

## Electron Microscopy Investigation of Cation Exchange Reaction to Synthesize Lateral Hybrid Nanostructures

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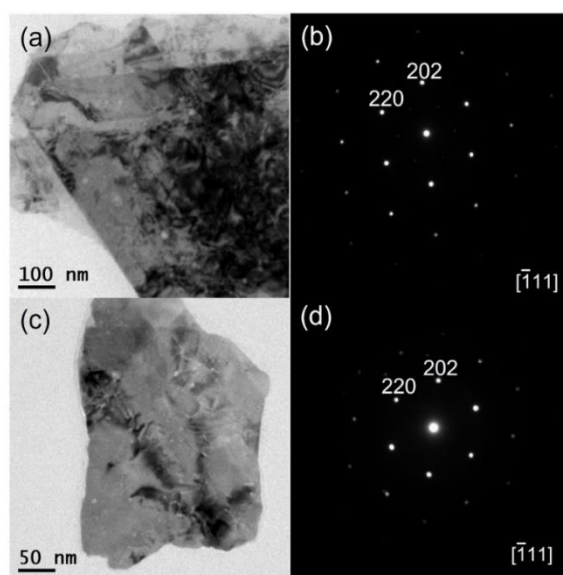
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Along with size, intriguing shape and composition-dependent properties of nanostructures have formed the core of growing nanotechnology [1]. Various approaches have been employed for the synthesis of the morphology-controlled nanostructure [2]. However, in recent years, ion exchange strategy (both cation and anion) has gained enormous attention in synthesizing nanocrystals with controlled morphology, composition, and high quality. The post-synthetic ion-exchange reaction provides an opportunity to synthesize complex nanostructures, including core-shell, metastable phase, lateral hybrids, or symmetry-broken nanostructures, which are challenging to synthesize via direct solution methods [3]. In cation exchange reaction, cation of the pre-synthesized nanocrystal is being replaced by guest cation. Generally, these ion exchange reactions are controlled by both thermodynamic and kinetic factors. The feasibility of these reactions is highly dependent on the crystal structure, lattice volumes and bond energy of reactants and products [4].

Due to the large number of Cu vacancies in  $\text{Cu}_{2-x}\text{Se}$ ,  $\text{Cu}_{2-x}\text{Se}$  nanocrystals have been explored for cation exchange reaction to synthesize various nanostructures of Zn and Cd [5]. However, cation-exchange reactions in symmetry broken 2D nanosheets has not been explored much. Herein, we have demonstrated the cation-exchange method to synthesize phase pure HgSe nanosheets from 2D  $\text{Cu}_{2-x}\text{Se}$  nanosheets. Crystallographically,  $\text{Cu}_{2-x}\text{Se}$  and HgSe have cubic crystal structures and has lattice parameter mismatch of ~6%. Electronically,  $\text{Cu}_{2-x}\text{Se}$  has been reported as p-type and HgSe as n-type materials [6]. A lateral hybrid nanostructure has been synthesized by controlled partial exchange reaction, leading to the generation of a p-n junction.

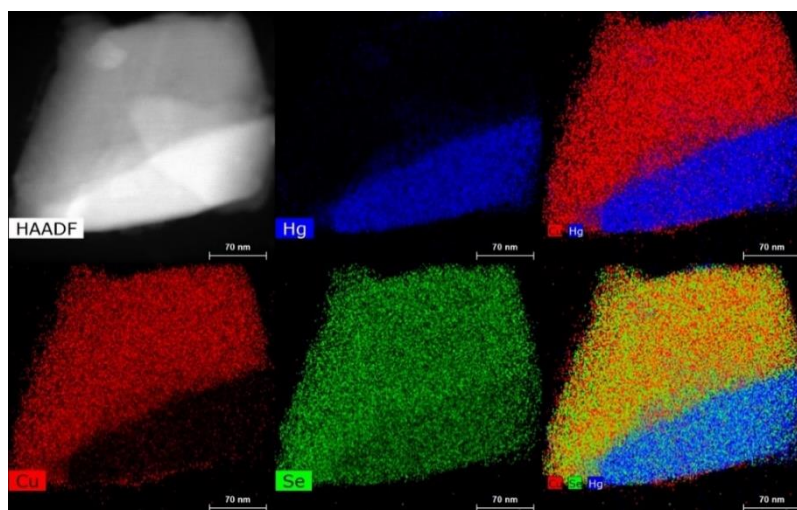
Template  $\text{Cu}_{2-x}\text{Se}$  has been synthesized via the solvothermal method. For typical complete conversion of  $\text{Cu}_{2-x}\text{Se}$  to HgSe, the exchange reaction was carried out at moderate temperature for 24 hr. To drive the cation exchange reaction faster, Tri n-octyl phosphine (TOP) has been used as it helps in breaking Cu-Se bond in  $\text{Cu}_{2-x}\text{Se}$ . Figure 1 shows the microstructure of the template  $\text{Cu}_{2-x}\text{Se}$  and HgSe nanosheet synthesized through the cation exchange strategy. Figure 1(a) shows the low magnification bright-field TEM micrograph of  $\text{Cu}_{2-x}\text{Se}$  nanosheet. The corresponding diffraction pattern taken from  $\text{Cu}_{2-x}\text{Se}$  nanosheet is shown in Figure 1(b). The hexagonal symmetric diffraction spots indicate the single-crystalline nature of the nanosheet and are indexed along  $\bar{1}11$  axis. Figure 1(c) shows the TEM micrograph of HgSe nanosheet obtained after cation exchange, and the corresponding diffraction pattern is shown in Figure 1(d). The sharp, bright spots with hexagonal symmetry reveal the single-crystalline nature of the as-obtained HgSe nanosheet.

The mechanistic study of the cation-exchange reaction was performed and observed that the exchange reaction initiates from one of the edges and move inwards. By adjusting the temperature of the exchange reaction to room temperature, partial exchange was performed. The microscopic investigation reveals a Janus-type structure of the partially exchanged product. HAADF-STEM micrograph of the partially



**Figure 1.** (a) Low-magnification TEM micrograph of Cu<sub>2-x</sub>Se nanosheet, (b) corresponding diffraction pattern; (c) Low magnification TEM micrograph of HgSe nanosheet and (d) corresponding diffraction pattern taken from HgSe nanosheet.

exchanged product is shown in Figure 2. Brighter contrast in low-magnification HAADF-STEM is due to the presence of heavier atom Hg, which can be further observed in EDS maps showing the elemental distribution of Cu, Hg, and Se in the sheet [7].



**Figure 2.** HAADF-STEM micrograph of partial exchange product and corresponding EDS map to show elemental distribution of Cu, Hg and Se respectively.

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