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_2 system using kelvin probe force microscopy (KPFM). Hot holes almost localized at Au/TiO_2 interface, indicating hot charge spatial separation. Combining with theoretical simulation, we demonstrate that the plasmonic near-field enhanced hot charge separation is generated at hot spots in Au/TiO_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.[1] The coherently oscillating localized surface plasmon can decay non-radiatively into an electron/hole pairs via Landau damping within a few hundred femtoseconds.[2] Generating hot charge with sufficient energy can be injected into adjacent semiconductor when incorporating plasmonic nanostructure into semiconductor device or catalyst.[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.[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_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_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_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_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 λ= 545 nm. The photon of this wavelength is expected to have efficientsufficient energy (～2.29 eV) to excite the electron overcome the Schottky barrier φ_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 injectedion 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 ΔCPD 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.

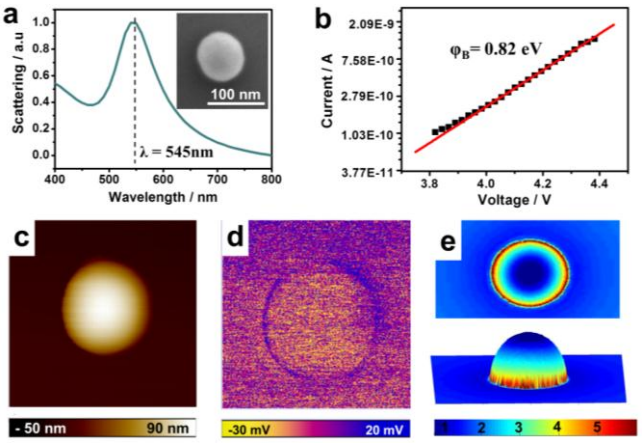

Figure 1

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

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