Inhibition of Catalytic Electron Transfer by Coulomb Blockade in Small Au Nanoparticles

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Abstract

Colloidal noble metal nanoparticles (NPs) are an emerging research topic in the field of nanotechnology because of their interesting catalytic properties.[1] They can actively participate in redox chemical reactions and are therefore attractive for various oxidation and reduction reactions including CO_2 reduction, H_2 dissociation, and so on. The metal NPs provide alternative reaction pathways, thereby significantly reducing the activation energies for these chemical conversions. There are several strategies to reduce the activation energies for these catalytic reactions, such as by changing the size, shape, and composition of the NPs and also by changing the reaction conditions.[2]

To investigate the reaction mechanism of sub-10 nm Au NPs of different sizes, we have used ferricyanide (Fe^{3+}) to ferrocyanide (Fe^{2+}) 1-electron transfer as a model reaction system.[3] We have found that the reaction rate significantly depends on the size of the NPs, and the highest reaction rate was achieved in presence of Au NP with a diameter of 5 nm. We also compared the reaction rate of Fe^{3+} to Fe^{2+} conversion in the presence and absence of a reducing agent triethanol amine (TEOA). It has been found that the reaction pathway is significantly altered with and without TEOA. TEOA, in general, transfers the electron to Au NP and causes a negative charging of the Au NP surface. However, when the size of the NPs is very small and especially below 5 nm, the negative charging of Au NPs is inhibited by the Coulomb Blockade effect. As a result, the catalytic electron transfer from Au NP to Fe^{3+} is also inhibited, thereby, decreasing the overall Fe^{3+} reduction rate. These experimental findings along with theoretical calculations will help the research community in designing novel metal NPs with better catalytic properties, which will open up new possibilities for various catalytic processes for environmental remediations.

References

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Figures

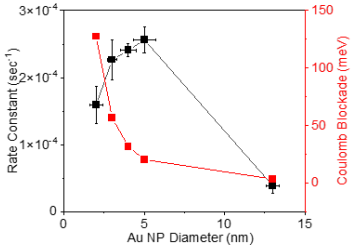

Fig 1. Catalytic rate constants of Fe^{3+} to Fe^{2+} reduction by different Au NPs with the diameter ranging from 2-13 nm. The calculated Coulomb Blockade energies are also plotted on the same graph for relative comparison.