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Probing Composition Distribution in Nanoalloy Catalysts with Correlative Electron Microscopy

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Introduction

Alloyed nanoparticles, also known as nanoalloys, are promising catalysts for many challenging but critical chemical processes. Examples include the Pt-M nanoalloys for the oxygen reduction reaction, Cu-M for the CO_2 reduction reaction, and Pd-M for selective hydrogenation and selective oxidation. [1, 2] Compared to their monometallic counterparts, unique active sites in nanoalloys can come from *(i)* electronic interactions, *(ii)* strain effects, *(iii)* bi-functionality and/or *(iv)* site separation effects. [1, 3] Controlled synthesis of nanoalloys is desired in order to understand their structure-property relationships and further optimize their performance. While many synthesis methods have been developed, information about the resultant composition versus size distributions amongst nanoparticles are usually not available, and the uniformity of the particle composition is often assumptive. Such an analysis would require extensive work on a high-performance analytical electron microscope, which is not always accessible.

In this presentation, we introduce an alternative way of performing composition analysis of nanoalloys via a correlative electron microscopy approach, separating the size measurement (imaging) and composition analysis between a conventional TEM and an SEM. This approach can be more efficient for composition analysis than using a high-resolution analytical electron microscope, and the instruments should be more readily available.

Materials and Methods

AuPd nanoparticles are prepared using a colloidal method [4] in aqueous media, using polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) as stabilizing agents. Particle sizes were measured using a JEOL JEM2100 TEM with a LaB_6 gun. The same sample was then subsequently transferred to a Hitachi Regulus 8230 SEM equipped with a cold field emission gun and a Bruker FlatQuad X-ray Energy Dispersive Spectrometer (XEDS), which was then used to measure compositions of individual nanoparticles.

Results and Discussion

Figure 1 demonstrates the correlative TEM and SEM imaging of a AuPd colloidal specimen, showing identical particles imaged using both instruments. The size and the composition of one particle were measured in the TEM and SEM, respectively. Compared to a high-resolution analytical electron microscope typically operated at a higher accelerating voltage (*e.g.* 200kV), XEDS analysis in an SEM with a much lower accelerating voltage (*e.g.* 20kV) is more efficient for many catalytically important elements with suitable ionization edges below 5 keV, such as Au M (M_5: 2.2keV), Pd L (L_{III}: 3.17keV).

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The efficiency gain in the low-kV SEM comes from *(i)* larger ionization cross-sections due to a smaller and more suitable beam energy; *(ii)* better X-ray detector geometry due to more available space in the SEM chamber; and *(iii)* a larger probe current (*e.g.* > 500pA) due to the absence of electron-beam knock-on damage to the sample. The necessity of performing composition distribution analysis was demonstrated using a pair of AuPd nanoparticles prepared the same colloidal route except for the stabilizing polymers (PVA and PVP). The two colloids were found to have very similar overall composition (by mass spectroscopy) and displayed very similar particle size distributions. However, their composition distributions are very different (Figure 2): AuPd-PVP particles have a more random composition distribution while the AuPd-PVA material shows a more esystematic composition variation with size. This difference may be the reason why they show different selectivity in the direct synthesis reaction of hydrogen peroxide.

Significance

This work introduces a new analysis protocol and demonstrates the necessity for probing composition distributions in nanoalloys catalysts, a key parameter that has been largely overlooked.

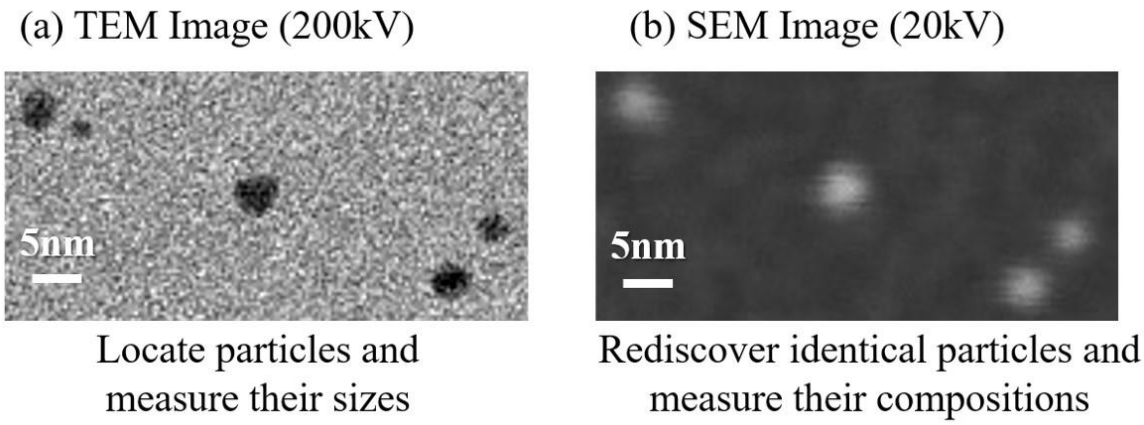

Figure 1. Correlative electron microscopy study of colloidal AuPd nanoparticles. (a) A bright field TEM image (b) A secondary electron SEM image of the same area as shown in (a).

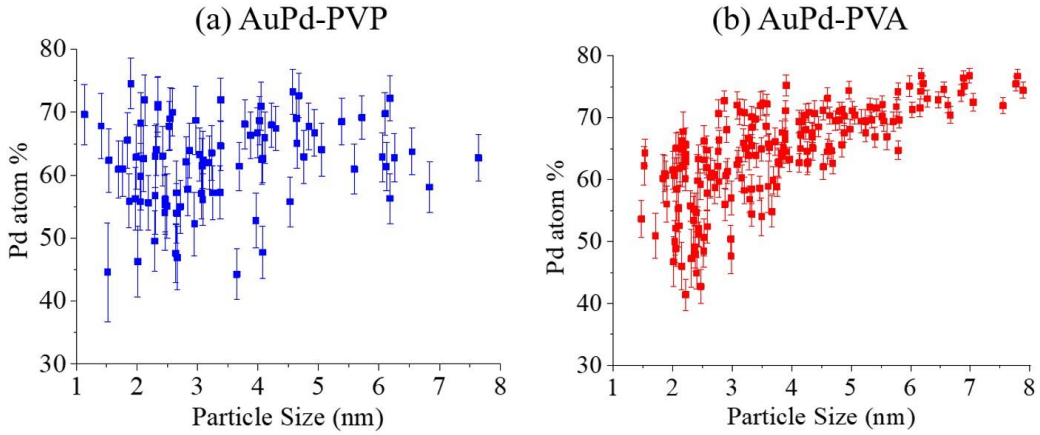

Figure 2. The composition distribution among individual AuPd nanoparticles prepared by the same colloidal method but using different stabilizing agents (PVP or PVA), plotted as the function of their sizes.

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Each data point represents a composition of one particle and the error bar represents a 95% confidence interval.

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