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Synthesis of Bimetallic Au-Au_3Cu Core-Shell Nanostructures Passivated with CuS_2 Surface and Atomic Resolution Images by Cs-Corrected STEM

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The synthesis of bimetallic (BM) nanoparticles such as core-shell, and alloyed structures has been established considerable efforts and attracted tremendous consideration from chemists and material scientists. Significant work has been done in recent years to control their morphology, as the physical and chemical properties can be tailored by controlling their chemical composition and structural shape.[1] Bimetallic nanoparticles have exhibited the ability to enhance their reactivity, selectivity and stability depending upon the variation of structure and composition.[2, 3] The modified polyol method is extensively used for the synthesis of Au core and Au_3Cu alloyed shell nanoparticles passivated with CuS_2 surface, which stabilized the final morphology of the nanostructure.

Transmission electron microscope (TEM) 1230 operated at 120 kV was employed to study the morphology of the sample. The STEM images were recorded in probe Cs-corrected JEOL JEM-ARM 200F operated at 200 kV. HAADF STEM images were obtained with a convergence angle of 26 mrad and the collection semi-angles from 50 to 180 mrad. These variations in semi-angles satisfy the conditions set forth for the detectors to eliminate contributions from unscattered and low-angle scattered electron beams. The probe size used was about 0.09 nm with the probe current of 22 pA. In addition, bright field (BF) STEM images were recorded by using a collection semi-angle of 11 mrad. Electron dispersive x-ray spectroscopy (EDS) spectra were obtained using a probe size of 0.13 nm with the probe current 86 pA. In X-ray diffraction (XRD) measurements, the crystal structure of the sample has been analyzed using XRD at 40 kV and 30 mA in the parallel beam configuration using RIGAKU Ultima IV X-ray diffractometer with Cu-Kα (λ = 1.54056 Å)

In this work, we present a comprehensive experimental investigation and atomic resolution images of Au-core, Au_3Cu-alloyed shell nanoparticles passivated with CuS_2 surface under 50 nm. Depending on the crystalline structure of Au seeds ($\sim$ 76% decahedral and others triangular, icosahedral and rod shaped) as seen by TEM observations, the final core-shell structure is mostly decahedral. The atomic resolution Cs-corrected STEM image allowed us to see the Au_3Cu type alloyed structure in the surface of Au seeds and passivated with CuS_2 surfaces, which is verified by XRD analysis. Atomistically, the diffusion of Cu atoms into the Au lattice site and the lattice mismatch between them leads to the formation of alloyed structure. The significant difference of the lattice parameter generates internal strain on the bimetallic.

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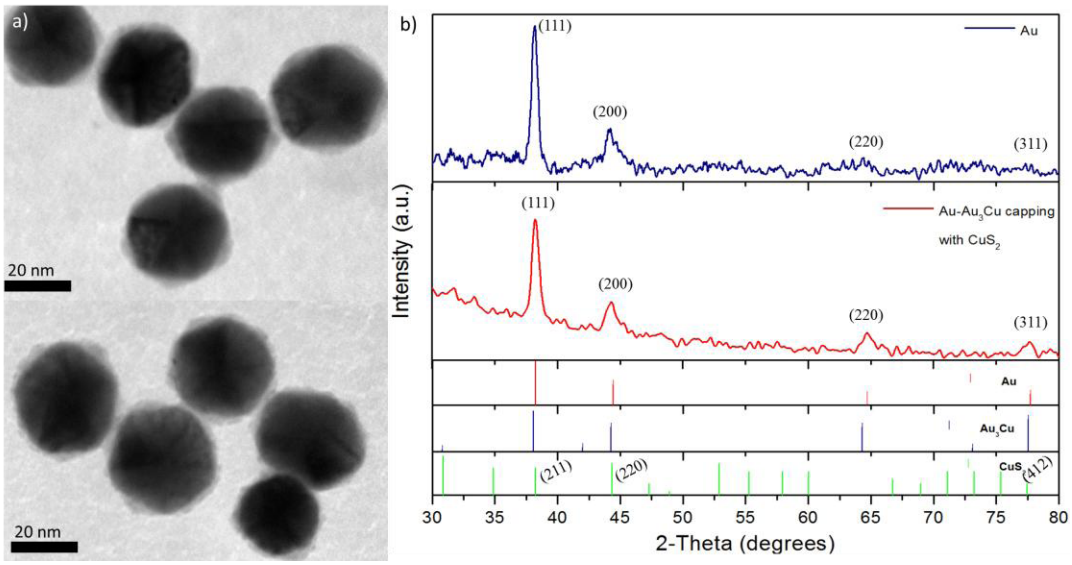

Figure 1. (a) TEM images of the Au core and Au_3Cu alloyed shell nanoparticles passivated with CuS_2 surfaces, (b) X-Ray diffraction patterns of Au and Au-CuS_2 nanoparticles studied to confirm the presence of Au_3Cu alloy and CuS_2 shell. Standard XRD patterns are also used for reference.

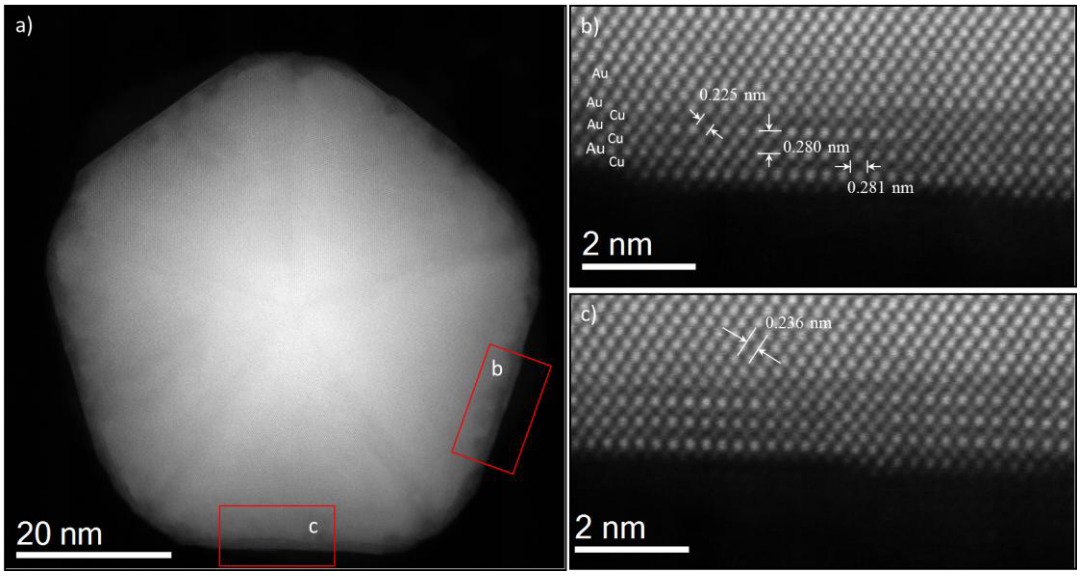

Figure 2. (a) HAADF image of decahedral core-shell nanoparticles in a [011] zone axis, (b) Amplified (b, c) Magnified shell region of the decahedral structure, where intensity of the atomic columns can be observed.

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