

Electron Beam-Induced Effects on Bi₆S₂O₁₅ Nanowires: An Insight into Stability and Applications

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Bismuth oxyhalides (BiOX, X: Cl, I, Br), a new promising photocatalyst for energy harvesting and environmental remediation, have attracted growing interest due to their unique layered structure and tunable bandgap [1]. While designing and tailoring the BiOX-based nanostructure for higher photocatalytic performance, its stability in practical application environments needs to be evaluated.

Bi₆S₂O₁₅ nanowires, hydrothermally synthesized, have a similar layered structure to other BiOX and an orthogonal crystal structure, with measured direct bandgap of $E_g = 3.34$ eV. We observed that at room temperature, amorphous nanoparticles (NPs) appeared on the surface of Bi₆S₂O₁₅ nanowires under beam irradiation within 5s, as shown in Figure 1. New NPs grew to 4-5 nm under continuous irradiation, then the amorphous NPs became crystalline and coalesced with neighboring NPs, while the main structure of nanowires themselves underwent no change. Upon further irradiation, nanowires were decomposed eventually into larger crystalline NPs. Cooling a specimen often mitigates the radiation damage of semiconductor materials [2]. However, we observed that new NPs on the nanowire surface appeared faster at liquid nitrogen temperature than at RT, and no NPs appeared when the specimen was at 300°C.

When beam irradiated nanowires embedded in thin vitreous ice, the surface changes was rapid, as shown in Figure 2. The new phase on the surface of the NPs did not change significantly after the surrounding ice was depleted, so cooling the specimen prevents further coalescence of NPs when water molecules are absent. When a large amount of liquid water surrounds the nanowires, the surface change occurs too fast to capture the dynamic evolution. Therefore a small amount of water was placed on carbon grid containing nanowires and sandwiched with another carbon film grid on top. In Figure 3, a water flow channel is formed between nanowires (exposed to the beam) and neighboring nanowires, where more water may be trapped. NPs appeared and grew on nanowire surfaces within seconds but then dissolved faster than they could coalesce. Upon further irradiation, the nanowires eventually decomposed.

Water radiolysis may contribute to all of the phenomena observed and is created by ionizing irradiation within the first picosecond [3]. Ionized radical species are then in contact with nanowire surfaces, where hydroxyl groups act as active sites, promoting stronger reaction at the oxide/water interface. Water depletion may imply that water splitting occurs under ionizing radiation, although surface modification may be needed to enhance the stability of nanowires in water-splitting applications. The nanowires may also be good candidates for organic pollutant removal or decay, their surfaces becoming trapping sites for pollutants under ionizing irradiation.

References:

- [1] J Di et al., *Nano Energy* **41** (2017), p. 172.
- [2] RF Egerton, *Ultramicroscopy* **127** (2013), p. 100.

[3] S Le Caë'r, *Water* 3 (2011), p. 235.

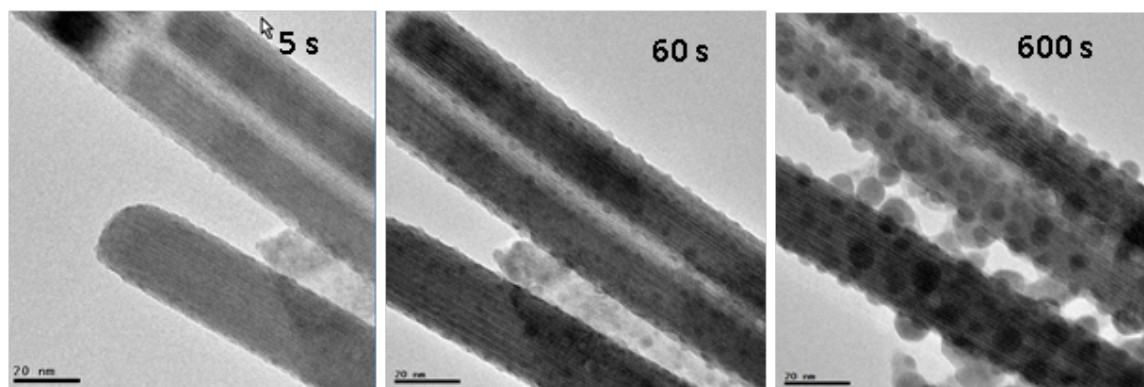


Figure 1. Evolution of a $\text{Bi}_6\text{S}_2\text{O}_{15}$ nanowire surface during electron-beam irradiation at room temperature (dose rate $J = 1.5 \text{ A/cm}^2$). Nanowires were placed on holey carbon and dried in vacuum before loading to the TEM.

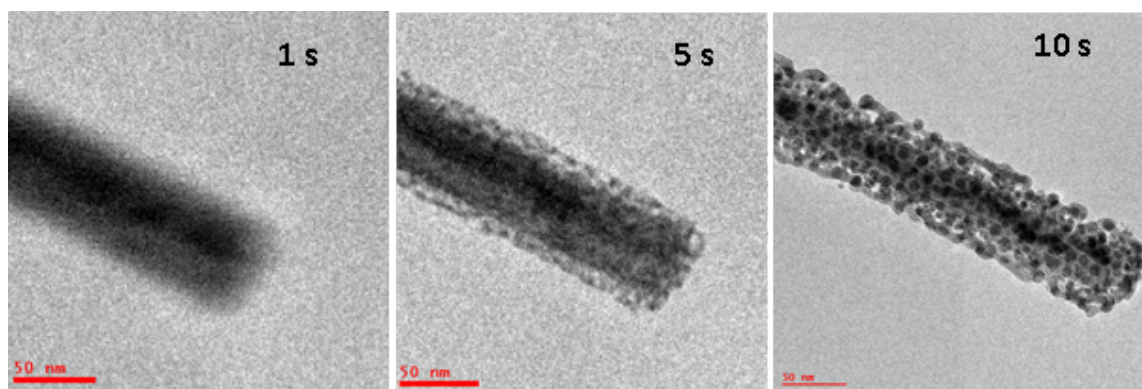


Figure 2. Evolution of $\text{Bi}_6\text{S}_2\text{O}_{15}$ nanowires embedded in vitreous ice during low-temperature electron-beam irradiation (dose rate $J = 0.1 \text{ A/cm}^2$). Nanowires in water were plunge frozen.

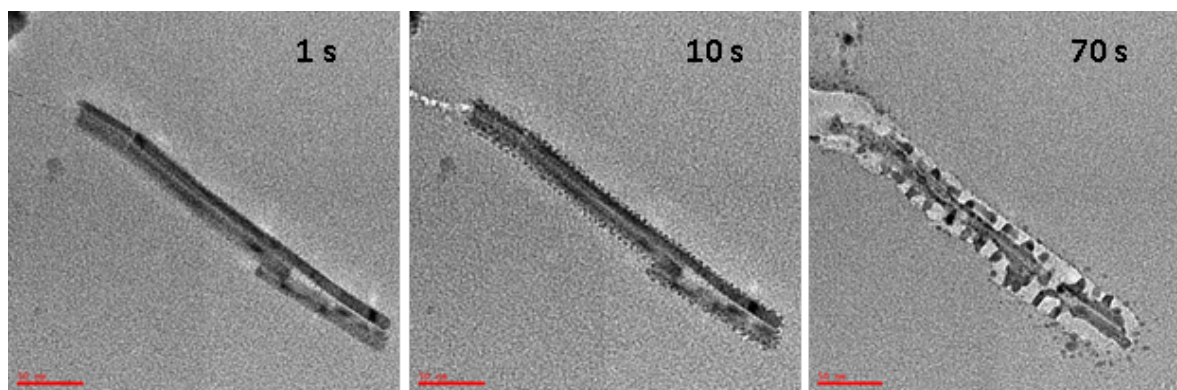


Figure 3. Evolution of $\text{Bi}_6\text{S}_2\text{O}_{15}$ nanowires in a liquid cell with beam irradiation (dose rate of $J = 0.1 \text{ A/cm}^2$). Nanowires with water were sandwiched between carbon films.