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Observing the Chemical Transformation of $MnBr_2$ Catalyzed by Cu under Electron Beam Irradiation

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Manganese bromide ($MnBr_2$) is a promising candidate in the syntheses of organic-inorganic hybrid compounds, especially the methyl lead bromide perovskites, with applications in the luminescence, lasing and solarcell [1]. Irradiation resistance of $MnBr_2$ is a critical material property utilized in its industrial applications. Materials under the irradiation of high-energy particles, including electrons, ions and neutrons, will lead to bond instability, forming defects and changing structures. Consequently materials' properties tend to deteriorate. On the other hand, particle irradiation sometimes results in certain *in situ* chemical transformations caused by the damage process [2]. Here we report a series of chemical evolutions of $MnBr_2$ with Cu grid under the electron beam irradiation by *in situ* TEM [3].

The structure of $MnBr_2$ powder was first examined by SAED and HRTEM. Then the sample was kept at room temperature in air for several days, XRD analysis was performed to confirm its structure and purity. XRD results demonstrate that $MnBr_2$ powder adsorbs the vapor from the air and some of them turn into $MnBr_2$ hydrate ($MnBr_2{\cdot}nH_2O$).

When the electron beam with a dose rate about 0.61A/cm^2 was focused on the sample ($MnBr_2{\cdot}nH_2O$) suspended on the copper grid for a few minutes, crystal whiskers were observed to grow from the edge of the matrix. The size of grown whisker is very sensitive to the electron dose. According to the exposure time, the accumulated total dose is about 2.29×10^6 e/nm^2. The EELS analysis reveals that one composition of the whiskers is Cu and no oxygen is detected. HRTEM images and the corresponding simulated images from different regions of the grown crystal indicate the crystal structures match the structure of β-CuBr along the [210] zone axis and γ-CuBr along the [110] zone axis, respectively (see Figure 1(a) and (b)). The formation of CuBr is likely to be caused by the chemical reaction between hydrous $MnBr_2$ and Cu grid under electron beam irradiation, and is induced by the following chemical equations: $MnBr_2{\cdot}nH_2O \rightarrow Mn^{2+}$(in solution)$+{\cdot}Br+HBr+{\cdot}OH$, $4{\cdot}OH \rightarrow 2H_2O\uparrow + O_2\uparrow$, $Cu+{\cdot}Br \rightarrow CuBr(s)$.

As the electron beam continued illuminating the sample, the lattice distances measured from the electron pattern in Figure 1(c) changed from CuBr to metal Cu. The chemical distribution of the grown whiskers was confirmed by the STEM-EDX measurement in Figure 2, which demonstrated that the region adjacent to the sample contains Cu and Br elements, and the region far from the sample contained only the Cu element.

In this report, we captured the *in situ* evolutions of the following sequence under electron beam irradiation: $MnBr_2 + nH_2O + Cu \rightarrow Mn^{2+} + HBr + {\bullet}OH + CuBr \rightarrow Cu + Br_2$. This helps us to understand the mechanism of the complex chemical transformations in sensitive halide materials under the electron

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beam irradiation at atomic scale in real time. In addition, the generation of Cu whisker at room temperature during the TEM experiment reminds us about the chemical instability of Cu grid and the influence of electron beam irradiation, which could produce some side effects in our TEM experiments.

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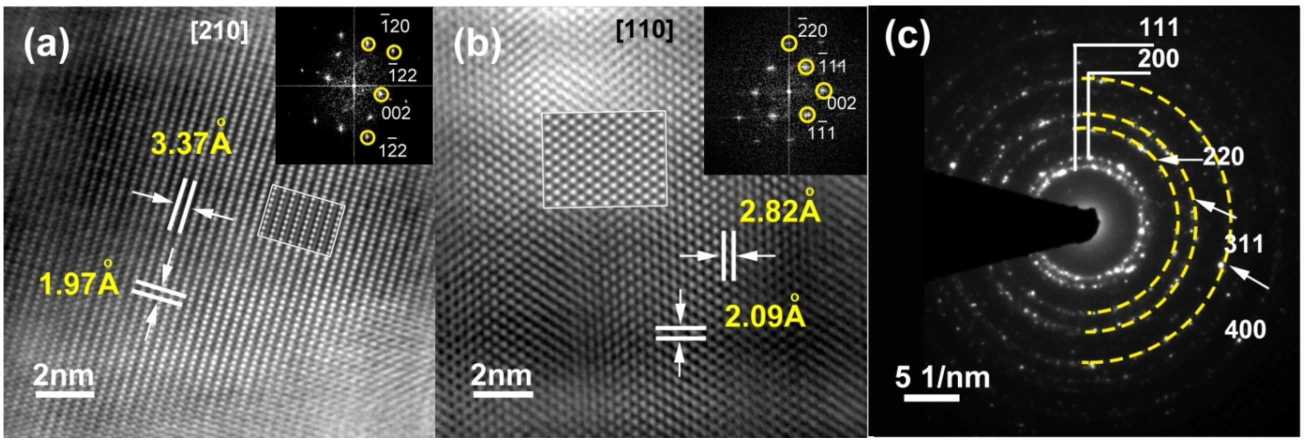

Figure 1. (a) and (b) HRTEM images of β-CuBr along the [210] zone axis and γ-CuBr along the [110] zone axis obtained from different regions; (c) SAED pattern taken after further beam irradiation, showing the structure of pure Cu.

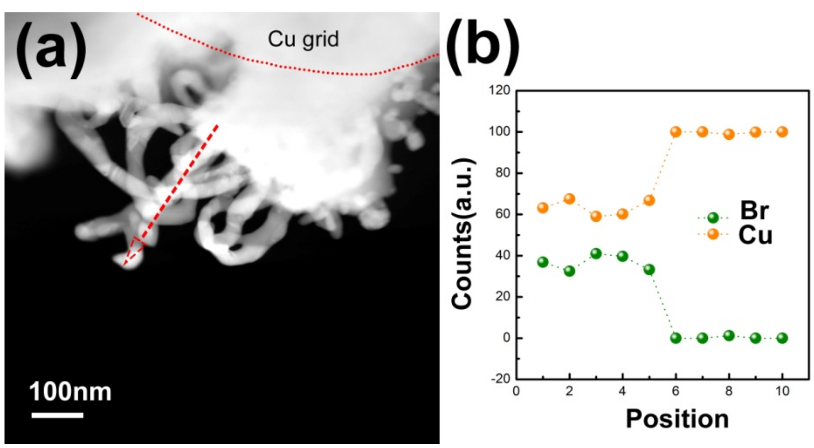

Figure 2. (a) STEM image of crystal whiskers. (b) EDX-linescan result in (a) along the dash arrow.

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