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Direct Visualization of Temperature Induced Phase Separation of Completely Miscible Au-Pd Alloy by In-Situ TEM

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Background incl. aims

Very recently, bimetallic nanoparticles (NPs) are getting a lot of attentions due to their superior efficiency in heterogeneous catalysis and potential to replace conventional fossil fuels. Bimetallic systems showed superior stability, and superior activity compared to any of their individual metallic counterpart. In this aspect, Au@Pd core@shell NPs and recently Au-Pd nano-alloys has been used for electrocatalytic production hydrogen peroxide (H2O2), ethanol oxidation reactions and they observed to show much better catalytic activity compared to bare Pd nanoparticles. However, Au NPs are less efficient for oxygen reduction but highly efficient for conversion of alcohols to aldehyde, which is completely opposite to the catalytic activity of Pd. These limitations were repressed by alloying both systems (Au and Pd), but the lower electrochemical potential of the metal alloy contrast to the individual metals decreases its efficiency towards alcohol to aldehyde conversion reaction. Thus, it should be highly beneficial to construct a bi-metallic Au-Pd system where both the phases are separated from each other in a single nanoparticle. In such systems, the oxidation and reduction reactions will take place at totally different locations of the same nanoparticle, leading to more superior catalytic activity and stability. Such systems are unique in this sense, as they retain the individual properties of separate constituents and also provide physical, chemical, optical interaction between them due to the presence of a common interface [1]. However, obtaining bi-metallic nanoparticle based on phase separation method depends on the fact that the lattice mismatch between two constituent metals must be large (>5%, ex. Au-Ni, Au-Cu). Metals with lower lattice mismatch tend to create an alloy system due to complete miscibility in their all composition range at all the temperatures according to their bulk phase diagram (i.e. Au-Pd) [2]. Though theoretical researchers predicted a miscibility gap of an Au-Pd bimetallic system, the conversion of Au-Pd nanoalloy to phase separated Au/Pd bi-metallic system with annealing could not be observed till now. Okamoto et. Al. observed Au-Pd alloy formation in face centered cubic (fcc) structure at high temperature for all Pd composition range [3]. Wu et. Al. observed formation of an alloyed nanoparticle upon in-situ heating of a core@shell Au@Pd nanostructure up to 600°C [4]. Precot et. al. studied the annealing effect of Au-Pd nanoparticles deposited on amorphous carbon at 873K and observed bi-modal distribution of nanoparticle upon annealing, where small nanoparticle and big nanoparticles became Au-rich and Pd-rich, resulting a bi-modal distribution of nanoparticles driven by Ostwald ripening mechanism [5].

We have shown by in-situ vacuum annealing high-resolution transmission electron microscopy (HRTEM) study of the generation of phase separated Au-Pd bimetallic nanoparticles from an initial Au nanotriangle (AuNT)@Pd core@shell nanoparticle system. We have observed through extensive aberration-corrected HRTEM, high-resolution scanning TEM (HRSTEM) and energy-dispersive X-ray spectroscopy (EDS) that the core@shell Au@Pd nanostructure forms an Au-Pd alloy during in-situ heating at 400°C and is very much stable up to 800°C, which is a completely normal behavior. Upon further heating at 900°C-1000°C range, the Au and Pd phase surprisingly got separated from each other and the separation is observed to be much prominent for initial core@shell NPs with higher Pd loading.

Methods

Au nanotriangles (AuNT) were produced by a previously described seedless method. Thickness of Pd layer was controlled by controlling the amount of H2PdCl4 in the AuNT solutions. The nanoparticles were initially identified by UV-Visible and X-ray photoelectron spectroscopy (XPS) technique. The in-situ HRTEM and selected area diffraction (SAD) studies were performed in an image-corrected FEI TITAN operated at 300 kV. HRSTEM, energy dispersive X-ray spectroscopy (EDS) analyses were carried out in a probe-corrected FEI TITAN TEM equipped with high-brightness gun and an Oxford Instruments Ultim X-MaxN 100TLE detector for EDS measurements. A DENSsolutions Wildfire MEMS based double-tilt heating holders was used for the in-situ heating measurements. The heating circuits were fabricated on a SixNy membrane and it can measure temperature until 1300 °C. A very dilute solutions of the AuNT nanoparticles were drop casted on the heating chips and kept overnight for drying.

Results

We have extensively studied the interface and surface of bare AuNT and AuNT@Pd core@shell nanostructures and identified presence of number of defects at the Au/Pd interfaces (i.e. stacking-faulst, dislocation pair etc.). Also, the melting point of bare AuNT is observed to be lower compared to the Pd doped sample and the melting point seemed to be increasing with increase in Pd content. Besides that, the relative change in lattice parameter with in-situ heating was also studied for bare NT and AuNT@Pd with different Pd thickness using fast Fourier transform (FFT) method and we observed the change in lattice parameter of (220) plane is much lesser for Au-Pd alloy compared to bare AuNT. However, the most important observation was the phase separation of Au-Pd alloy triangular nanostructure producing distinctive Au and Pd region at higher temperature which was verified by HRTEM and EDS measurement. The Pd region increased in size with higher Pd loading. The in-situ microscopy reveals the Pd atoms outward movement from the core due to their higher mobility at high temperature while Au atoms move inwards to finally produce a phase separated structure. This structure was also observed to be very stable as the EDS spectra taken from the sample at room temperature after 7 days revealed that the nanoparticle still remains in the phase separated form.

Conclusion

We have done in-situ heating experiment on bare AuNT and AuNT@Pd core@shell nanostructure up to 1000°C. The Pd deposited AuNT showed much more stability in terms of structure and thermal resistance as observed. Most importantly, though Au and Pd are miscible in all temperature range and all compositions. We observed when Pd content is higher, it can produce phase separated region at High temperature which was observed to be very much stable in ambient atmosphere over a month. This result will be of very much important to understand not only the catalytic activity of Au-Pd alloy but also to produce phase separated bi-metallic nanostructure consisted of separated Au and Pd region for superior catalytic activity.

Graphic:

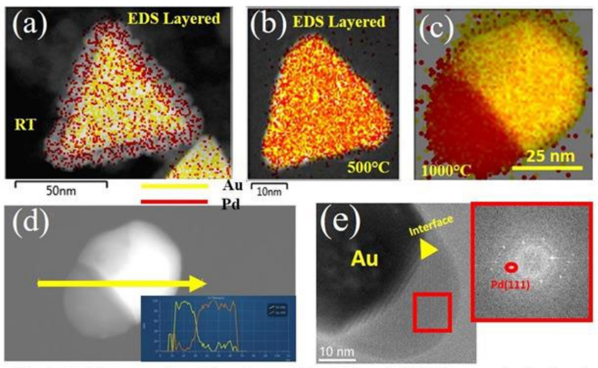

Fig. (a-c) EDS map of Au-Pd region at RT, 500°C and 1000°C, respectively showing complete phase separation at high T. (d) Line spectra (e) HRTEM image. The FFT [inset] taken from the Pd region [red square] showing lattice parameter corresponds to (111) planes of Pd.

Keywords:

Au-Pd alloy, Phase separation, in-situ

Reference:

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