

Orientation Preference during Heterogeneous Nucleation on Amorphous Substrates: Implications for Heterogeneous Catalysis

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Hybrid nanostructures are extensively used for heterogeneous catalysis. The effect of particle size and particle-substrate combination on the efficiency of the catalyst has been extensively studied in the literature. However, the effect of orientation of the catalyst nanoparticle with respect to the substrate on the catalytic efficiency has not been investigated so far. Homogeneous nucleation of an FCC crystal leads to a cuboctahedral nucleus which is its Wulff shape. Heterogeneous nucleation of an FCC metal will generate truncated cuboctahedron, called the Winterbottom (WB) shape, with the extent of truncation depending on the substrate particle interfacial energy (γ_s). For a particular substrate-particle combination there can be infinite possibilities of WB shapes depending on the orientation of the particle. Our analytical calculations show that in the case of heterogeneous nucleation on a planar and isotropic substrate, there exists one WB shape which has the least nucleation barrier. Hence, for a given γ_s value one particular orientation/WB shape is preferred. With the change of γ_s , the preferred orientation of the particle changes.

Experimentally, we have nucleated single crystalline Au on oleylamine functionalized amorphous carbon substrate, Au on butanedithiol functionalized amorphous carbon substrate and Ag on oleylamine functionalized amorphous carbon substrate as shown in figure 1(a) and (b). Functionalization with different organic surfactants alters the interfacial energy between the nucleating particle and the amorphous carbon substrate. By precession electron diffraction technique, we have acquired diffraction patterns from about 250 particles and analyzed the nucleation orientation of each of these particles on the substrate, as illustrated in figure 1 (c) and (d). We have observed that for each of the systems there is a preferential nucleation orientation and the preference of nucleation orientation alters with change in the interfacial energy, as is evident from the inverse pole figures in figure 1(e). Nucleation being a stochastic process there exists a distribution in the preferred orientation, the majority being around a particular direction. The experimental observation correlates well with the analytical calculations.

By density functional theory (DFT), we also show that the orientation of the catalyst particle with respect to the substrate has significant effect on the adsorption energy of CO and the kinetics of CO oxidation. Hence, it is important and intriguing to find out the orientation preference of the catalyst particles and manipulate the nucleation conditions to obtain a desired orientation for a specific application. The knowledge gained through this work¹ will help in choosing a suitable substrate-particle combination for which the desired orientation can be obtained for a specific catalytic application.

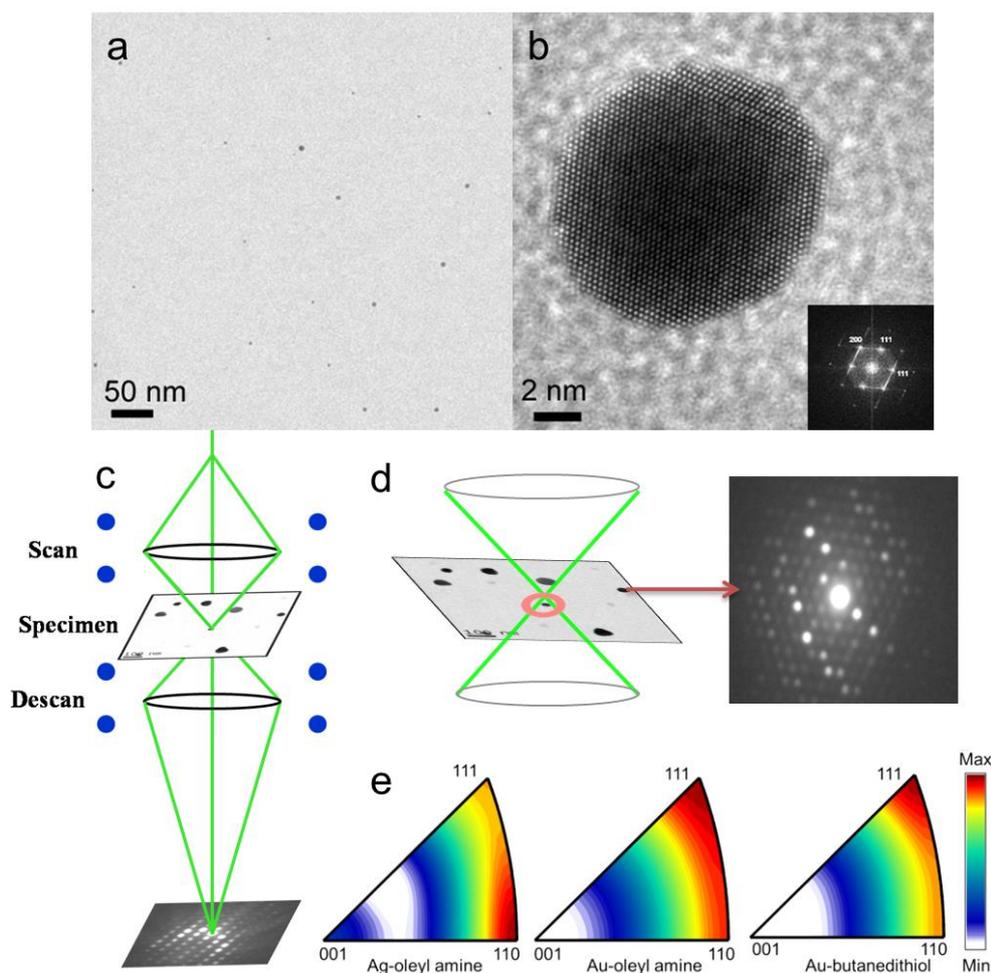


Figure 1. Representative low magnification and high resolution images of Au nuclei on amorphous Carbon grid functionalized with Oleyl amine shown in (a) and (b) respectively, schematic showing the precession electron diffraction technique used to acquire diffraction pattern from each of the single crystalline nuclei as shown in (c) and (d). Inverse pole figures in (e) show that there is orientation preference for each systems and the preference is different for different systems.

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References

1. Dipanwita Chatterjee; Akash R; K. Kamalnath; Rafia Ahmad; Abhishek Kumar Singh; N. Ravishankar, Orientation Selection during Heterogeneous Nucleation: Implications for Heterogeneous Catalysis. *The Journal of Physical Chemistry C* **2017**, *121* (18), 10027-10037.