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Electronic supplementary information

The role of boron in the carrier transport improvement of CdSe-sensitized B,N,F-TiO$_2$ nanotubes solar cells: a synergistic strategy

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1. **Characterization of light source used during photoelectrochemical measurements**
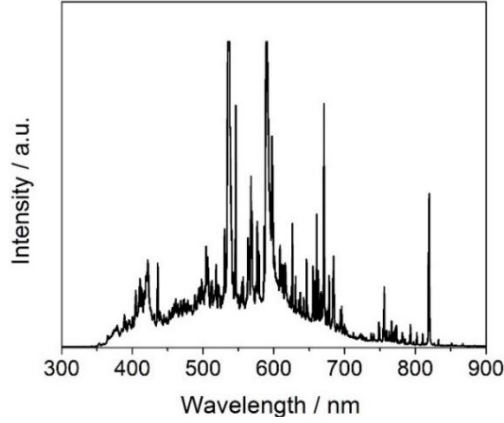

Fig. S1 Emission spectrum of the halide lamp used in photo(electro)chemical tests (60 mW cm^{-2}).

2. **Dependence of depletion layer (W) on the boron doping in the photoanodes**

One alternative to observe changes in the charge carrier density by impurity doping, is through the estimation of depletion layer width (W) produced during band bending of TiO_2 (See Fig. S2a). W can be determined by the following relationship taking into account the terms used in the M-S analysis:

$$W = \sqrt{\frac{2\varepsilon\varepsilon_0(E_{app} - E_{fb})}{eN_d}} \qquad (1)$$

Here, e is the electron charge. W was plotted vs E_{app}-E_{fb} for all photoanodes, obtaining a decrease of depletion layer for E_{app}-E_{fb} = 1.0 $V_{Ag/AgCl}$ to vary the amount of H_3BO_3 in the following order: 0.09 wt% < 0.06 wt% < 0.04 wt% < bare NF-TNT. Some works have reported that a wide W is vital for an efficient charge carrier separation to increase the photoresponse of TiO_2.[1,2] Nonetheless, X-BNF-TNT showed a diminution of W (See Fig. S2b). So, ¿what allows the PEC performance of modified photoanodes increases although W is decreased by boron doping? The answer was addressed in terms of the donor species function into X-BNF-TNT formed by interstitial boron. After boron doping, the amount of Ti^{3+} species was increased than that bare NF-TNT, mediating a suitable electron-hole separation by using a H_3BO_3 content of 0.06 wt%. It is suggested that a high amount of Ti^{3+} was formed in the bulk and the depletion layer of B-photoanodes (N_d of 0.06-BNF-TNT was 3.6 times higher than that NF-TNT). This modification facilitated electron-hole pair separation to generate a high photocurrent.[3,4] Conversely, an excess of Ti^{3+} in the bulk and W of TNT favoured charge-carrier recombination, which inhibited photoholes migration to the photoanode surface and electron transport to the current collector. On the other hand, E_{fb} can be considered as indication of the energy required to carry out charge carrier

separation. Thus, the flat band condition (absence of W) into TNT could be easily achieved at more negative values to increase the amount of H_3BO_3.
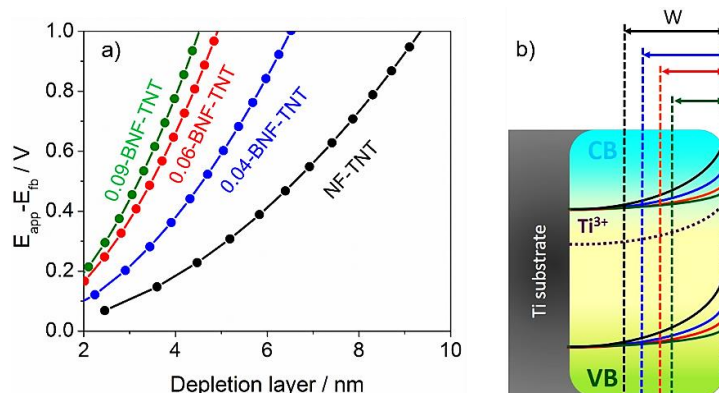

Fig. S2 a) Depletion layer (W) as a function of applied potential for the NF-TNT and X-BNF-TNT photoanodes, and b) schematic representation of W compaction varying the amount of H_3BO_3.

3. Wettability of CdSe-sensitized photoanodes

Contact angle (CA) measurements were carried out for 0.06-BNF-TNT photoanodes before (Fig. S3a) and after 5-CdSe sensitization (Fig. S3b), dropping 10 µL of DI water on the photoanode at room temperature. Bare BNF-TNT presented a high CA about 93.1°, which indicates a low wettability in its surface. The high surface tension of water provides a poor wetting ability on the solid surface, hindering the penetration of the liquid into the BNF-TNT matrix. In addition, after annealing, the hydroxyl groups in the TNT surface are replaced by oxygen molecules, which decrease their hydrophilicity.[5] This evidence have been considered to avoid the use of SILAR aqueous solutions to carry out sensitization processes.[6] Conversely, after 5-CdSe sensitization, the CA was decreased until 53.0°, indication of the improvement in the hydrophilicity of composite material. The chalcogenides deposition generates a more roughness surface[6], facilitating the permeability of liquid. It favours an intimate contact between the composite and the electrolyte to promote the diffusion of redox species and the charge carrier transport in the photoanode/electrolyte interface.[3]
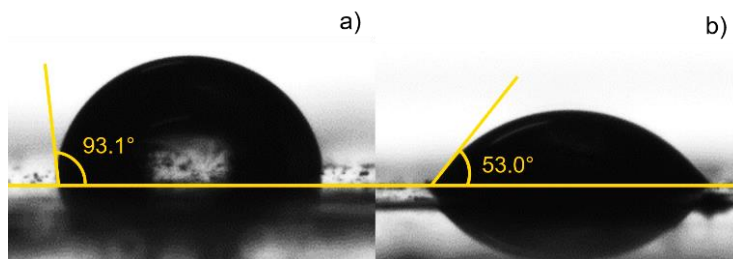

Fig. S3. Contact angle measurements for 0.06-BNF-TNT a) before and b) after 5-CdSe sensitization.

4. **Influence of boron modification and CdSe sensitization on the conducting properties of composites**

As mentioned in the main manuscript, electrochemical impedance spectroscopy (EIS) spectra were acquired to investigate the interfacial charge carrier transfer behaviour into individual BNF-Y-CdSe materials. Under dark, typical Nyquist plots for each composite in function of number of SILAR cycles (Fig. S4a) were fitted to a serie resistance (R_s) and two-Randles type circuits in serie, which indicate the existence of two interfaces into the 0.06-BNF-Y-CdSe. From the impedance parameters depicted in Table S1, R_s was associated to the ITO resistance and the electrical contact from the external circuit of cell. R_l and CPE_1 corresponded to the resistance and constant phase element of the ITO/BNF-Y-CdSe interface (inset of Fig. S4a), while the interfacial charge carrier resistance (R_{ct}) and capacitance (CPE_2) were associated to the BNF-Y-CdSe/electrolyte interface.[4,7] It could be noted from Table S1, that R_l showed a decrease-to-increase behaviour with the increase of SILAR cycles until 5. The declining of R_l indicates the enhancement of charge carrier transfer from CdSe to BNF-TNT assisted by the type-II heterojunction in the BNF-TNT/CdSe interface.

Moreover, the R_{ct} also displayed a notable decrease to sensitize the BNF-TNT with 5-CdSe, which means an effective photogenerated electron hole pairs separation inside CdSe mediated by Ti^{3+} donor states, and the inhibition of electron recombination with the S^{2-} based electrolyte.[8,9] In addition, the accumulation of electrons in the heterostructure was promoted, leading to the highest CPE_2. Conversely, upon 6-CdSe sensitization, R_l and R_{ct} were increased, as result of a low electron recombination resistance into the heterostructure, and the photoanode/electrolyte interface. It facilitates fast electron recombination in CdSe with the electrolyte. This was corroborated to obtain a lower CPE_2 than 5-CdSe. On the other hand, the effect of B-doping on the improvement of photogenerated charge carrier transport into the BNF-5-CdSe was also observed in EIS spectra performed under visible illumination (Fig.S4b). By comparing with a NF-5-CdSe, a decrease in R_l (inset of Fig. S4b) and R_{ct} were observed. A high Ti^{3+} content promoted by B-doping increases the charge carriers separated and transported from the B-composite photoanode/electrolyte interface to the back contact. The increase of carriers transferred from BNF-TNT to CdSe into BNF-5-CdSe was corroborated by a higher CPE_2 than that NF-5-CdSe composite.
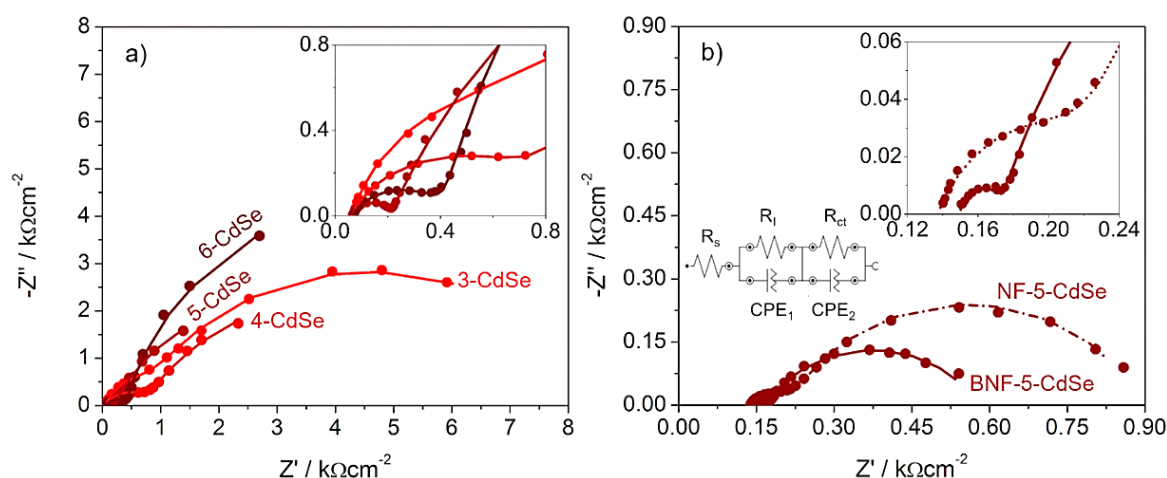
Fig. S4 Electrochemical impedance spectroscopy (EIS) spectra (10 kHz-0.01Hz) for a) BNF-Y-CdSe photoanodes under dark. b) EIS spectra of NF-5-CdSe and BNF-5-CdSe composites under visible light. Electrolyte: 1.0 M Na$_2$S (pH 12). Insets of Fig. S4a,b show the Nyquist plots at high frequencies for the composites and the equivalent circuit after EIS spectra.

Table S1. Parameters determined from EIS fitting of NF-5-CdSe and BNF-Y-CdSe sensitized composites

Photoanode	Rs / Ωcm^{-2}	R$_l$ / Ωcm^{-2}	R$_{ct}$ / Ωcm^{-2}	CPE$_1$/ μFcm^{-2}	CPE$_2$/ μFcm^{-2}
3-CdSe, dark	68	697	7742	67	238
4-CdSe, dark	63	675	7205	53	954
5-CdSe, dark	66	145	6583	11	1267
6-CdSe, dark	67	344	11423	34	692
NF-5-CdSe, light	137	92	660	348	2344
BNF-5-CdSe, light	150	23	403	106	3803

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