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Silver atoms of nanoparticles are mobile, IIT Madras team finds

The rapid exchange of silver atoms in solution might have implications in real-life situations

While atoms in silver metal remain in their positions forever in bulk material, their behavior changes completely at the nanoscale, researchers at the Indian Institute of Technology (IIT) Madras have discovéred.

When nanoparticles made of two silver isotopes (107Ag and 109Ag) 'having just 25 atoms each were mixed in solution, a team led by Prof. T. Pradeep of the Chemistry Department found that the atoms from the two particles rapidly exchanged their positions. New particles composed of nearly 50% mixture of both isotopes were formed. This is akin to the exchange of hydrogen and deuterium atoms when normal and heavy water (D_2O) are mixed. Even in an alloy of silver and gold, a rapid exchange of silver atoms was seen.

“This is a surprising find for the nanoscience community. We have always been thinking that silver and gold particles are rigid, well-defined structures even at the nanoscale. But we observed silver atoms undergoing dynamic changes in solution,” says Prof. Pradeep. “Unlike bulk silver, silver nanoparticles are not rigid and fixed at specific locations we thought them to be.” The results were published in the journal *Science Advances*.

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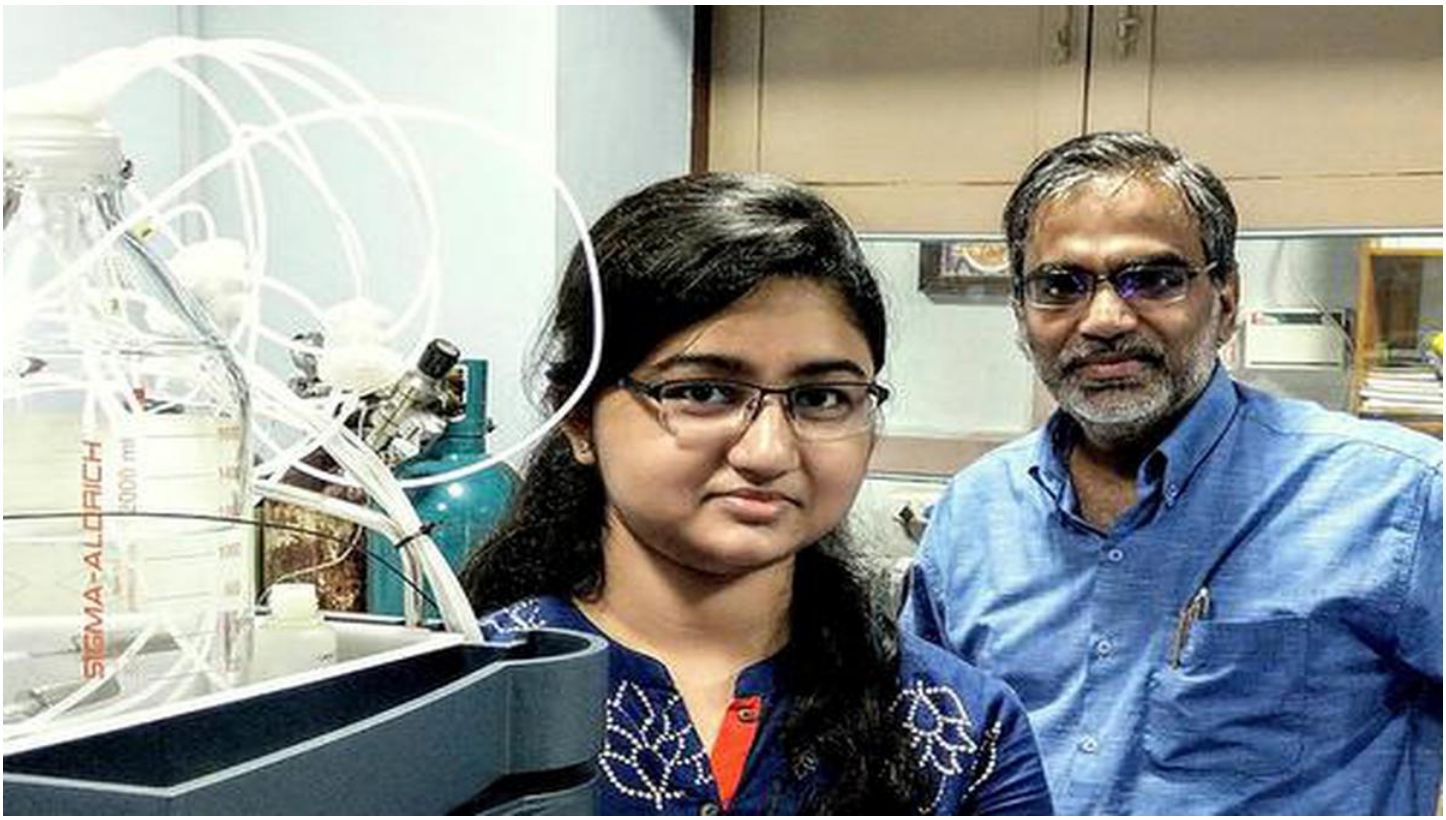

Mixing of silver atoms is akin to the exchange of hydrogen and deuterium atoms when normal and heavy water are mixed, say Pradeep (right) and Papri Chakraborty.

“The properties of nanoparticles such as catalysis, drug delivery, and biological sensing may all be viewed differently in view of this rapid atom exchange,” Prof. Pradeep says. “In homogeneous catalysis involving nanoparticles, the site at which chemistry occurs could be changing continuously,” the authors write.

The silver particles composed of 25 atoms were protected by ligands to form clusters. Despite the protection offered by the ligand, the atom exchange between the two clusters happened in millisecond time scale. The new cluster, which was formed by the mixing of atoms belonging to two isotopes, had almost 50:50 ratio of the isotopes. The researchers found that the rate at which the atoms exchanged could be controlled by changing the temperature. While the exchange was rapid at room temperature, at -20 degree C, the exchange rate was slower and took about 30 seconds to attend equilibrium distribution. The

relatively longer time taken to reach equilibrium allowed the researchers to observe the in-between states of atom exchange. They found that the atom transfer rate is similar to that in water.

Slower exchange rate

The atom exchange rate slowed down drastically when silver nanoparticles were composed of 29 atoms - it took about 3 hours to reach dynamic equilibrium at room temperature compared with Rapid exchange in the case of 25 atom clusters. The slower exchange rates allowed the researchers to study the dynamics in greater details. The exchange went through multiple steps. First, there was rapid exchange of atoms at the surface of the nanoparticle. Then the exchange atoms diffused into the core of the nanoparticle making more exchange at the surface possible. Finally, there was the equilibrium of the mixed isotope system.

"The difference in the exchange rate between the clusters made of 25 and 29 silver atoms is not due to the difference in the number of atoms but due to the like and used for binding to the silver atoms," says Papri Chakraborty from the Department of Chemistry at IIT Madras and first author of the paper. "The ligand binds to each silver atom at just one site in the case of the cluster compost of 25 atoms. But it binds at two sites of the silver atoms in the 29-atom cluster thus rendering the structure rigid."

"Such dynamics can occur in any nanosystem. Fundamental insight the study provides is that nanoparticles are indeed molecules close Professor Pradeep says.

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https://www.thehindu.com/sci-tech/science/silver-atoms-of-nanoparticles-are-mobile-iit-madras-team-finds/article25920352.ece

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R. PRASAD

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The rapid exchange of silver atoms in solution might have implications in real-life situations. "The properties of nanoparticles such as catalysis, drug delivery, and biological sensing may all be viewed differently in view of this rapid atom exchange," Prof. Pradeep says. "In homogeneous catalysis involving nanoparticles, the site at which chemistry occurs could be changing continuously," the authors write.

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