Electronic Supplementary Material (ESI) for Dalton Transactions.

Enhanced photo-voltaic performance and time varied controllable growth of CuS nanoplatelets structured thin film and its application as an efficient counter electrode for Quantum dot-sensitized solar cells via cost-effective chemical bath deposition

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Digital images of precursor preparation of CuS using with HCl and without HCl (hydrochloric acid) along with corresponding thin films.

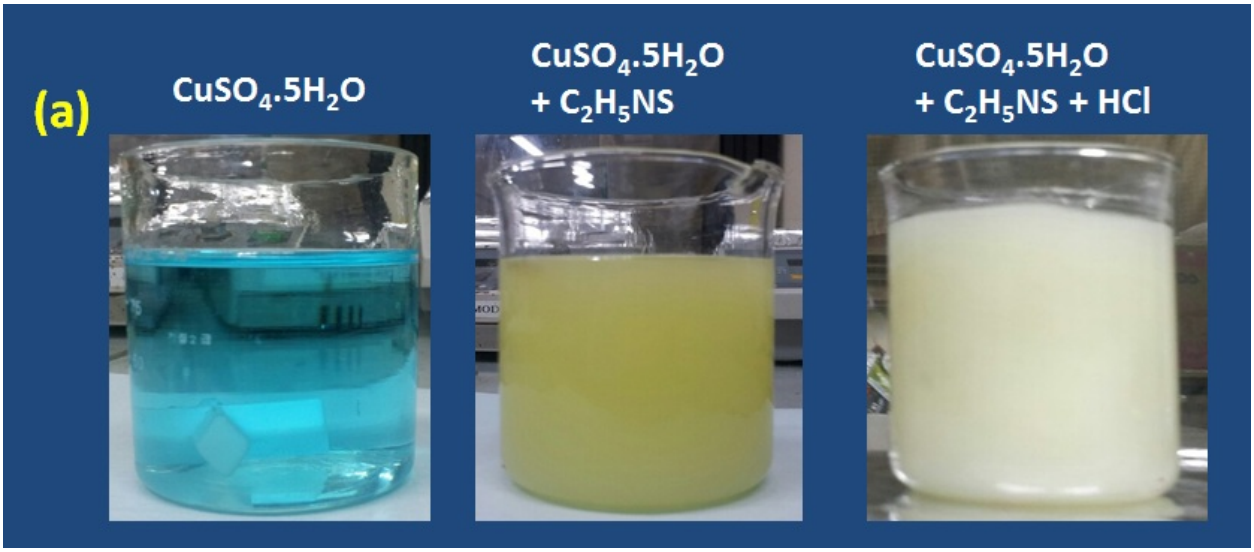

Fig. S1 Degital images of copper sulfide precusor solution with HCl and without HCl.

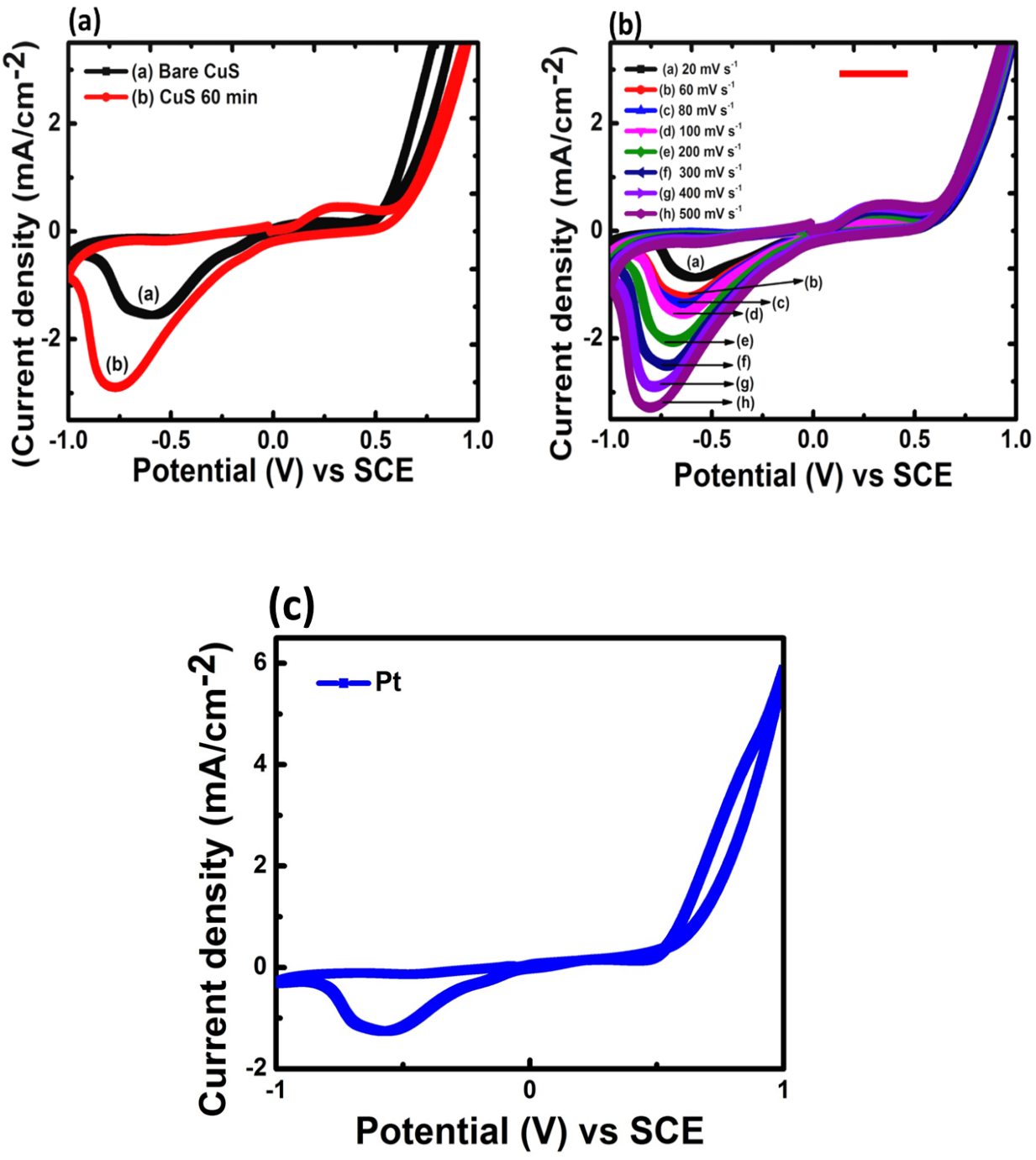

Fig S2. (a) shows the Cylic voltammetry of bare CuS and CuS 60 min CEs, (b) shows the CV performance of CuS 60 min at different scan rates, (c) Pt CE, respectively.

To better understanding the J-V performance of CuS CEs, we have conducted cyclic voltammetry (CV) analysis with fresh electrolyte using 0.1 M KCl, 0.1 M Na_2S, and 0.1 M S, in the presence of with HCl and with-out HCl, respectively. The peaks in the CV curve significantly explain the catalytic reaction at the interface of the CE/electrolyte interface as follows.[1]

$$S_X^{2-} + e^- \rightarrow xS^{2-} \quad (1)$$

Generally, from the CV curve the positive currents are related to the oxidation of S^{2-} ions in the polysulfide electrolyte, while their negative currents represent the reduction of S_x^{2-} ions to S^{2-} ions respectively. The role of CE materials in the QDSSCs, the reduction peak currents of CV curve of the electrodes directly reflect the electro catalytic ability of the CEs for S_x^{2-} reduction.[1] The current density of Pt CE shows lower than that of CuS CEs. Therefore Pt exhibits the lowest electro catalytic activity for the reduction of polysulfide electrolyte due to irreversibility and physisorption of sulfur compounds presents on the Pt surface.[1] The HCl CuS 60 min shows highest current density and good reversibility with superior electro catalytic activity, while with-out HCl CuS shows considerable current density and moderate reversibility with the shift of redox peaks and reduced current density, as shown in figure (CV). This results accordance with best energy conversion efficiency in QDSSC and as well as surface morphology, surface roughness,[2] increased surface to volume ratio from surface uniformity[3] and improved carrier concentration enhanced by the both copper and sulfur ions presence as well. Finally from this results we conclude that the CuS CEs effectively acts as a catalyst in the reaction of the S^{2-} / S_x^{2-} redox couple and Pt does not because of physisorption of sulfur compounds presents on the Pt surface.

Fig. S2(b) shows the CV curves of with HCl CuS 60 min deposition time at different scan rates: 20, 40, 60, 80, 100, 200, 300, and 400 mVs^{-1}, respectively. When we increasing the scan rates from 20 to 400, the current density of CuS 60 min CE gradually increasing, which means the J_{sc} value strongly depends upon the electrocatalytic ability of the CEs, resulting CuS 60 min deposition time shows best photo-voltaic performance in comparison with CuS 50 min, CuS 70 min, and with-out HCL. Based on the CV results we conclude that, the CBD of CuS 60 min CE is consistent with the highest J_{sc} , fill factor (FF), and outstanding PCE of QDSSCs.

References:

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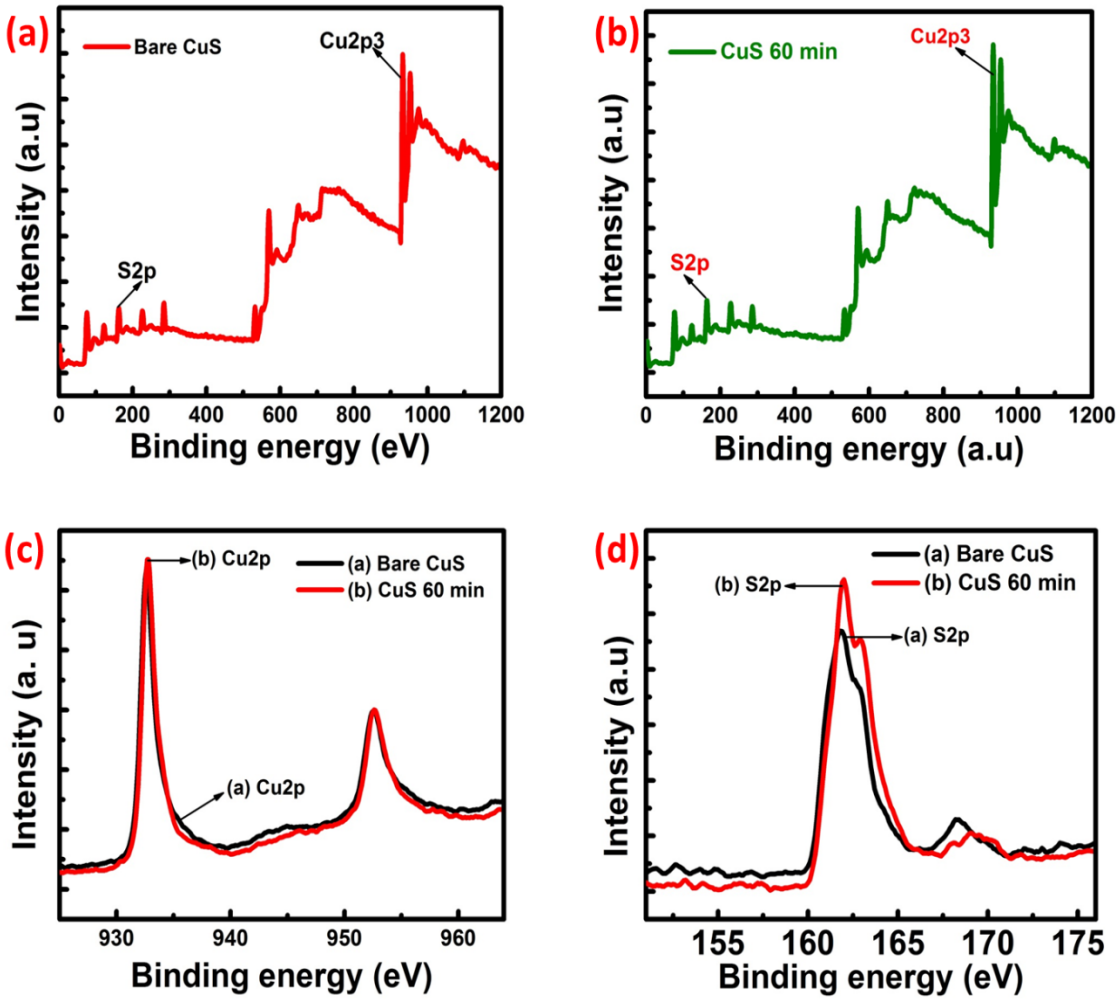

Fig S3. XPS spectra of bare CuS and CuS 60 min CEs using chemical bath deposition.

--- We introduced X-ray photoelectron microscopy (XPS) to better understand the chemical bonding state of the as-prepared CuS nameplates. The XPS spectra indicated the presence of Cu and S from the CuS nanoplatelets in the range of 925 965 eV for bare CuS and CuS 60 min CEs, respectively. No obvious impurities were found on the surface of both samples, indicating that the as-prepared CuS CEs is relatively pure. The peaks for the Cu located 932.74and 952.6 eV were assigned to $Cu2p_{3/2}$ and $2p_{1/2}$ while the binding energies of the S $2p_{3/2}$ for bare CuS and CuS 60min CEs are 61.81, and 162.12 eV respectively. The most important

future in the S 2p spectra is the enhanced intensity of the CuS 60 min in comparison with bare CuS CE. These values are in good agreement with the literature reported results.[1-3] From the XRD and XPS analysis confirmed the presence of Cu vacancy in the as synthesized copper sulfide nanoplates predominantly.

References:

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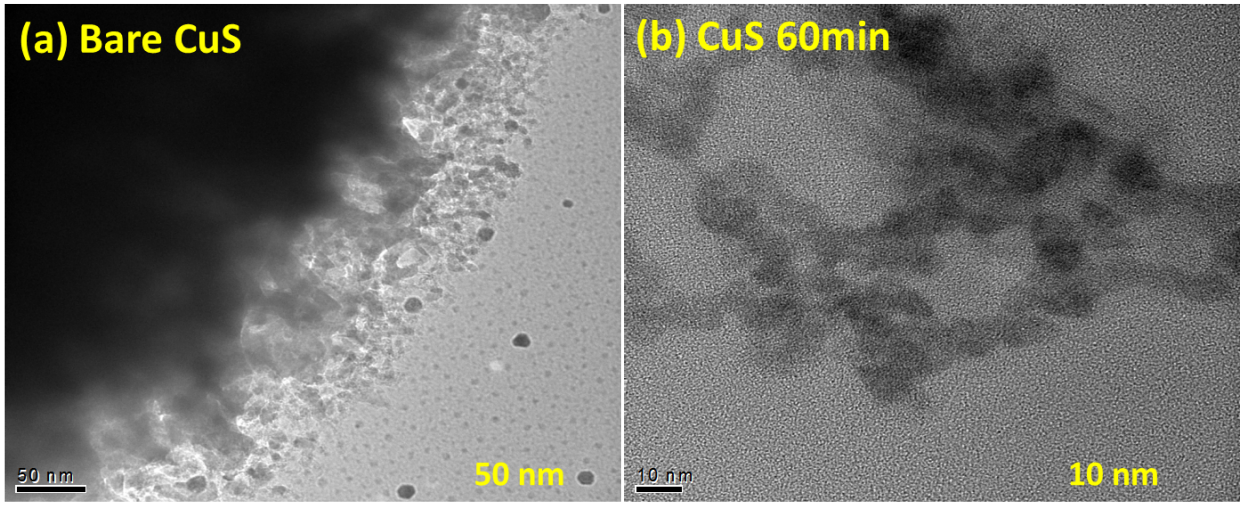

Fig S4.Tem images of bare CuS and CuS 60 min CEs using chemical bath deposition.