Mapping near-field enhanced hot charge separation in plasmonic nanostructure

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Abstract: Plasmonic hot charge separation is an important step in plasmon-induced photochemical reaction, which closely interrelated with solar energy utilization efficiency and reactive sites. Here, we present the feasibility of mapping the spatial heterogeneity of hot charge separation in Au/TiO\textsubscript{2} system using kelvin probe force microscopy (KPFM). Hot holes almost localized at Au/TiO\textsubscript{2} interface, indicating hot charge spatial separation. Combining with theoreatical simulation, we demonstrate that the plasmonic near-field enhanced hot charge separation is generated at hot spots in Au/TiO\textsubscript{2} nanostructure. Our work offers a thorough understanding the relationship of localized plasmonic near-field and hot charge separation in plasmon-induced photochemistry.

Keywords: Hot spots, Charge separation, Hot charge, Plasmonic near-field.

1. Introduction

Surface plasmon resonance (SPR) in metallic nanostructures has sparked diverse applications in photochemistry reactions, super-resolution spectroscopy, optical switching and biological sensing.\textsuperscript{1} The coherently oscillating localized surface plasmon can decay non-radiatively into an electron/hole pairs via Landau damping within a few hundred femtoseconds.\textsuperscript{2} Generating hot charge with sufficient energy can be injected into adjacent semiconductor when incorporating plasmonic nanostructure into semiconductor device or catalyst.\textsuperscript{3}

Hot charge separation and relaxation dynamics of energetic plasmonic carriers generated in hot spots have attracted much attention and studied predominantly by optical spectroscopy.\textsuperscript{2, 4} Despite these significant progresses in investigation of hot charge behavior on time scale, there are still open questions that understanding the spatial hot charge separation and correlate it with reaction activity site on spatial scale need to be addressed. Specially, the highly inhomogeneous electromagnetic field produced at spatially narrow region of gold dimers nanogap, known as ‘hot spots’. However, how localized electromagnetic field affect the hot charge carrier separation at hot spots in metal/semiconductor nanostructure remains unexplored and is becoming the critical puzzles for the improving of subsequent chemical reaction activity.

Here, we demonstrated, on individual Au nanoparticle, the feasibility of mapping the spatial heterogeneity of hot charge separation in Au/TiO\textsubscript{2} system using kelvin probe force microscopy (KPFM). Combining with theoretical simulation, we demonstrate that the plasmonic near-field enhanced hot charge separation is generated at hot spots in Au/TiO\textsubscript{2} nanostructure. These findings provide a strong basis for disclosing the active sites with high hot carrier density for initiating reaction at nanoscale in plasmonic hot-carrier science.

2. Experimental

Au NPs with an average diameter of 64 nm were synthesized according to the previously reported method. Au NPs were then dispersed onto cleaned 0.05 wt% Nb-doped rutile TiO\textsubscript{2} (100) crystal by spin coating method. The adsorbed surfactant on gold NPs was removed by oxygen plasma etching. The obtained samples were annealed at 673 K. SEM and AFM images show that the monodisperse Au NPs were successfully deposited on TiO\textsubscript{2} substrate.

3. Results and discussion
The scattering spectrum (Fig. 1a) of this Au particle deposited on with TiO$_2$ nanostructure show a single scattering peak centred near $\lambda = 545$ nm. The photon of this wavelength is expected to have sufficient energy ($\sim 2.29$ eV) to excite the electron overcome the Schottky barrier $\varphi_B$ (Calculated as 0.82 eV) (Fig. 1b) at the interface between gold and TiO$_2$, which is a prerequisite for the excited plasmonic hot electrons injection into TiO$_2$. KPFM has a high signal-to-noise in our measurement while recording AFM morphology and surface potential simultaneously (Fig. 1c). The contact potential difference (CPD) at interface between Au and TiO$_2$ was distinctly lower than that gold and TiO$_2$ crystal surface. This can be ascribed to the band bending due to the formation of Schottky barrier at the interface of annealed Au NPs/TiO$_2$. We found that the CPD changes are mainly detected and highly localized at Au/TiO$_2$ interface (Fig. 1d). The positive $\Delta$CPD indicate the hot holes localized at Au/TiO$_2$ interface. We then performed the finite element method (FEM) to calculate the spatial distribution of electromagnetic near-field in order to get a closer insight into the origin of the spatial heterogeneity for the hot charge separation (Figure 1e). It is shown that the electromagnetic near-field is highly confined at the Au/TiO$_2$ interface due to the symmetry breaking of this nanostructure. We can unambiguously assign the observed features of hot charge spatial separation to the heterogeneous near-field distribution inside a plasmonic nanostructure with hot spots, i.e., near-field enhanced hot charge spatial separation.

Figure 1. Spectral properties and Kelvin probe force microscopy (KPFM) images of Au nanoparticle on TiO$_2$ substrate. a, Normalized simulated scattering spectra of Au/TiO$_2$ nanostructure. Inset: a magnified SEM view of Au/TiO$_2$ nanostructure. The simulated model is gold particle size of 72 nm on TiO$_2$ (n=2.5). b, the I-V curve of Au/TiO$_2$ nanostructure. The curve is fitting by thermionic emission conduction mechanism to get the Schottky barrier height. c, d, AFM image (c) and differential surface potential image (d) of Au/TiO$_2$ nanostructure by KPFM. The differential image (d) is derived by subtracting the surface potential in the dark from excited surface potential. e, calculated local near-field intensity distribution using finite element method.

4. Conclusions

In summary, we showed the possibility of mapping hot charge separation at single particle level in Au/TiO$_2$ nanostructure. It is found that, the near-field enhancement directly corresponds to the spatial heterogeneity in hot charge distribution. The method opens a new door to understand the charge separation in more complex plasmonic metal/semiconductor nano structure, such as bowtie nanoantenna or heterometallic antenna.

References