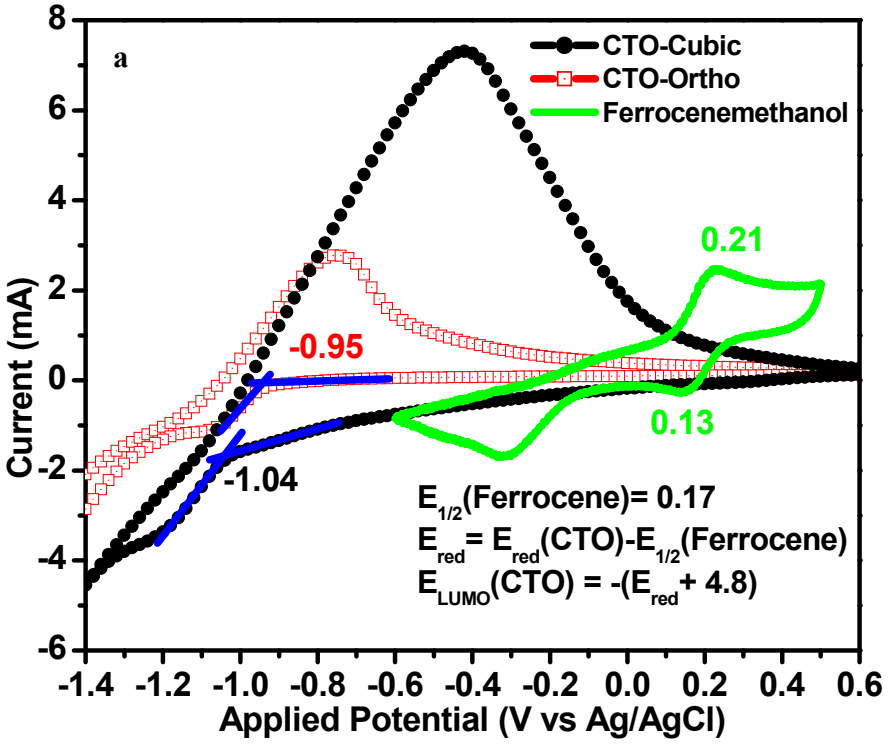
Electronic Supplementary Information

ESI-I

In order to detmine the conduction band/valance band positions of cubic and orthorhombic Cd_2SnO_4, Cyclic Voltammetry was performed as shown in figure ESI-I (a). For this we performed used the Cd_2SnO_4 film as working electrode under the same three electrode system as described in the experimental section and identified the reduction potential. The electrolyte used was 0.1 M lithium perchlorate in 1M NaOH. Using the reduction potential of ferrocenemethanol as the reference, the absolute position of the lowest unoccupied molecular level (E_{LUMO})/conduction band was determined using the equations presented in the figure. From the optical band gap obtained from the DRS measurement, the absolute position of the valance band was determined. The band positions obtained from this method are depicted as part (b) of figure ESI-I and found to be quite close to those deduced from the Mott-Schottky analysis.



b

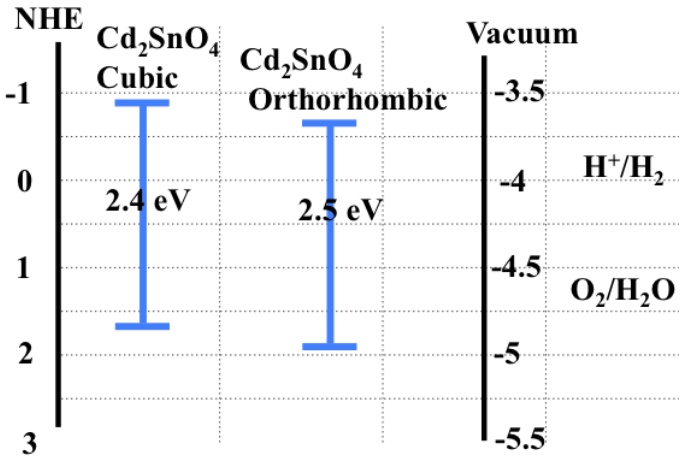
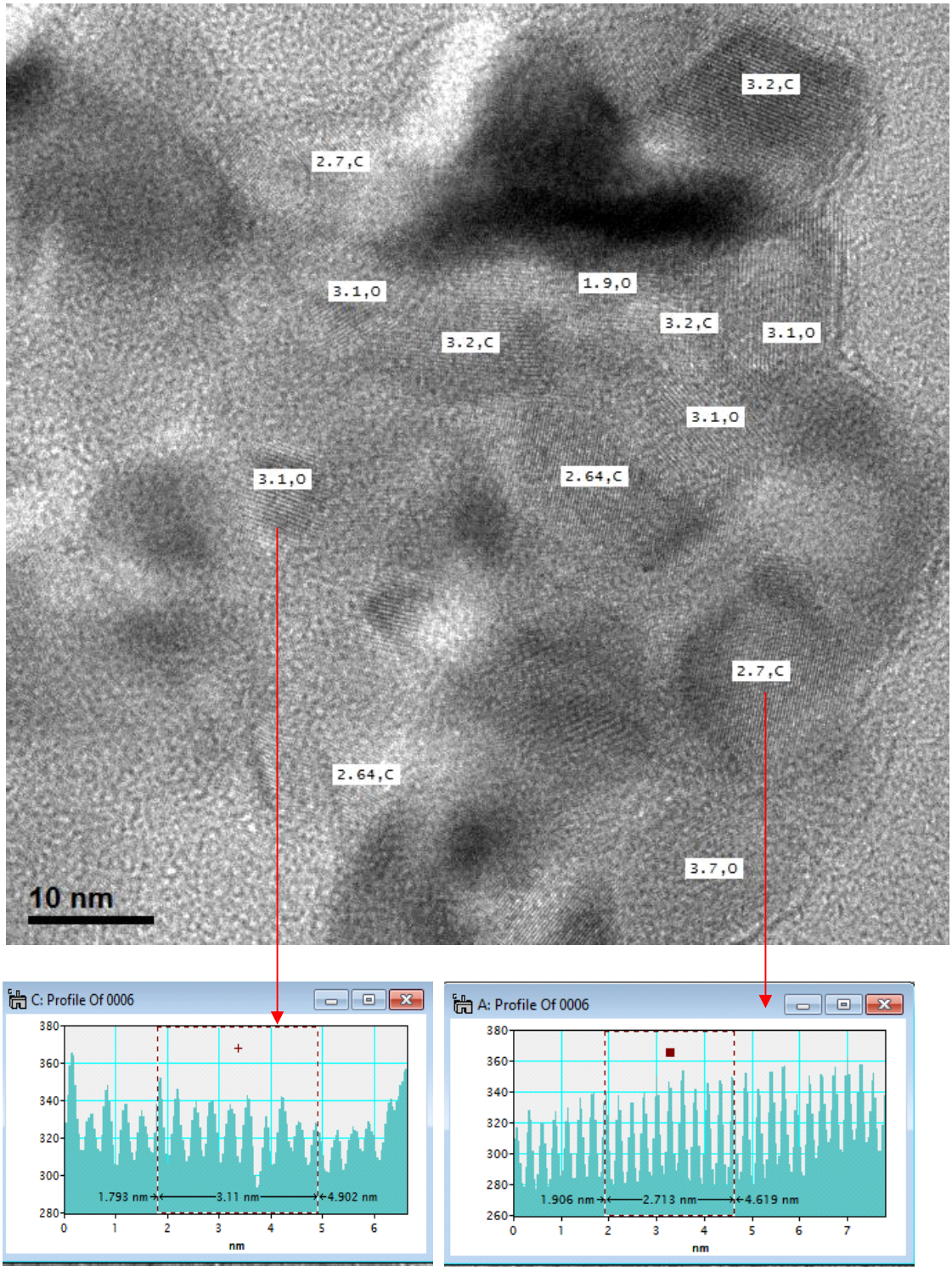


Figure ESI-I: (a) Cyclic Voltammetry of cubic and orthorhombic Cd_2SnO_4 electrodes. From the onset of the reduction reaction, conduction band positions are determined using ferrocene as the standard (b) Corresponding relative band alignment diagram

ESI-II-A

HRTEM Images and Nano-grain Lattice parameter evaluation

"C" stands for Cubic phase and "O" for Orthorhombic Phase

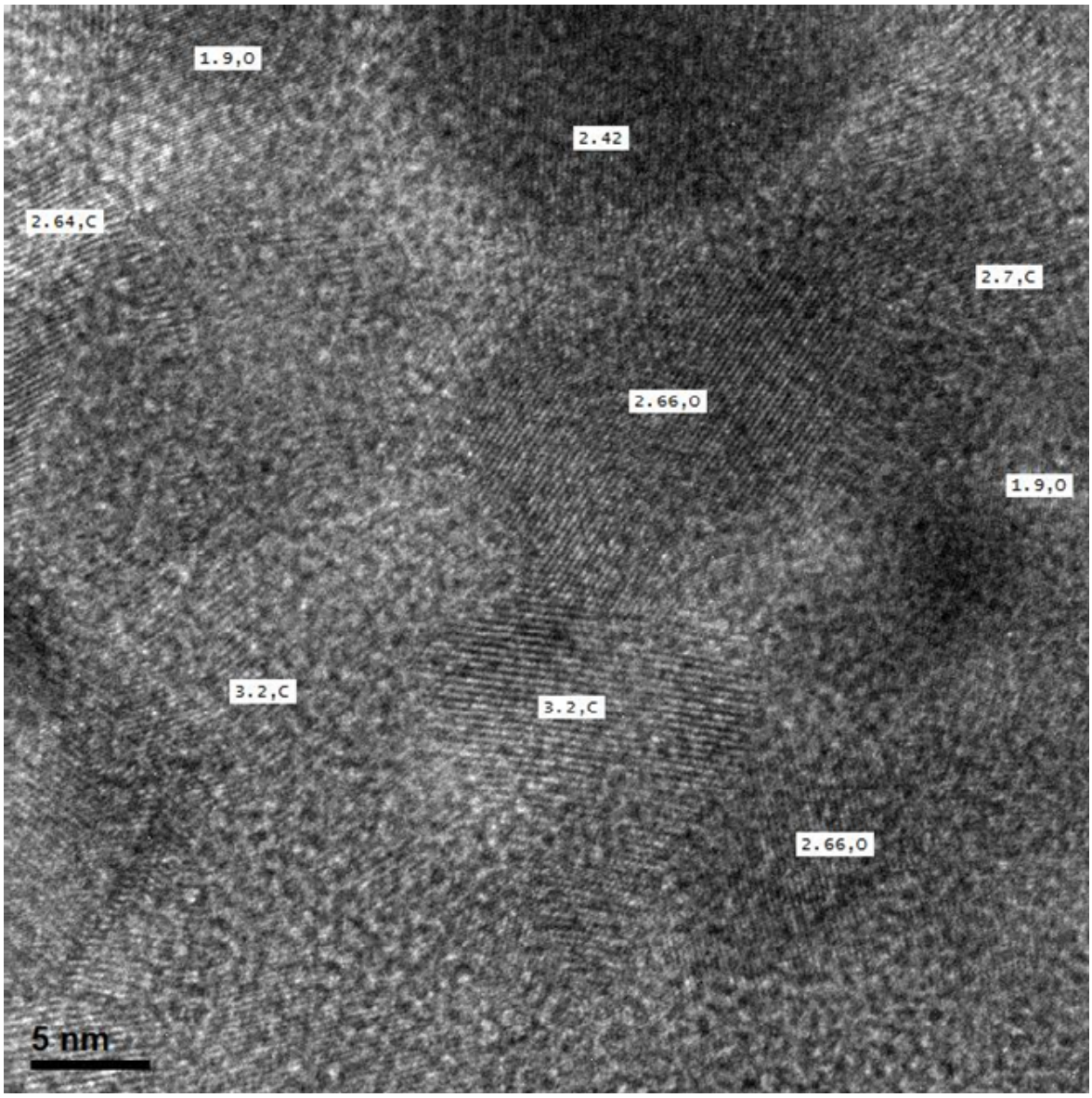


Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

ESI-II-B

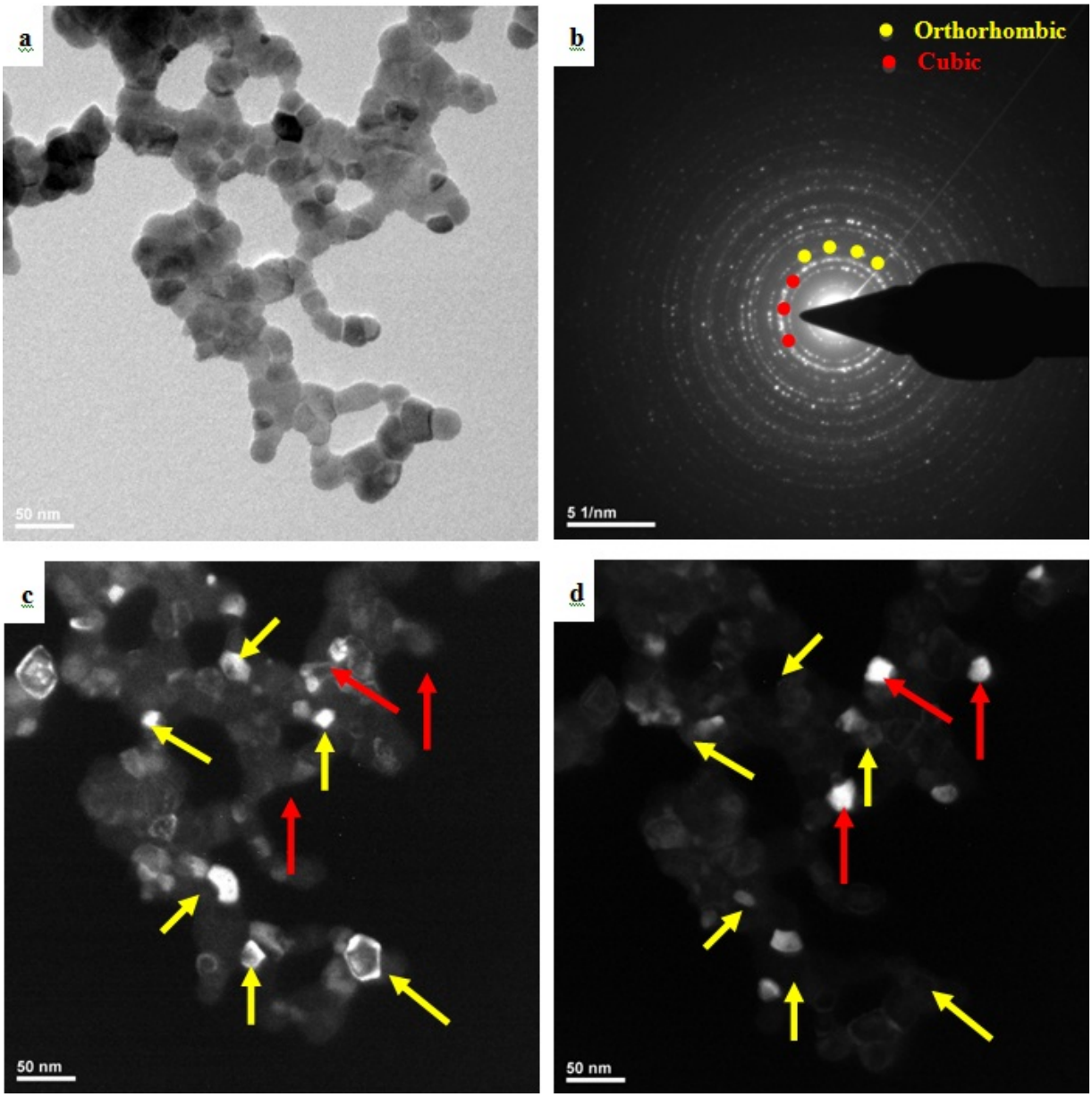
HRTEM Image and Nano-grain Lattice parameters

"C" stands for Cubic phase and "O" for Orthorhombic Phase



ESI-III

Figure ESI-III (a) (please see next page) shows a typical image of the interconnected grain structure of the Cd_2SnO_4 nanoparticles in our urea-based combustion synthesized biphasic sample. In order to identify the locations of orthorhombic and cubic grains therein we performed dark field imaging using the diffraction spots corresponding to the two phases as shown below. The diffraction pattern shown in Figure (b) was used and a few spots on the rings representing lattice parameters of 0.26 nm (orthorhombic (0 2 1)) and 0.27 nm (cubic (3 1 1)) were selected for acquiring the dark field images. The dark field image taken with diffraction of a few spots representative of orthorhombic phase is presented in Figure (c) and that taken with a few spots representative of cubic phase is presented in Figure (d). The complementary nature of grain structure is apparent from these images. It should be noted that only a few grains of each type appear bright because only a few spots from the ring were used. Had it been possible to use a full ring representing a specific set of planes for each type, all grains corresponding to each phase would have been visible in each image. Importantly, the orthorhombic and cubic grains are seen to be well distributed and electronically well connected supporting the charge separation argument.



a) HRTEM of Biphasic Cd_2SnO_4 prepared by urea based-combustion synthesis having interconnected orthorhombic and cubic nanoparticles, b) SEAD pattern showing diffraction rings associated to orthorhombic and cubic phases of Cd_2SnO_4, c) dark field image regenerated from the selected points of the diffraction pattern representing the orthorhombic phase, d) dark field image regenerated from the selected points of the diffraction pattern representing the cubic phase.

ESI-IV

Figure ESI-IV shows the plot of photocurrent enhancement obtained with the biphasic Cd_2SnO_4 prepared with urea over the pure orthorhombic and pure cubic Cd_2SnO_4 cases. It can be seen that the enhancement ensues at much lower voltage value (Vs Ag/AgCl) but increases rapidly until it saturates, and finally tapers off as the electrochemical water splitting voltage (about 0.7V with reference to Ag/AgCl) is approached. The photocurrent enhancement factor for biphasic case over the pure orthorhombic case is **23**, while that *vis-a-vis* the pure cubic case Cd_2SnO_4 is nearly **8.5**.

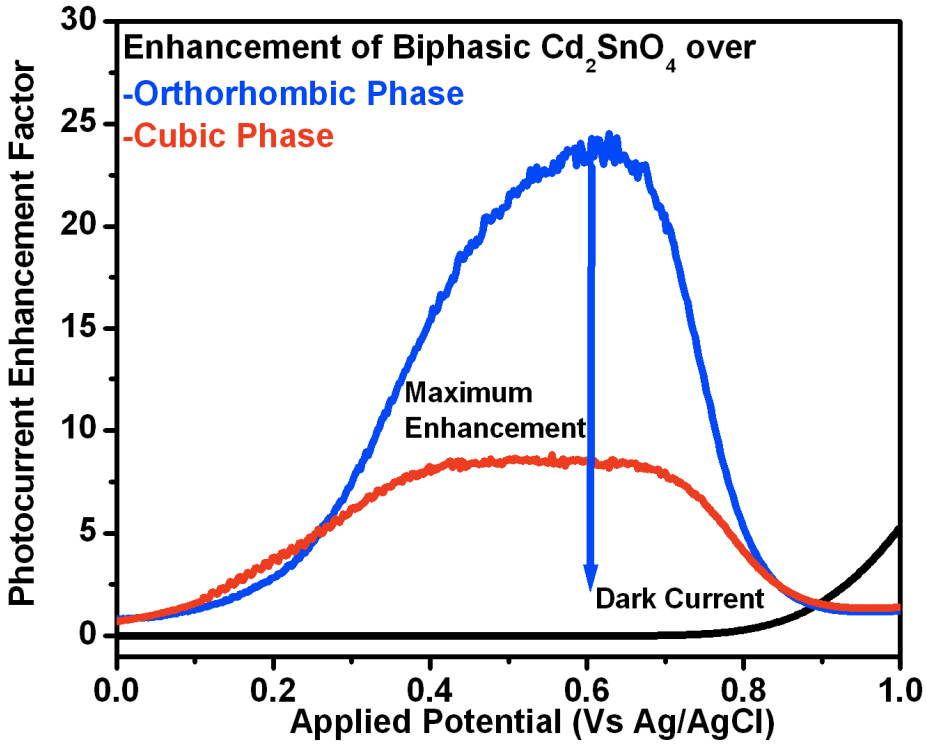


Figure ESI-IV: Plot of photocurrent enhancement factor in biphasic Cd_2SnO_4 over pure orthorhombic and cubic Cd_2SnO_4 cases against applied potential Vs Ag/AgCl.