Cathodoluminescence (CL) Spectroscopy and Imaging: A Powerful Tool in the Field of Plasmonics

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Abstract. Plasmonic nano-structures have received a great deal of attention lately because of their exceptional ability to confine light at the nanoscale. The highly enhanced E-M field around the plasmonic structure is frequently confined on a length scale of 10~50 nm. Furthermore, the enhanced E-M field varies greatly depending on the size, shape, periodicity, and composition of the nanoparticles (NPs). To understand the light-matter interaction at the nanometer level, an experimental tool that can directly visualize the nanoscale optical phenomena is required. In this respect, Cathodoluminescence (CL) spectroscopy and imaging technique have emerged as a novel experimental tool for directly visualising the local field enhancement around the NPs. We use CL spectroscopy and imaging to investigate the plasmonic behaviour of a gold (Au) nano particle with decahedral or pentagonal bi-pyramidal geometry.

Keywords: Cathodoluminescence (CL), Plasmon, Nanoparticle.

1. INTRODUCTION

Surface Plasmons (SPs), first predicted by Ritchie in 1957 , are coherent electron oscillations that exist at the interface between any two metal-dielectric interface [1]. Metals have large number of free electrons. When we excite the MNPs with an external EM wave (which could be a light wave or an evanescent wave associated with the first moving e-beam), these free electrons collectively respond by oscillating in resonance with the external EM wave. Surface Plasmons (SPs) are basically EM waves trapped in a metal dielectric interface. Due to their capacity to sustain localised surface plasmons (LSPs), noble metal nanoparticles (MNPs) have gained significant research interest in recent years [1, 2]. One of the important property of LSP is that it can decay into radiative photons that can be collected into far field. At localized surface plasmon resonance (LSPR) condition, the fields associated with these modes are strongly enhanced; they are also evanescent in character i.e. decaying exponentially with distance away from the particle and the decay length is about wavelength order.

Therefore at resonance local EM field is highly enhanced and localized around nanoparticle volume having a dimension of only 10-50 nm in x, y, z direction that is well below the light diffraction limit. In order to know the EM field distribution associated with the MNPs sufficient degree of spatial and spectral resolution is needed. LSP resonances can show highly localised enhancement in the near field around the nanoparticles also same enhancement around the far field intensity. The commonly used optical imaging techniques, such as UV-VIS spectroscopy or dark-field microscopy (DFM) are diffraction limited. As a result of this, these optical imaging techniques are not capable to correlate spectral and spatial distribution of an individual nanoparticle, rather they show the optical response over collection of particles at a time. Therefore, in order to understand the nanoscale optical phenomena an experimental tool with sufficient degree of spatial and spectral resolution must be used. In this respect, electron beam based spectroscopy [2-5] such as electron energy loss spectroscopy (EELS) in transmission electron microscope (TEM) [3-4] or cathodoluminescence (CL) [5-8] in a scanning/transmission electron microscope (SEM/TEM) has shown to be a marvellous tool for probing light matter interraction even sub nanometer resolution information in the spatial domain. The rebirth of plasmonics was partially triggered by our ability to visualize surface plasmons (SPs) through imaging with nm scale spatial resolution. The significance of imaging plasmons lies on the control over the propagation and control over the localization. And in this context, the electron microscopy techniques like EELS and CL are at the forefront. In 2001 Yamamoto et al. [5] showed for the first time that CL can be used to image plasmon excitations. Although the CL signal is much weaker compared to EELS signal,

there are few advantages of CL, such as it can be performed in SEMs which are more widely available and cheaper than TEMs. The remarkable aspect of CL microscopy lies in the fact that it presents a 'valse' between an electron, a plasmon, and a photon.

In this article we will discuss about CL spectroscopy and imaging technique, a novel experimental tool to directly visualize the local field enhancement around the single MNP in high resolution spectral and spatial domain.

2. ELECTRON BEAM EXCITATION AND CL

When an kiloelectronvolt (keV) electrons interact with an object, it can produce a variety of emitted signals such as secondary electrons (SE), backscattered electrons (BSE), X-rays as well as photons. The luminescence or emission of photon induced by a high-energy electrons (historically called as 'cathode ray') is known as cathodoluminescence (CL). In CL microscopy one generally analyze the emitted light from a sample in an electron microscope. The emitted light may be in the ultraviolet, visible, and infrared wavelength portions of the electromagnetic spectrum. Depending upon the degree of coherence [2] with respect to their field of impinging electrons, we can generally classified the CL emission process broadly into two categories, coherent and incoherent CL. Incoherent emission is commonly related with creation of electron-hole pairs and it is widely used in semiconductor technology and mineralogy for the characterization of materials. In metals electronic relaxation channels are much faster than radiative recombination. So that for metals, incoherent radiation has only a minor contribution to CL. Coherent CL radiation includes Cherenkov radiation, transition radiation and diffraction radiation. Although the creation of surface plasmons (SPs) is an indirect emission process, but also falls into the set of coherent emission. The CL emission generally comes from the skin depth under the sub-surface of metals (~ 20 nm in the visible and NIR for noble metals). This drastically minimizes any other effects arising from the electron solid collision cascade produced by the impinging electron probe in deeper region. Thus for metallic nanostructure emitted CL signal mainly generated from the decay of plasmon modes into photons, that constitute one of the prominent decay channels for the plasmons [2,3].

When a first moving electron beam is focused onto or close to the nanostructure of interest, it will transfer some part of it's energy to the nanostructure via electromagnetic interaction (Figure 1). During this process the electron beam loose some amount of energy while the nanoparticle gain same amount of energy that electron is lost. The amount of energy that is lost by the electron is generally measured through electron energy loss spectroscopy (EELS). However the sample re-emits a part of the absorbed energy in the form of photon to return to equilibrium via a radiative decay channel. This gives rise rise to the CL signal for metallic nanostructures. The energy from the incident electron beam is coupled to the plasmon modes of the metal nanostructure and consequently these excited surface plasmon mode decay into radiative photons.

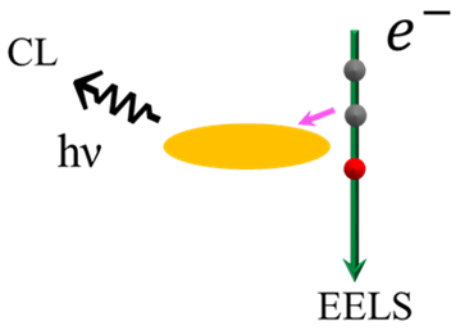

Figure1. Schematic diagram of the basic principle of cathodoluminescence in metallic nanostructures.

From CL spectra one can easily access the energy of the emitted photons. CL spectra gives the energy characteristics of the radiative decay channel. In particular, CL probes the scattering physics, while EELS probes the extinction physics. i.e. total loss due to both scattering and aborption.

3. METHODOLOGY

Cathodoluminescence (CL) in a SEM: The schematic diagram of CL-SEM set up is shown in Figure 2. It consists of two units; a probe forming unit that delivers few nanometer size focused electron beam (ZEISS SUPRA40 field emission gun (FEG) SEM) and an optical detection unit (MonoCL3, Gatan)[6]. Zeiss Supra 40 SEM consists of several units such as column chamber, specimen chamber, detectors and vacuum unit. The CL unit is equipped with a retractable paraboloid mirror, a monochromator grating, and a photon detector unit.

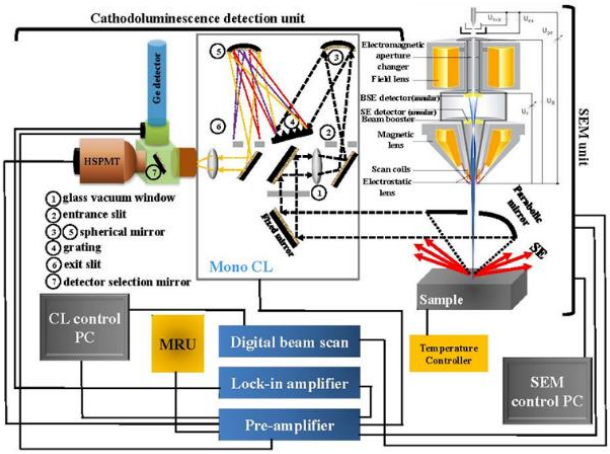

Figure 2. Schematic diagram of cathodoluminescence in scanning electron microscope (CL-SEM) system installed at the Saha Institute of Nuclear Physics, Kolkata. Image adapted from Ref. 6.

The light detection unit (Gatan MonoCL3) is mainly controlled by Digital Micrograph TM software controls system. Details of the CL-SEM unit has been described elsewhere [6]. During CL operation, the energetic e-beam from the SEM impinges on the sample surface through the 1 mm diameter hole of the retraceable mirror that is inserted manually to a position directly beneath the pole piece of SEM. The photograph of the CL parabolic mirror is shown in Figure 3.

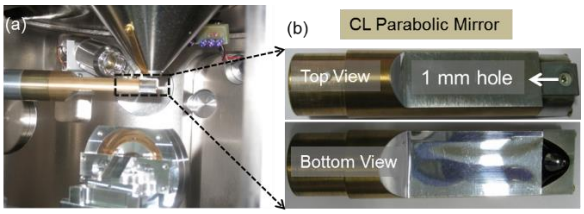

Figure 3: (a) Photograph of the CL parabolic mirror and SEM pole piece. (b) Zoomed view of CL parabolic mirror (views from top and bottom).

During CL operation, the top surface of the sample was placed at the focal plane of the parabolic mirror for maximum efficiency of light collection. Otherwise, no meaningful CL spectroscopy and imaging is possible due to very small signal-to-noise ratio. The light emitted from the sample surface is collected through the parabolic mirror. The angular range covered by the parabolic mirror is 1.42π sr of the full 2π of the upper half sphere. The gathered light signal is then collimated through a hollow aluminium tube and delivered to an optical monochromator of the Czerny-Turner type with a 300 mm focal length. Finally, the signal from the monochromator is fed to a Peltier-cooled high sensitivity photomultiplier tube (HSPMT). It is possible to use the combined CL-SEM system in panchromatic or monochromatic mode. When operating in monochromatic mode, light travelling through the monochromator enables the creation of CL images and spectra at a chosen peak wavelength. A dispersive element has been included between the CL collector and the detector in the monochromic mode of operation. Since a diffraction grating monochromator (in our case either 1200 lines/mm or 600 lines/mm) makes it simple to choose a desired spectral wavelength, it has been utilised as a dispersive element. When obtaining spectra, the electron beam is either swept over the specimen's area of interest or is fixed in place (spot mode), and the produced luminescence is examined spectrally. After averaging over three to four spectra for each e-beam point, final spectra are obtained and the substrate background is removed. Then, by scanning the e-beam over the sample, the monochromatic photon map is constructed at a chosen peak wavelength of the emission spectrum. The luminescence is gathered over the entire sample for each e-beam point. The regions where the strongly excited plasmon mode emits the photons are then represented by the bright pixels. We obtain a full CL map of the plasmon mode associated with a specific wavelength by adding all of the position dependent partial maps obtained for each e-beam position. Contrarily, in the panchromatic mode of imaging, light avoids the monochromator and is sent directly to the HSPMT to create the panchromatic photon maps. The contrast in the CL image is therefore brought about by the difference in photon counts or light intensities between any two places. We emphasise that CL mapping for metallic nanostructures reveals the efficiency with which electron energy is coupled to far-field radiation as a function of electron injection position.

4. RESULTS AND DISCUSSION

Mapping plasmons on an Individual Au Decahedron.

To demonstrate the versatility of the CL-SEM technique, we present plasmon-induced luminescence from an isolated Au decahedron. The SE image of a Au nano decahedron of side edge length 220 nm is shown in the Figure 4 (a). The panchromatic CL image of this Au nano decahedron is shown in Figure 4 (b). The PanCL image clearly shows the plasmon-induced luminescence in the Au nanoparticle. It is interesting to note that almost no photon is emitted from point 4 and 5. This is due to the fact that in our experiment, the decahedron is supported on the Si substrate with one of its faces in contact with it, and as a result, that face has

a strong interaction with the high index substrate Si. Because the LSPR mostly radiates towards the high index Si substrate, very few photons will reach the upper hemisphere CL detector. This reduces the amount of photons emitted in the upper hemisphere, explaining the negligible emission intensity for e-beam excitation at corners 4 and 5. The pan CL images, however, do not offer wavelength-specific data that would enable us to pinpoint the precise plasmonics modes responsible for the radiative response. CL spectroscopy and imaging in monochromatic mode are required to obtain spectrally resolved features. The experimentally depicted CL spectra from different beam injection position of the decahedron has been shown here in Figure 4c. The decahedron's various e-beam impact positions are indicated here with numbers from 1 to 7, as in Figure 4. (a)

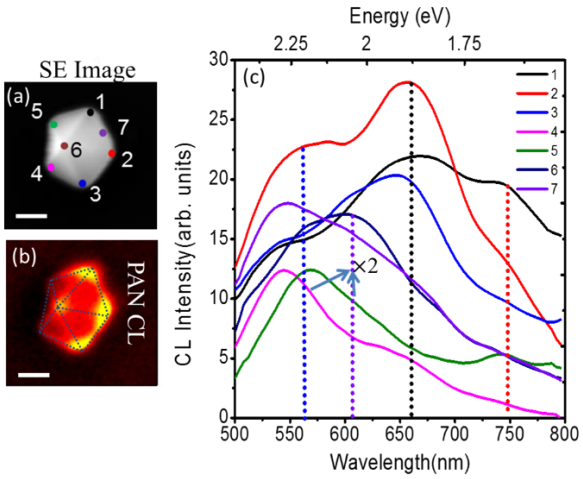

FIGURE 4. a) SEM image and (b) corresponding panchromatic CL image on an isolated Au decahedron of side edge length 220 nm. (c) Experimentally obtained CL spectra from different beam injection positions of the decahedron. The SE image shows the e-beam impact points (marked as 1, 2, 3...7) with different colored dots.

As shown in Figure 4c, the spectral peak intensity and peak position are highly dependent on the position of the electron beam. When we excite point 1, we see three distinct peaks at approximately 570 nm, 670 nm, and 750 nm. For excitation over point 2, the first two peak positions were noticeable, but the 750 nm peak was very weak. The various peak positions correspond to various plasmonic modes. We mapped the spatial distribution of photon emission at different resonant wavelengths to better understand plasmon-induced photon emission, as shown in Figure 5. The spatial distribution of photon emission can be directly visualised over a length scale much smaller than the wavelength of light. The monochromatic CL image at 570 nm shows maximum intensity along the side and corner edges.

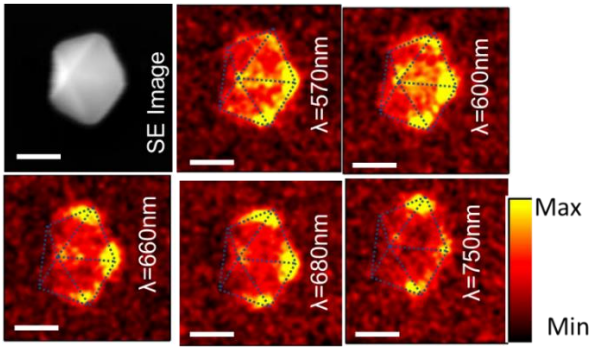

Figure 5. Monochromatic CL emission maps on an isolated gold decahedron on silicon.

Photon maps at 660 and 680 nm, on the other hand, show maximum luminescence coming from the pentagonal base corner points. Aside from the 750 nm peak, monochromatic photon maps of all other resonant wavelengths show significant luminescence from the tip apex (point 6), which is consistent with our spectroscopic data. Using finite-difference time-domain (FDTD) simulations we have explicitly shown that origin of 750 nm mode is purely from a substrate induced LSPR mode [8]. Using FDTD numerical analysis we have also demonstrated that the longer wavelength (660 nm) mode has the dipolar charge pattern in both directions, whereas the shorter wavelength (570 nm) mode has a mixture of in-plane quadrupolar and out-of-plane quadrupolar charge distribution pattern. [8].

5. CONCLUSIONS

It is clear from the preceding analysis that using CL-SEM, one can not only capture high resolution spectroscopic information but also record maps of spatial variation of light emission, or the EM local density of states (EMLDOS) with high spatial resolution (10-50 nm range). CL detects radiative modes without disturbing the local environment, making CL-SEM a powerful tool for direct LDOS analysis at the single nanoparticle level.

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