions [1,2]:

$$H_2SeO_{3(aq)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons Se_{(s)} + 3H_2O_{(l)} \qquad (1)$$
$$H_2SeO_{3(aq)} + 6H^+_{(aq)} + 6e^- \rightleftharpoons H_2Se_{(aq/g)} + 3H_2O_{(l)} \qquad (2)$$
$$Se_{(s)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2Se_{(aq/g)} \qquad (3)$$

The voltammetric profile of the binary system can be observed from black solid line CV showed in Figure 1, which had two cathodic peaks (C_3 and C_4) andone anodic peak (A_4). Also, it can be observed that the broad peak attributed to the Se species disappeared, appearing a new cathodic peak at about -0.71 V (C_3). As the free energy of CdSe formation is large negative ($\Delta G^o_{f, 298 K}$ = -141.5 kJ mol^{-1}[2]), we believe that this process can be related to the reaction 4 showed below[1,2].

$$Cd^{2+}_{(aq)} + H_2SeO_{3(aq)} + 4H^+_{(aq)} + 6e^- \rightleftharpoons CdSe_{(s)} + 3H_2O_{(l)} \qquad (4)$$
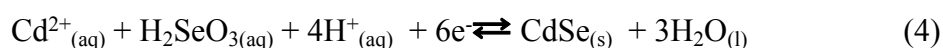
The C_4 and A_4 peaks can be respectively associated to Cd^{2+} reduction anddissolution. The peak potential of the C_4 reaction was shifted to more negative potential with de Se species presence, probably, the CdSe phase formed at C_3has become the electrode surface more resistive, inhibiting the Cd reduction. A similar behaviour was observed for Cd dissolution peak, which can be explained of the same way. The charge of the Cd dissolution decreases in relation to the system without Se species, which can be evidence of the CdSe formation.

Thus, the pulsed deposition of CdSe intro TiO$_2$NTswas carried out during 1000 s; the potentials of -0.76 V and -0.64 V were used in the cathodic and anodic pulse and the duration of each pulse per cycle was of 25 s and 15 s, respectively. The anodic pulse was applied to eliminate the Cd excess. The profile of the pulse deposition can be seen in Figure 2.
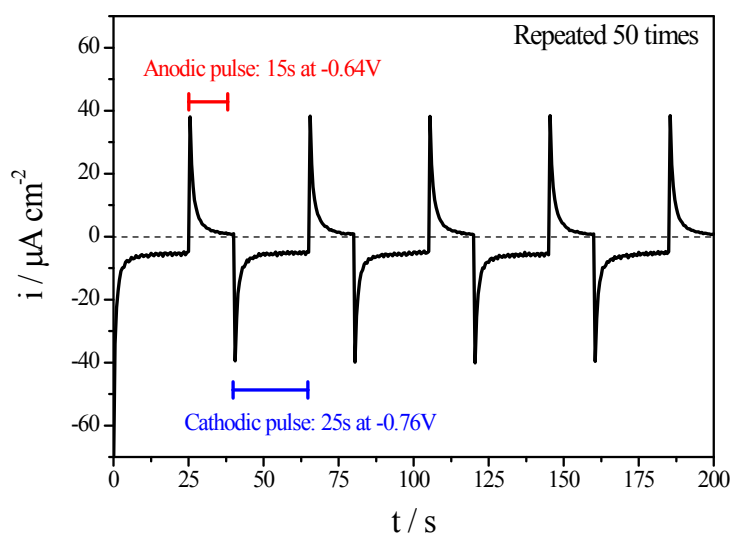

Figure S2 -Chronoamperogram representing the pulsed deposition profile foran electrolytic bath containing 5 mmol L^{-1} Cd^{2+}, 1 mmol L^{-1} SeO$_2$, and 0.5 mol L^{-1} H$_2$SO$_4$ (as supporting electrolyte).

Ordered Desordered CdSe@TiO$_2$NT TiO$_2$-anatase Unit Cell

Theoretical calculus involving *density functional theory* (DFT) [3,4] were carried out to elucidate the band structure and correlate theoretical band gap with experimental values.

Based on the results of Rietveld refinement and TiO$_2$-anatase CIF obtained after the refinement procedure, the crystallographic databasewere used as input in order to compute the referred properties. DFT computations for the geometric and electronic structures of TiO$_2$ surfaces have been carried out within the generalized gradient approximation (GGA) using PWscf code included in the Quantum-Espresso package[5]. Electron ion interaction were described by ultrasoft pseudopotentialsb[6]. Plane-wave basis set cut-offs for the smooth part of the wave functions was 500 Ry. Electronic structure calculations were performed using a 4 x 4 x 2 Monkhorst-Pack *k*-points grid to sample the Brillouin zone. The resulted TiO$_2$-anatase for ordered and disordered unit cell can be observed in Figure S3, respectively.
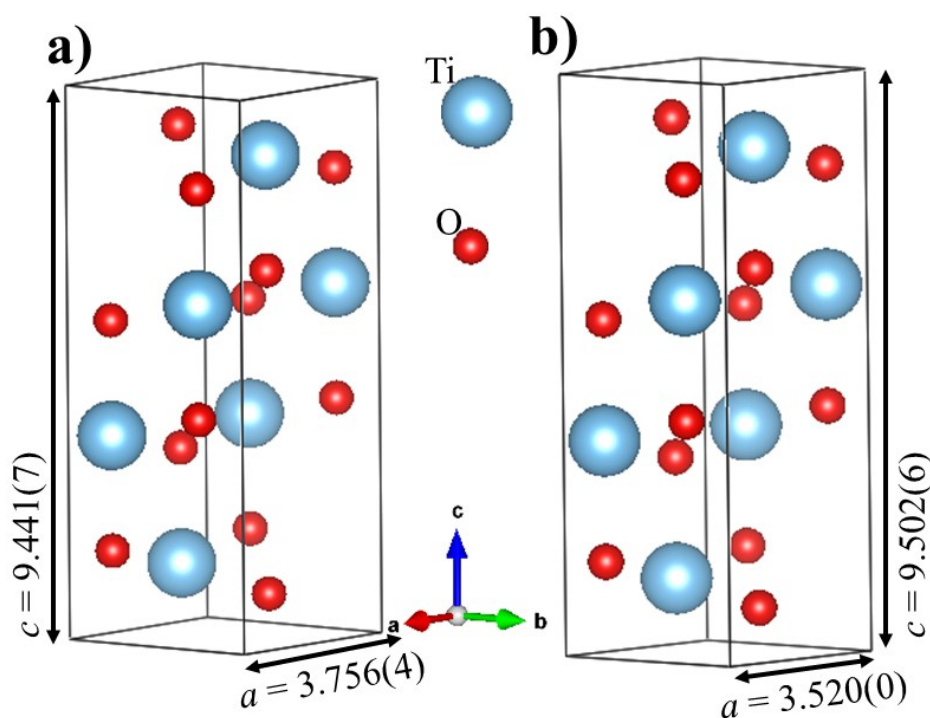

Figure S3 -a) ordered and b) disordered Sample-PTT and Sample-LTT -related TiO$_2$-anatase unit cell.

TiO$_2$ Cartesian Coordinates obtained from Rietveld Refinement – Sample-PTT

Ti   0.000000   0.939128   3.541238

Ti   3.756510   0.939128   3.541238

Ti   0.000000   2.817383   5.902062

Ti   3.756510   2.817383   5.902062

Ti   1.878255   2.817383   8.262888

Ti   1.878255   0.939128   1.180413

O   0.000000   0.939128   1.503373

O   3.756510   0.939128   1.503373

O   0.000000   2.817383   7.939927

O   3.756510   2.817383   7.939927

O   1.878255   2.817383   6.225024

O   1.878255   0.939128   3.218277

O   0.000000   2.817383   3.864199

O   3.756510   2.817383   3.864199

O   0.000000   0.939128   5.579102

O   3.756510   0.939128   5.579102

O   1.878255   0.939128   8.585849

O   1.878255   2.817383   0.857452

TiO$_2$ Cartesian Coordinates obtained from Rietveld Refinement – Sample-LTT

Ti   0.000000   0.947450   3.562387

Ti   3.789800   0.947450   3.562387

Ti   0.000000   2.842350   5.937312

Ti   3.789800   2.842350   5.937312

Ti   1.894900   2.842350   8.312237

Ti   1.894900   0.947450   1.187462

O   0.000000   0.947450   1.795443

O   3.789800   0.947450   1.795443

O   0.000000   2.842350   7.704256

O   3.789800   2.842350   7.704256

O   1.894900   2.842350   6.545293

O   1.894900   0.947450   2.954406

O   0.000000   2.842350   4.170368

O	3.789800	2.842350	4.170368
O	0.000000	0.947450	5.329331
O	3.789800	0.947450	5.329331
O	1.894900	0.947450	8.920218
O	1.894900	2.842350	0.579482

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