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Electron Energy-Loss Spectrometry (EELS) and Energy-Filtered TEM (EFTEM) Analyses of Organic-Inorganic Nanoparticles

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Composite Organic-Inorganic Nanoparticles (COINs) [1,2] are novel surface-enhanced Raman scattering (SERS) nanoclusters formed by aggregating inorganic silver nanoparticles in the presence of organic Raman-active molecules (Fig. 1 and [3,4]). They are then encapsulated with bovine serum albumin and cross-linked with glutaraldehyde to facilitate subsequent functionalization with antibodies. COINs exhibit higher Raman scattering efficiency and narrower emission peaks than traditional fluorescent labels, and can be used to detect antigens in tissue sections [5].

We applied EELS and EFTEM techniques to study COINs to gain insight into their SERS enhancement effects. Low-loss EELS analyses were performed using the FEI Tecnai F20 UT located at the National Center for Electron Microscopy (NCEM), Lawrence Berkeley National Laboratory (Berkeley, CA) [6]. The microscope was operated at 200kV in monochromated STEM mode. We found that COINs exhibit a range of surface plasmon energies, from 3.5eV to 3.7eV, at junctions between the silver nanoparticles (Fig. 2). These values do not correspond exactly to the 3.5eV surface plasmon energy nor the bulk plasmon energy of 3.8eV that have been reported in the literature [7,8]. Using the TEAM 0.5 microscope at NCEM [6], we applied EFTEM spectrum imaging (EFTEM SI) in the low energy-loss region (1 to 6 eV, in intervals of 0.1eV) to obtain maps showing the plasmon energy distribution in COINs (Fig. 3). So far, our results show that COINs exhibit different surface plasmon modes, possibly due to their heterogeneous nature. We demonstrate that EELS and EFTEM SI techniques can be applied to investigate plasmons in COINs.

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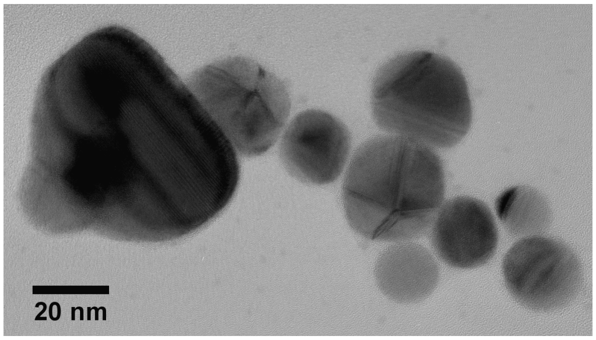

Fig. 1. TEM bright field image of a COIN. COINs are clusters composed of smaller silver nanoparticles of different dimensions.

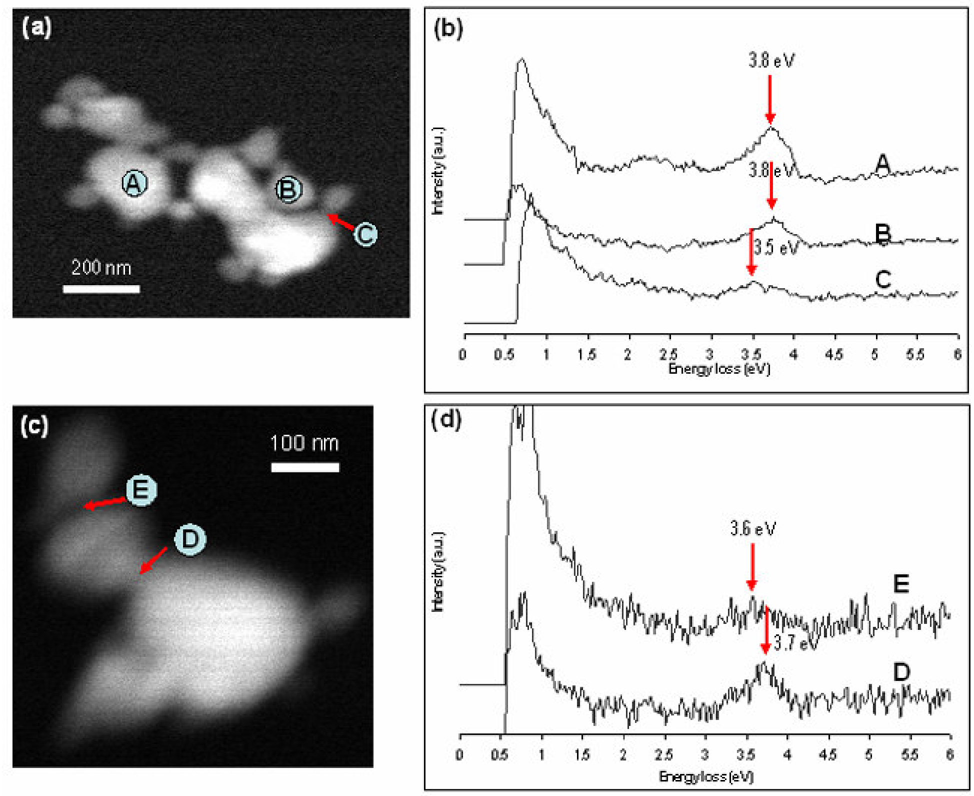

Fig. 2. (a) and (c) are HAADF-STEM images of COINs whose corresponding low loss spectra are shown in (b) and (d). COINs exhibit a range of surface plasmon energies.

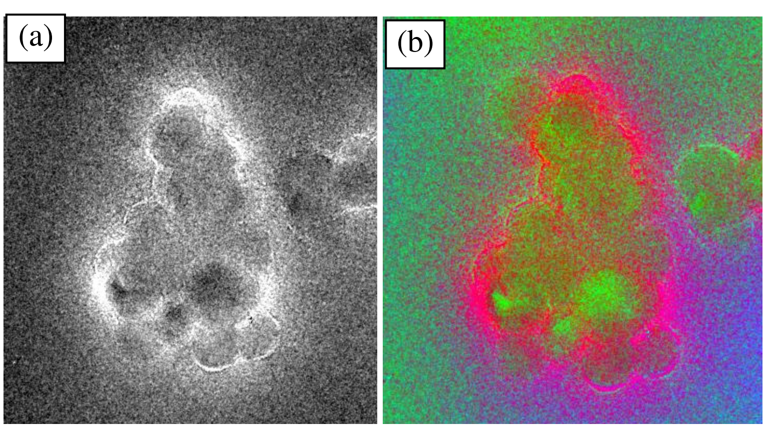

Fig 3. (a) EFTEM spectrum image slice of a COIN and (b) the corresponding map showing the distribution of surface plasmon (Red), bulk plasmon (Green) and background (Blue) after multiple least squares fitting was applied.

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