Supporting Information

Figure S1-S2, continuous observation of selected nanoparticles of different sizes, indicating the fluctuation states of nanoparticles.

Figure S3, statistics of the states of Bi nanoparticles.

Figure S4, irreversible transformation from crystalline to non-crystalline structure caused by long exposure time of electron beam irradiation.

Figure S1. HRTEM images of selected nanoparticles of different sizes at different moments. The diameters of the particles in (a–e) are about 2.6 nm, 3.2 nm, 3.8 nm, 4.3 nm and 5.2 nm, respectively. It is found the nanoparticles in (a–c) keep non-crystalline state while those in (d–e) fluctuate between non-crystalline and crystalline states under irradiation.
Figure S2. HRTEM images of selected nanoparticles of different sizes at different moments. The diameters of the particles in (a–e) are about 13.6 nm, 14.7 nm, 15.1 nm, 16.9 nm and 18.2 nm, respectively. The nanoparticles in (a–c) fluctuate between non-crystalline and crystalline structures while those in (d–e) keep crystalline state under irradiation.
Figure S3. Statistics of the non-crystalline and crystalline states based on 55 Bi nanoparticles, showing that the critical sizes of crystalline fluctuation are about 4 nm and 15 nm for lower and upper boundaries, respectively. The nanoparticles were exposed to electron beam in TEM facility for 24 min each.

Figure S4. Irreversible transformation from crystalline to non-crystalline structure caused by a long exposure time of electron beam irradiation.