Catalysis-Induced Fluxionality at the Single Nanoparticle Level with Single Turnover Resolution

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Introduction and Objectives

Metal nanoparticles are key components in the advancement of future energy technologies since they are catalytically active for several organic-inorganic syntheses, electron-transfer, and energy conversion reactions[1]. The nanoparticle surface before, during, and after a catalytic turnover event is not static in nature, but dynamic due to the movement of surface atoms. This rearrangement is both intrinsic due to the metastability of nanoparticles or extrinsic[2]. Extrinsic sources leading to fluxional behaviour of nanoparticles include adsorption and reaction of small molecules. This fluxionality cannot be studied by ensemble methods because catalytic turnover and reaction-induced fluxional behaviour is asynchronous among nanoparticles.

In order to probe fluxional behavior at the most fundamental level, we propose to study catalytic turnover events on single nanoparticles with single turnover resolution in a two-state (off-on) reaction using fluorogenic reactants at different temperatures and reactant concentration. We have used a single-molecule fluorescence approach similar to Xu *et al.*[3] to monitor the real-time catalysis of individual gold nanoparticles (Au NPs) for the reduction of resazurin (non-fluorescent) to resorufin (fluorescent) in the presence of NH_2OH and small molecule adsorbates with single turnover resolution. Coupled with adsorbate-induced restructuring effects and temperature considerations, we aim to fundamentally understand how real-time structural variations influences reactivity and energy transfer in nanoparticle catalysts. Ensemble level reactivity measurements and isothermal titration calorimetry (ITC) complement the body of single nanoparticle reactivity data.

Results and Discussion

We have studied the real-time reduction of resazurin to resorufin by NH_2OH on the surface of 5, 10, and 20 nm Au NPs at the single nanoparticle level using total internal reflection fluorescence (TIRF) microscopy. In order to quantify the adsorbate-induced fluxional behavior of Au nanoparticles, we added a sufficient amount of the adsorbate; 3-mercaptopropionic acid (3-MPA) or β-alanine, to cover 10-100% of Au surface atoms (Au_s) based on their stoichiometric binding ratio. ITC results obtained for the binding of 3-MPA to Au NPs indicate strong irreversible binding (with a binding ratio of 3 Au_s to one 3-MPA molecule) with a binding constant of 10^7 M^{-1} while the binding of β-alanine

is weak and in the order of 10^3 M^{-1}. β-alanine and 3-MPA were chosen because of their aqueous solubility, similar structure, but different functional group interacting with Au.

In single molecule TIRF experiments, we recorded trajectories of stochastic fluorescent bursts from localized spots corresponding to Au NPs on a cover slip inside a flow cell. These fluorescent bursts (off-on signals) represent the formation and desorption of resorufin (Figure 1). The consistent heights of these bursts (Figure 1A-F) indicate each fluorescent burst comes from a single resorufin molecule. The fluorescence trajectories with increasing 3-MPA coverage show a clear transition from being stochastic to trajectories that appear more digital in nature. The waiting time for both product formation and desorption increase with increasing 3-MPA coverage (Figure 1A-F) indicating 3-MPA covered Au NP provides increased resistance towards product formation and desorption. The increased coverage of β-alanine on the 5 nm Au NP surface does not cause any significant change in the waiting times and the fluorescence trajectory remains stochastic in nature even with 100% coverage of the Au_s. A statistical evaluation of the single nanoparticle trajectory has been averaged over at long times to arrive at average properties, <TOF> that can be compared directly with ensemble measurements. The adsorbate-induced fluxional behavior can be quantified by observing the non-uniformity in the off-on waiting times but more importantly by the change in the standard deviation (S.D.) of the waiting times. In the presence of increasing 3-MPA coverage, we observe a significant decrease in the S.D. of $<\tau_{off}>$ and $<\tau_{on}>$, while no change in the S.D. was observed even in the presence of 100% β-alanine.

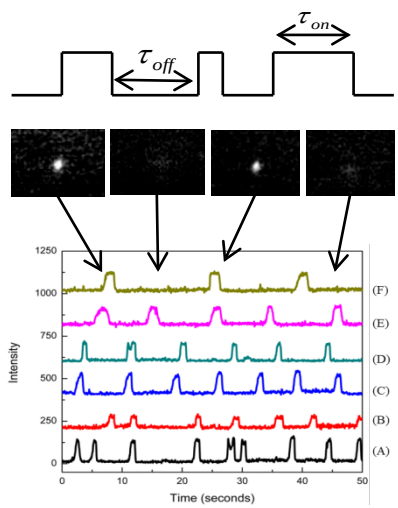

Figure 1. Schematic representation of a single molecule turnover trajectory displaying the off-on behavior. Image of the fluorescent spot shows the formation of a product molecule and the blank image shows its desorption. A segment of the fluorescent trajectory with increasing 3-MPA coverage on the 5 nm Au nanoparticle surface; (A) 0% (B) 1 0% (C) 25% (D) 50% (E) 75% (F) 100% Au surface atoms covered by 3-MPA.

Conclusions

Single molecule experiments with single turnover resolution allow the measurement of intrinsic kinetics of individual nanoparticles which are masked during ensemble measurements. This study provides insight into the structure-activity and the size-activity relationship of a catalyst thereby promoting the development of highly selective catalysts.

References

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