2002
doi:10.1017/S1431927622007772
Microsc. Microanal. 28 (Suppl 1), 2022

Nanoscale Imaging of Plasmonic Hot Spots in Au Nanocapsule Dimers by Ultrafast Electron Microscopy

Haihua Liu[1]*, Prem Singh[2], Amit Jaiswal[2], Thomas E. Gage[1], Ilke Arslan[1]

[1] Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL, USA
[2] School of Basic Sciences, Indian Institute of Technology Mandi, Kamand, Mandi, Himachal Pradesh, India
*Corresponding author: haihua.liu@anl.gov

The localized surface plasmon resonances (LSPR) investigations of nanoscale metal particles have been widely expanding in chemical and biological sensing [1], surface-enhanced raman scattering (SERS) [2], waveguiding [3], etc. LSPR resonance energies are highly sensitive to the shape, size, and composition of the plasmonic materials and the surrounding dielectric environments [4]. Tuning of the plasmonic energies is important for the design of metal nanostructures capable of providing large electric field enhancements at the hot spots for surface-enhanced spectroscopies [5] and biological sensing. Metallic nanorods (NRs) are among the most popular highly tunable plasmonic nanostructures because their plasmon resonances in both the longitudinal and transverse directions depend on the aspect ratio of the NRs (the ratio of the long to short axes) [6]. The nanorod dimer provides an alternate way to tune the plasmonic energies and generate hot spots according to plasmon hybridization theory [7]. Nanoscale imaging of the hot spots is critical for nanophotonics applications. Photon-induced near field electron microscopy (PINEM) developed within ultrafast electron microscopy (UEM) enables scientists to capture the evanescent electromagnetic field on its intrinsic time scale (picoseconds) on the nanometer scale [8, 9]. In PINEM, the free electrons gain or lose quantized photon energy when electrons spatiotemporally travel through the plasmonic field near the nanostructures. PINEM images formed by those electrons gaining photon energy are used for plasmonic field imaging in UEM at the nanometer scale.

Figure 1a shows a bright field image of one single Au nanocapsule (GNC) with a Au shell and Au solid core. Figure 1b and 1c are two PINEM images recorded at the delay time of t=0 ps under 1030 nm optical excitation with light polarization directions parallel to and perpendicular to the long axis of the GNC, respectively. Figure 1b shows electric field enhancements (hot spots) at the two tips of the GNC. The field enhancements are quite weak at the tips in Figure 1c because the longitudinal plasmon resonance of the GNC is close to 1030 nm and the transverse plasmon resonance is around 530 nm [10]. However, for the dimer of two side-by-side GNCs in Figure 1d under 1030 nm optical excitation, the PINEM image in Figure 1f under transverse light polarization excitation shows similar field enhancements at the tips compared with the PINEM image in Figure 1e under longitudinal light polarization excitation. In contrast with a single GNC in Figure 1c, the transverse plasmon energies of the GNC dimer in Figure 1f is highly tuned according to the nanorod dimer plasmon hybridization, in which the hot spots of the plasmonic field are clearly imaged by UEM with high spatial resolution. The nanoscale understanding of the electric field enhancements (hot spots) in plasmonic nanostructures by UEM is critical for advancing biological sensing and SERS methods [11].

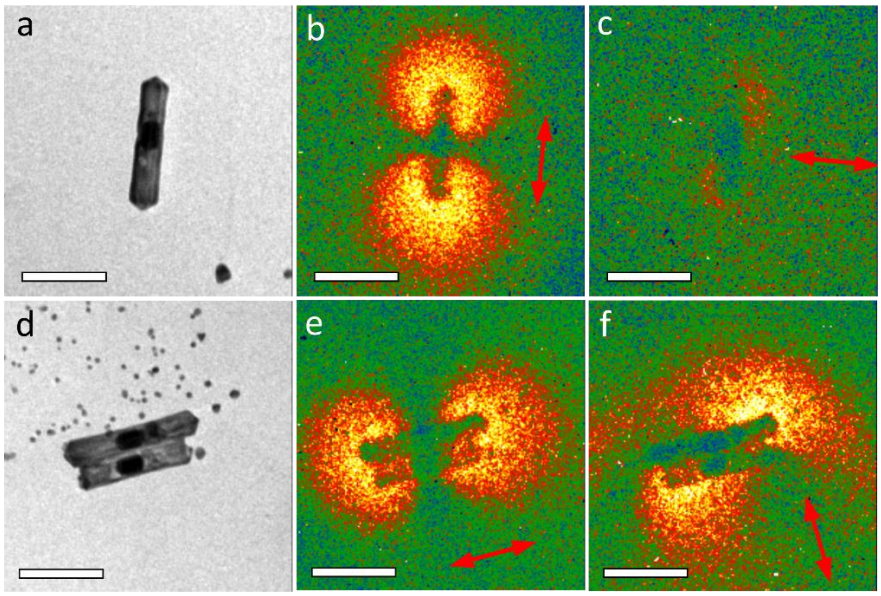

Figure 1. **a**, Bright field image of one Au nanoapsule. **b** and **c**, PINEM images of the Au nanocapsule obtained at the delay time of 0 ps with different light polarizations, respectively. **d**. Bright field image of one Au nanocapsule side-by-side dimer. **e** and **f**, PINEM image of the Au nanocapsule dimer with different light polarizations. The optical excitation wavelength is 1030 nm. The arrows in above images indicate the light polarization directions. The laser fluence is 1.3 mJ/cm^2. The scale bar is 200 nm. The false color in above images represents the PINEM image intensity for clear visualization of the plasmonic field distributions.

References:

[1] JN Anker et al., Nat. Materials **7** (2008), p. 442.
[2] R Laura et al., J. Am. Chem. Soc. **131**(13) (2009), p. 4616.
[3] SA Maier and HA Atwater, J. App. Phys. **98** (2005), p. 011101.
[4] KL Kelly et al., J. Phys. Chem. B. **107**(3) (2003), p. 668.
[5] M Moskovits and DH Jeong, Chem. Phys. Lett. **397** (2004), p. 91.
[6] S Link, MB Mohamed and MA El-Sayed, J. Phys. Chem. B. **103** (1999), p. 3073.
[7] B Willingham, DW Brandl and P Nordlander, Appl. Phys. B. **93** (2008), p. 209.
[8] AH Zewail, Science **328** (2010), p. 187.
[9] B Barwick, DJ Flannigan and AH Zewail, Nature **462** (2009), p. 902-904.
[10] P Singh, TAF König and A Jaiswal, ACS Appl. Mater. Inter. **10** (2018), p. 39380.
[11] This work was performed, in part, at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357 and in part, supported from the Department of Biotechnology (DBT), Government of India, under project number BT/PR14749/NNT/28/954/2015.

https://doi.org/10.1017/S1431927622007772 Published online by Cambridge University Press