Supporting Information

Site-specific Growth of Au Particles on ZnO Nanopyramids under Ultraviolet Illumination

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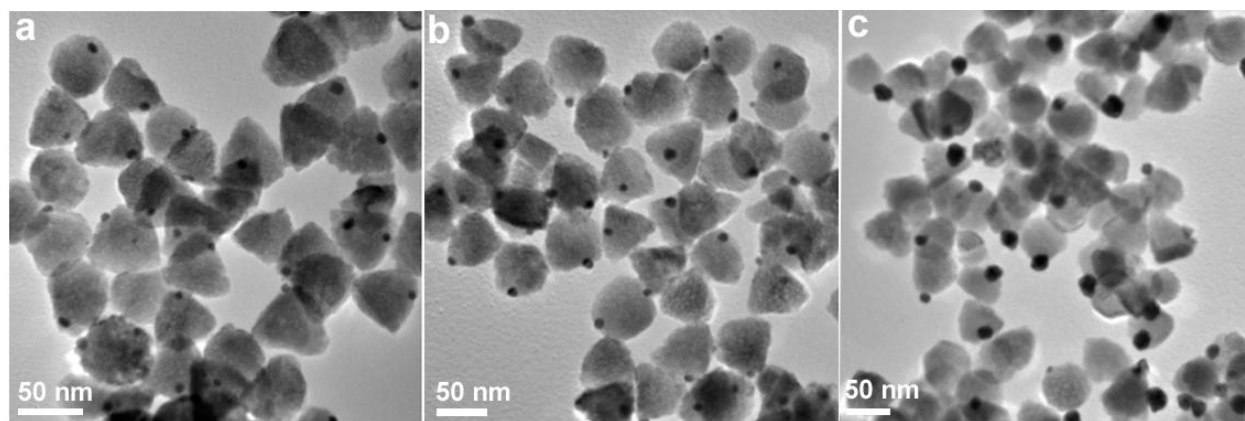[⊥] These authors contribute equally to this work.

Figure S1. TEM images of Au/ZnO nanocomposites with Au nanoparticles in different sizes: 8 nm (a), 10 nm (b) and 20 nm (c).
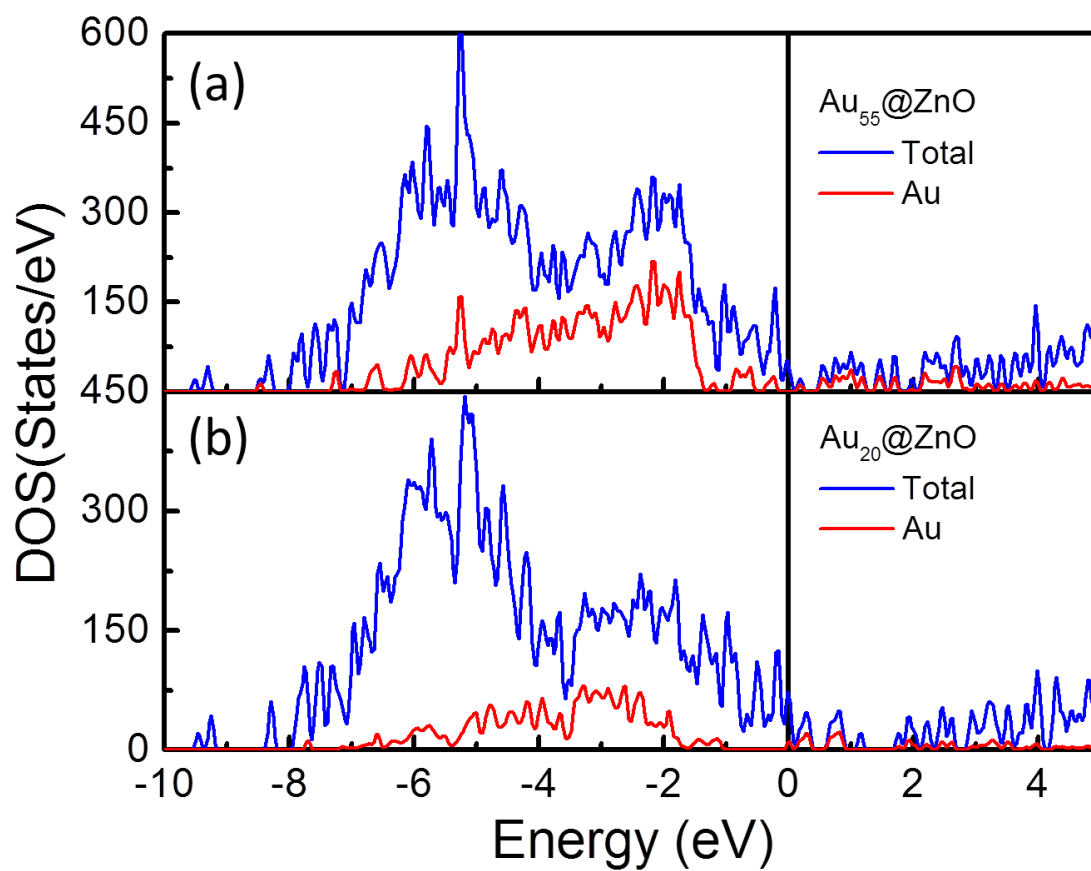
Figure S2. Projected density of states of Au_{55} (a) and Au_{20} (b) deposited on ZnO (001) surface.

First-principles Calculations Details

Extensive first-principles based calculations were performed with Vienna ab initio simulation package (VASP).[1-4] The wave functions are expressed by plane waves with a cutoff energy 400.0 eV. Ionic potentials are represented by PAW pseudopotential [5,6] with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) correction.[7] The Brillouin-zone integrations were performed using Monkhorst–Pack (MP) grids. K-point sampling convergence was achieved with ($7 \times 7 \times 4$) MP grid for the bulk, ($7 \times 7 \times 1$) MP grid for the surfaces, and only Γ point sampling for nanorods, nanopyramids and the nanocomposites. A denser ($11 \times 11 \times 7$) MP grid was also tested for bulk calculation, and confirmed the convergence. All the atomic geometries were fully relaxed until the forces on all the atoms were less than 0.02 eV/Å, except for the nanocomposites.

The calculated lattice and internal parameters ($a_0 = 3.256$ Å, $c_0 = 5.240$ Å) of ZnO are in good agreement with experimental results ($a_0 = 3.25$ Å, $c_0 = 5.21$ Å).[8-10] Thus, the Zn-O bond length is 2.00 Å. And, the DFT-PBE fundamental band gap at Γ point, E_g is 0.78 eV, though different from the experimental value of 3.37 eV which is due to the well-known problem of GGA functional, is still in line with the previous theoretical results.[11]

The w-ZnO nanorods grown along c-axis with finite length were truncated to have both (001)-Zn and (00-1)-O termination. To avoid the possible influence of size effect and the interaction between surface terminations on the electronic structure analysis, these nanorods were constructed to contain 4, 8, and 12 Zn-O double atomic layers (equivalent to rod dimension along c-axis of 0.9 nm, 1.9 nm and 2.9 nm), together with vacuum layers of at least 30 Å. The resulting rectangular cells for calculation are about 4 nm, 5 nm and 6 nm in dimensions.

The w-ZnO nanopyramide of 4 Zn-O double atomic layers thickness was optimized in a 25.0 Å × 25.1 Å × 25.2 Å rectangle cell, with dipole corrections in all three dimensions. The calculated band gap is 1.81 eV, which is higher than the bulk gap due to the well-known confinement effect.

Au_{20} and Au_{55} clusters were selected to as models of Au nanoparticles to study the interfacial interaction between the particle and the (00±1) surface, as their electronic structures are well studied experimentally and theoretically, and were extensively used to study the electronic structure of nanoparticle-substrate interface.[12-17] The interfaces were constructed by putting the compact surface of Au particle onto (001)-Zn and (00-1)-O surfaces the ZnO nanosubstrate. The calculation was performed in a 25.0Å × 25.1 Å × 25.2 Å rectangular cell. The top 4 layers of the ZnO substrate surface and the Au particles are fully optimized until the forces on all the atoms were less than 0.02 eV/Å.

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