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COMMUNICATION

Can information of chemical reaction propagate with plasmonic waveguide and be detected at remote terminal of nanowire?

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We attempt to provide experimental and theoretical evidence that information of chemical reaction can propagate with plasmonic waveguide along the nanowire and be detected at the remote terminal of nanowire, where the chemical reaction is the surface catalyzed reaction of DMAB produced from PATP assisted by surface plasmon polaritons.

Introduction

Surface plasmons (SPs), are coherent electron oscillations that exist at the interface between any two materials where the real part of the dielectric function changes sign across the interface.[1] When SPs couple with a photon, the resulting hybridised excitation is called surface plasmon polaritons (SPPs). This SPP can propagate along the surface of a metal until energy is lost either *via* absorption in the metal or radiation into free space. The local SPPs and plasmonic waveguide have been widely applied to surface plasmon resonance,[2,3] surface enhanced Raman scattering (SERS),[4] quantum communication,[5] super-resolution microscopy,[6] metal materials,[7,8] plasmonic circuitry for next generation IT,[9–11] cloaking,[12] photothermal cancer therapy,[13] holography[14] *etc.* The latest novel application of plasmonics is in the chemical reactions assisted by SPPs,[15–22] where the PATP and 4NBT can dimerize to DMAB through surface catalyed reaction by local SPPs and plasmonic waveguide, respectively.

As we know, optical information can propagate in optical fiber and be received at a remote terminal. Similarly, can the information of chemical reaction propagate with plasmonic waveguide and be detected at a remote terminal of nanowire? In this communication, we attempt to answer this question experimentally and theoretically, where the information of chemical reaction is the SERS spectra on a surface catalyzed reaction.

Experimental

The Ag single crystalline nanowires were prepared by chemical synthesis.[23] The SERS active Ag colloids were synthesized, according to ref. 24. PATP was purchased from Aldrich Chemical Co. and used without further treatment or purification. The Ag nanoparticles were mixed with PATP ethanol solution (0.04 M) for 24 h, and were diluted with ethanol. Then the mixture Ag nanoparticles were dropped on the SiO_2 substrate. Lastly, the Ag nanowires were dropped on the SiO_2 substrate. The method that Ag nanoparticles with PTAP and Ag nanowires were dropped on the SiO_2 substrate guarantees that PATP adsorbed on Ag nanoparticles, while there is no PATP on Ag nanowires. Fig. 1 is the SEM imaging of the Ag nanowire–nanoparticles system. The remote SERS measurements were performed using Leica microscopy equipment in the confocal Raman spectroscopic system (Renishaw, Invia) through an objective of 100× with a numerical aperture (NA) of 0.85, which is the same objective used for all Raman measurements. The detailed description of remote SERS measurement can be seen from ref. 25–28. The optical image was recorded by a TE cooled CCD detector equipped on the microscope. For remote SERS measurement, the 632.8 nm laser (He–Ne laser) radiated on nanoparticles (point b in Fig. 1), and the Raman signals were collected at the remote terminal of nanowire (point a in Fig. 1), and remote-excitation SERS signals were integrated 20 times, and the laser power is about 7 mW.

Theoretical

Our theoretical study revealed that the SPPs on nanoparticles can be efficiently excited, and coupled to the Ag nanowire; then the SPPs can

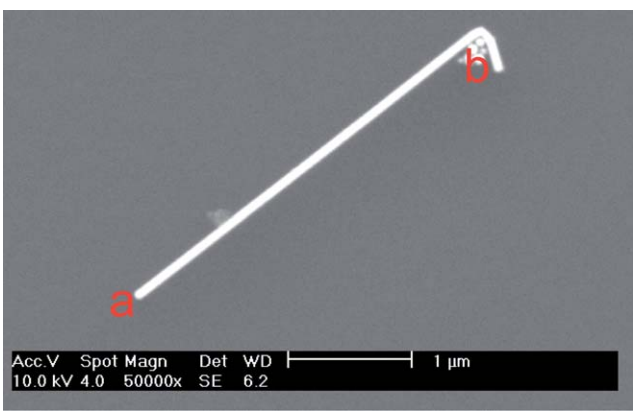

Fig. 1 SEM imaging of Ag nanowire and Ag nanoparticles system, where the PATP molecules were adsorbed on Ag nanoparticles.

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propagate efficiently along the nanowire (plasmonic waveguide). And lastly, plasmonic waveguide can be coupled out at the remote terminal of Ag nanowire. The theoretical calculations were done with the finite difference time-domain (FDTD) method,[29] using FDTD Solutions software.[30] The model in the calculations can be seen from Fig. 2. The substrate is SiO_2 with a thickness of 200 nm, the diameters of nanowire and nanoparticle are 80 nm, respectively, the length of nanowire is 4 μm, the nanogap between nanoparticle and nanowire is 10 nm, and the electric dipole light is set in the center of nanogap. The Cartesian coordinate is shown in Fig. 2. The permittivity of Ag and SiO_2 at 632.8 nm was taken from ref. 31.

Results and discussion

Fig. 3 (a) and (b) show the near field distribution at the remote terminal and 5 nm ahead of the remote terminal (Cartesian coordinates can be seen from Fig. 2). It is found that plasmonic waveguide can efficiently propagate to the terminal of the nanowire—when it is ahead of the remote terminal of nanowire, the intensity of SPPs significantly decrease, and has a tendency to localize to the surface of the substrate. Fig. 3(c) and (d) are the near field distribution 110 and 140 nm above the remote terminal from the substrate. We can see that with the increase of the height, the intensity of SPPs decrease gradually. Fig. 3(e) and (f) are the near field distribution of SPPs near the side of the remote terminal (cross the diameter and near the terminal from 2 nm, side view). It can be found that near the terminal, there are strong SPPs. So, from Fig. 3(a)–(f), we can derive the conclusion that intensity of SPPs is on the order of 10^4 near the remote terminal of nanowire.

Experimentally, we firstly measured the local Raman signals at the remote terminal of nanowire (excitation and collection are at the same point a, see Fig. 1). It is found that there were no SERS signals (see Fig. 4), so there are no molecules adsorbed on the remote terminal of Ag nanowire (point a in Fig. 1).

Then, we measured the propagation of SPPs along the nanowire. The 632.8 nm laser is radiated on point b in Fig.1, and the signals were collected at point a in Fig. 1. From Fig. 5, we can see that the SPPs can efficiently propagate along the nanowire, and can be coupled out at the remote terminal of nanowire (see point a in Fig. 5). It is expected that spectral information can propagate with plasmonic waveguide along the Ag nanowire, and be detected at the remote terminal of Ag nanowire.

Thirdly, when the laser is radiated on the region of nanoparticles (point b in Fig. 1), we measured remote excitation SERS spectrum at the remote terminal of the nanowire (point a in Fig. 1 and 5). When the SERS signals were integrated 20 times, the SERS spectrum of

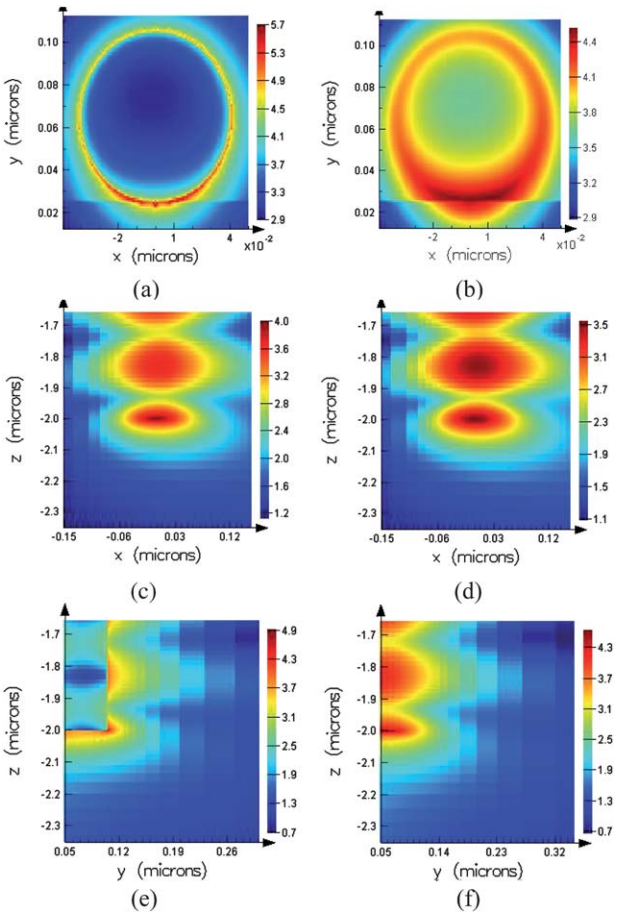

Fig. 3 SPPs propagate along nanowire from different side views. The color bars shown are in log scale.

DMAB can be clearly obtained (see Fig. 6). As we have mentioned in the measurement in Fig. 4, there are no molecules adsorbed on the remote terminal of the nanowire (at point a in Fig. 1), so the SERS signal must be the propagating SERS signals with plasmonic waveguide. The SERS signals are firstly excited on the nanoparticles by directly radiating by laser, then the surface catalyzed reaction occurs on the nanoparticles, thirdly the SERS signals coupled to nanowire with strongly local surface plasmon in the nanogaps. Lastly, the SERS signals that coupled to nanowire propagate with plasmonic

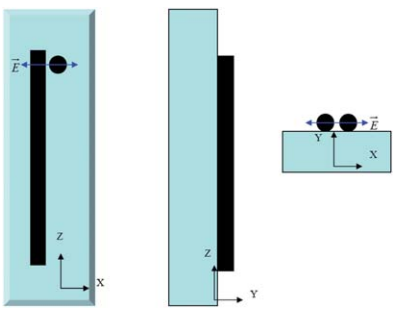

Fig. 2 The theoretical model in the calculations.

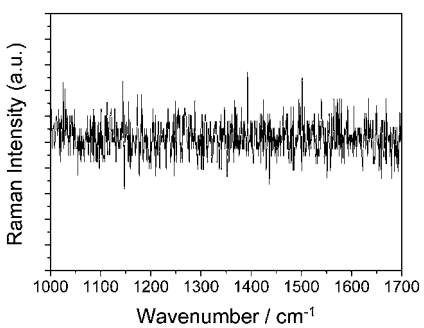

Fig. 4 The measurement of local SERS spectrum at point a in Fig. 1.

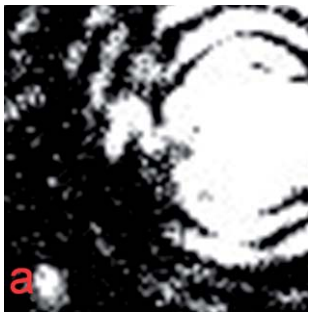

Fig. 5 SPPs propagate along nanowire, where point a is the point of the remote terminal of Ag nanowire.

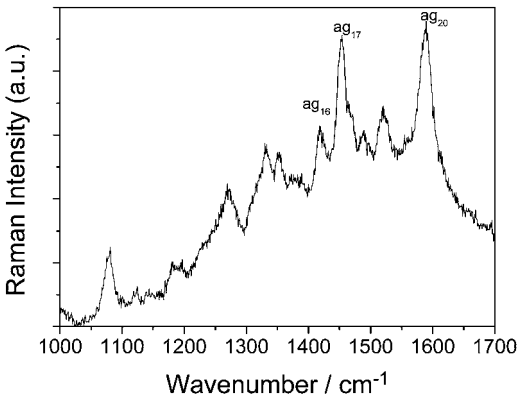

Fig. 6 The remote-excitation SERS spectrum measured at the remote terminal of Ag nanowire (point a in Fig. 1), and the laser is radiated on the nanoparticles (point b in Fig. 1).

waveguide. At the remote terminal of nanowire (point a in Fig. 1), the SERS signals were coupled out and measured, shown in Fig. 6.

Conclusions

We have demonstrated that the chemical information of surface catalyzed reaction can be propagated with plasmonic waveguide along the nanowire, and can be detected at the remote terminal of nanowire. So, the nanowires can be used as a sensor to propagate SERS spectra with plasmonic waveguide.

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