Supporting Information

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging is performed to visualize the atomic structure of ZnO clusters with an average diameter of approximately 2 nm. An electron beam with a relatively low accelerating voltage of 120 kV is used to avoid beam damaging of the sample. The ZnO clusters are found to be rotating due to the electron beam irradiation. This is illustrated in the series of HAADF-STEM images (acquired with short acquisition times of 0.8 s) in Fig. SI 1. The cluster exhibits zinc blende structure and reveals a transformation from the [100] zone axis (upper left) to the [110] zone axis (lower right).

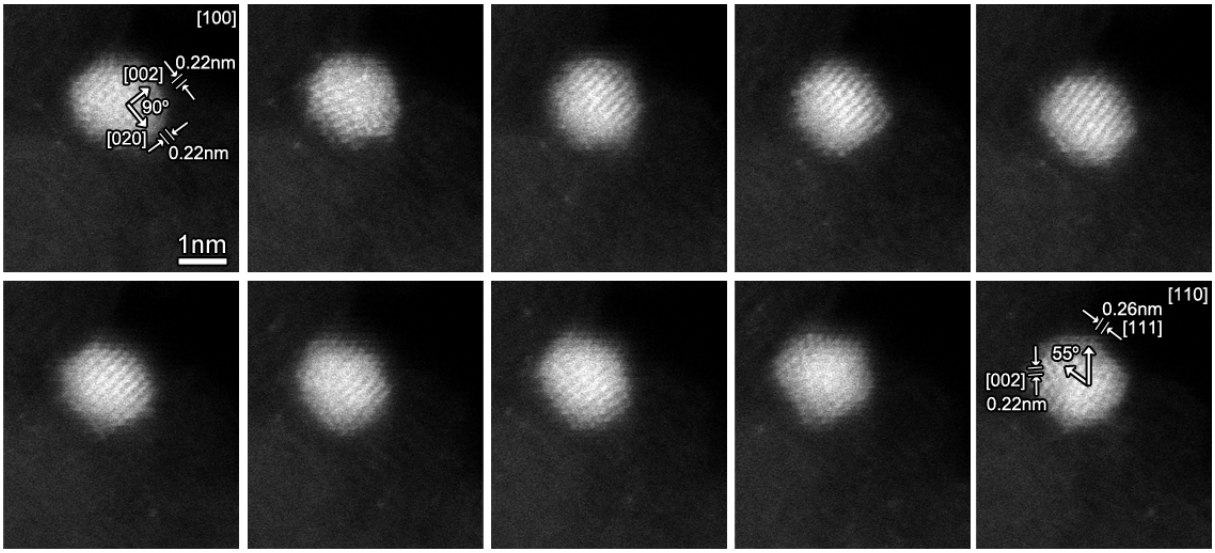

Fig. SI 1 Series of HAADF-STEM images of a ZnO nanoparticle with a diameter of 2 nm. A transition is observed from the [100] to the [110] zone axis in the zinc blende structure. The crystal facets, the lattice distance, and the angle between two crystal facets are indicated by labels for the two different cluster orientations in the upper left and lower right image.

In Fig. SI 2(b) we present a color visualization of (dI/dV)(V) spectra recorded along the white dotted arrow in the scanning tunneling microscopy (STM) topography image in Fig. SI 2(a)

(cluster height is about 2.0 nm). Bright (dark) colors correspond to a high (low) local density of states (LDOS). It is clear that the energies at which the maxima occur are constant (within the accuracy of the measurement) across the spherical cluster surface, i.e. the quantized energy levels of the cluster can be probed at all locations on the cluster surface. This is surprising since the wave functions and hence the LDOS of the quantized states are expected to exhibit atomic-like *s*, *p*, *d*, ... symmetries. This discrepancy may be attributed to the possible existence of multiple asperities at the tip apex, which implies that multiple locations of the ZnO clusters are involved in the tunneling process and that the atomic-like symmetries cannot be clearly resolved.

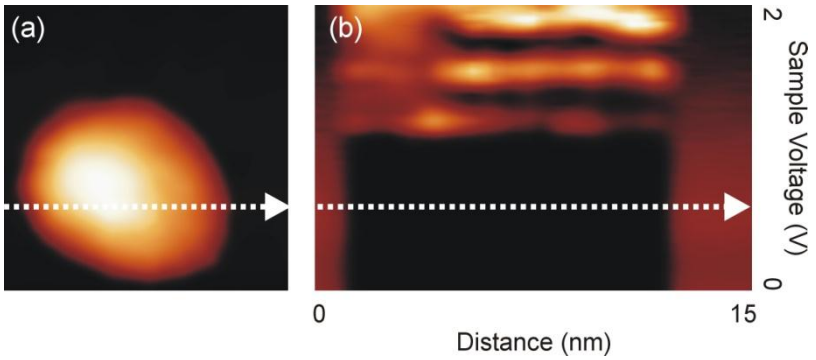

Fig. SI 2 (a) 15×15nm^2 STM topography image of a ZnO cluster (I = 2.0 nA, V = 2.0 V) and (b) corresponding 15 nm×2.0 V visualization of (dI/dV)(V) spectra recorded along the white dotted arrow in the topography image.