Cation exchange is the process by which the cation in a compound is replaced by another cation from a suitable precursor. It is very difficult to replace any cation by Au, since the high electron affinity of Au leads to reduction of the precursor to form metallic Au rather than undergoing cation exchange. The competition between cation-exchange and reduction is not well understood. For the case of Au or other elements, one of the processes may be dominant over the other depending on the choice of system and the experimental conditions. Knowing the criterion and having a rational understanding of the process is essential for rational synthesis of heterostructures. In our study, we show that cation exchange is unexpectedly dominant over reduction for the case of CdS-Au.

Bright-field TEM imaging (Figure 1) reveals the presence of small, faceted particles of Au on the CdS nanorods. However, on careful observation it shows the formation of more particles under the electron beam. When the concentration of the Au precursor is low, most of the Au$_2$S$_x$ (x=1 & 3) formed as a result of cation-exchange is on the surface, which on exposure to the electron beam leads to the formation of faceted Au particles. In the case of a higher precursor concentration, the beam effects are highly accentuated as the Au$_2$S is present across the depths of the sample which results in shortening of the nanorods; in some cases along with the formation of Au nanoparticles. Energy dispersive X-Ray mapping in STEM mode (Figure 2) clearly depicts the change taking place due to beam irradiation. The HAADF-STEM image in Figure 3a further shows three different regions of contrast. Careful investigation of the high magnification STEM images (Figure 3b) reveals the presence of the cubic Au$_2$S phase which confirms that cation-exchange indeed takes place under the reaction conditions. Thermodynamic calculations have been carried out to understand the experimental observation that paves the way for better predictability of the viable product for various systems under different reaction conditions.

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Fig. 1: Bright field TEM image showing Au attached to CdS nanorods.

Fig. 2: More of such Au nanoparticles form under the electron beam as is evident from the HAADF-STEM image and the corresponding EDS map.

Fig. 3: (a) At high magnification we observe three different regions of contrast as marked by the blue dotted line. (b) Atomic resolution imaging clearly shows the Au$_2$S and CdS domains.