

When unmixable metals mix

At the bulk scale, gold and rhodium separate like oil and water, but at the nanoscale, they can mix completely. The reason for the miscibility is on the particles' surface.

Phase diagrams change at the nanoscale. When particles are shrunk down to small-enough sizes, the fraction of atoms on the surface increases, and the free-energy balance of atomic interactions changes. Although that phenomenon has been common knowledge in the nanoscience community for decades, the details have remained fuzzy. Now Peidong Yang of the University of California, Berkeley, and colleagues have filled in some of the gaps by documenting the nanoscale phase transition of gold–rhodium mixtures down to diameters of 1–4 nm.¹

At bulk scales, gold and rhodium are incompatible metals. Even in particles as small as 3.8 nm, the metals remain mostly separate. In such particles, the two metals segregate into separate regions, as shown in figure 1; they are thus sometimes called Janus particles after the Roman god of duality, who had two faces. But below 2 nm, the thermodynamic balance shifts, and the researchers found that a completely mixed alloy forms.

Gold and rhodium have several qualities that make them an appealing pair to investigate. Nanoparticles of those elements are already used for electrocatalysis reactions, such as the separation of water to make hydrogen fuel. Both elements have cubic lattice structures, so the analysis wouldn't have to account for structural differences. Materials with larger atomic numbers show up brighter in the scanning transmission electron microscopy (STEM) imaging used to study them. Gold, with a relatively high atomic number of 79, thus stands out from rhodium, with atomic number 45.

Small is different

Beyond miscibility, optical and mechanical material properties also change at the nanoscale. For example, semiconductor nanocrystals, known as quantum dots,

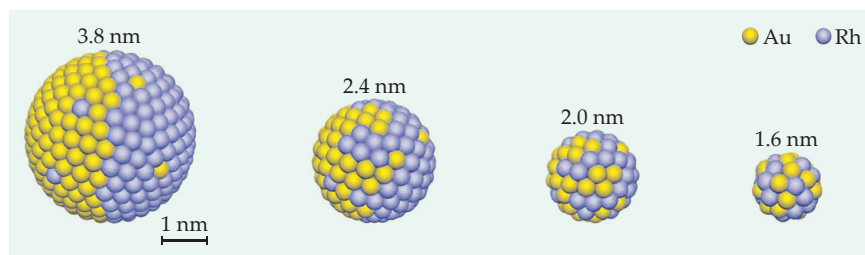


FIGURE 1. GOLD AND RHODIUM ATOMS are phase separated in particles with diameters as small as 3.8 nm. At smaller sizes, the metals begin to intermingle, and in particles less than 2 nm across, mixing of the elements becomes thermodynamically stable. (Adapted from ref. 1.)

emit different wavelengths of light depending on their size. Quantum dots' extraordinary properties were highlighted by last year's Nobel Prize in Chemistry. (see *PHYSICS TODAY*, December 2023, page 16). Some materials, such as certain ceramics, are also stronger at the nanoscale (see *PHYSICS TODAY*, November 2013, page 14).

Previous studies had documented the mixing at nanoscales of otherwise immiscible materials, such as silver with nickel and gold with rhodium.² Yet it was unclear whether the nanoparticles were composed of thermodynamically stable alloys or had been kinetically trapped in a mixed form by rapid cooling. Previous work by Yang's research group had found that in particles with diameters of 4–12 nm, gold and rhodium remain mostly separate but begin to mix a little bit.³ The new study now extends that earlier work to even smaller particles.

The reason the community had been missing data on the changes to multielement phase diagrams at nanoscales, explains Yang, is that it was a formidable task to take on. It's difficult to produce bimetallic nanoparticles of 1–4 nm, and once they've been made, analyzing their mixing state is also a challenge. Such small particles are easily knocked out of place by the electron beams used to image them, and they can't be measured if they're no longer in the beam. To deal with that issue, Yang and colleagues used low-dose STEM.

To reliably estimate the mixing of gold and rhodium in the smallest nanoparticles, the researchers developed a random-walk algorithm that measures the domain size and distribution of the gold in the samples. The algorithm first

identifies the brightest pixel in a STEM image of a nanoparticle, which will always be gold (thanks to its large atomic number), and then investigates neighboring pixels until it reaches a threshold decrease in brightness, indicating that it has left the gold domain. Then the algorithm looks at the remaining region. By repeating that process dozens of times, it maps the size and location of all gold domains. Rhodium domains are then mapped simply by subtracting the gold domains from the total image. When the domain sizes become small enough, on the scale of one to four atoms across, the material is considered completely mixed.

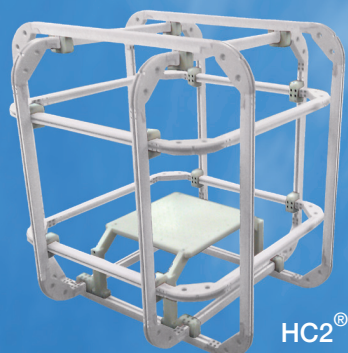
In addition to looking at the effects of particle size, the researchers investigated how different mixing ratios of the two metals affected the results. They found that the elements best mix when the composition is far from 50-50. When a particle has roughly equal volumes of the two metals, they exhibit maximum repulsion. But particles larger than 2 nm do mix when there is much more of one metal than the other. For example, mixtures that are 80% either gold or rhodium will fully mix at 4 nm.

A thermodynamic mystery

After building a detailed experiment-based phase diagram for the metals' miscibility, Yang and colleagues turned to thermodynamic models to confirm their findings. But there was a problem: Theory-based models disagreed with what they had observed. Instead of the evenly mixed alloys seen in experiments, thermodynamic simulations suggested that small nanoparticles should separate into a core of rhodium surrounded by a shell of gold, as shown in figure 2a.

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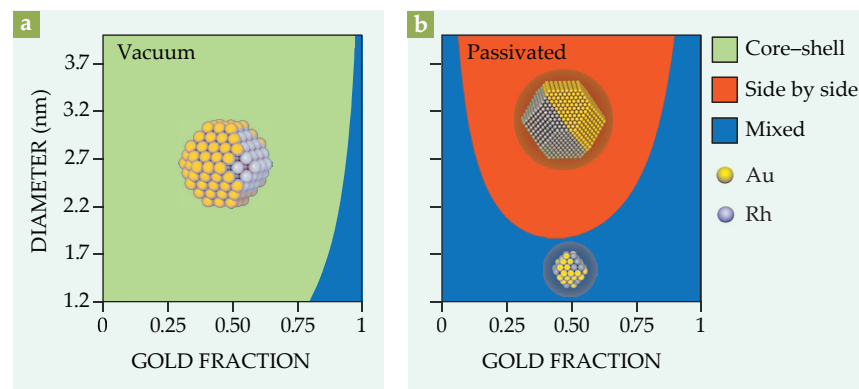


FIGURE 2. THERMODYNAMIC MODELS predict the structure of gold–rhodium nanoparticles. **(a)** Pure gold and rhodium mixtures synthesized in UHV should stratify into a core of rhodium surrounded by a shell of gold. **(b)** Surface passivation of nanoparticles changes their stable structure to either fully mixed or unmixed side-by-side domains. (Adapted from ref. 1.)

The apparent conflict between theory and observation revealed a hidden element that the researchers had missed in their simulations. The nanoparticles of gold and rhodium are synthesized using droplets of organic polymers that are then burned away, and the samples are washed with argon and oxygen plasma. Despite the cleaning step, the polymers used in the synthesis process left behind remnants, such as carbon and oxygen atoms, that had attached to the surface of the nanoparticles. Those remnants, undetectable in the STEM images, reduced the free-energy difference between rhodium and gold, making them less repellent to each other.

Surface passivation occurs when any material is coated with another material that makes it less reactive. It is a method often intentionally used in engineering to reduce weathering and corrosion, but it also occurs naturally. Many metals, such as aluminum and titanium, naturally form a layer of passivating oxides on their surface just from normal air exposure.

Once the researchers accounted for the effects of surface passivation, the experimental phase diagram finally aligned with thermodynamic simulations, as shown in figure 2b. Despite the impossibility of directly imaging the passivating elements, their presence is confirmed by the agreement between the corrected model and experimental observations. The model, like the experiments, showed that 50-50 gold–rhodium compositions are the most resistant to

mixing but that they will still mix below a particle size of 2 nm. Only nanoparticles synthesized in UHV should form the core-shell structure, a hypothesis that could be tested in the future.

One might wonder whether the discovery of surface passivation on those nanoparticles could forebode problems for the electrocatalysis reactions that they are valued for, but most nanoparticles are synthesized using polymers, so what is already understood about their catalytic properties should not change. Other recent research shows that passivating elements will dissociate from the surface of nanoparticles during electrocatalysis and may even help enhance reactivity.⁴

“Knowing the phase diagrams at this nanoscopic level will help us design better catalysts,” says Yang. The phase diagrams provide a path to targeted engineering of specific structures and pave the way to understanding the behavior of other multielement nanomaterials. For engineers and researchers who want to synthesize gold–rhodium nanoparticles that are phase separated, alloyed, or in a core-shell structure, the conditions needed to achieve those structures are now mapped out.

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References

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