Cathodoluminescence Nanoscopy of 3D Plasmonic Networks

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ABSTRACT: Nanoporous metallic networks are endowed with the distinctive optical properties of strong field enhancement and spatial localization, raising the necessity to map the optical eigenmodes with high spatial resolution. In this work, we used cathodoluminescence (CL) to map the local electric fields of a three-dimensional (3D) silver network made of nanosized ligaments and holes over a broad spectral range. A multitude of neighboring hotspots at different frequencies and intensities are observed at subwavelength distances over the network. In contrast to well-defined plasmonic structures, the hotspots do not necessarily correlate with the network morphology, emphasizing the complexity and energy dissipation through the network. In addition, we show that the inherent connectivity of the networked structure plays a key optical role because a ligament with a single connected linker shows localized modes whereas an octopus-like ligament with multiple connections permits energy propagation through the network.

INTRODUCTION

Nanoporous metallic networks constitute a new class of advanced materials comprising multimodal nanosized blobs connected to each other to form a disordered 3D structure. Their distinct structural properties, including high surface-to-volume ratio, ability to host guest materials, pure solid connectivity, and high surface curvature, endow them with optical properties that can be found neither in conventional (well-defined) plasmonic structures nor in bulk metals.1–14

It has been previously shown by us15–17 and others18–33 that this class of connected metallic nanomaterials (two-dimensional (2D) networks as well) exhibit strong local fields over a broad optical range. These fields are confined to subwavelength volumes and are termed hotspots. The associated strong electric fields that exist in these hotspots lead to exceptional enhancement of the nonlinear optical properties of the network,13,16,20–23,33–38 and even to the occurrence of photothermal processes and reactions inside and on the network.1,2,15,39–41 Both phenomena are outcomes of the high local density of optical states (LDOS) expected on the basis of the strong field enhancement and spatial localization,18,31,38,42–44 raising the necessity to map the optical eigenmodes with high spatial resolution.

Diffraction-limited far-field optical measurements are not adapted for characterizing these local effects, as field fluctuations and spectral resonances are averaged and result in a broad spectral response.4,41,45–47 Even near-field techniques, like near-field optical microscopy, are limited in their ability to retrieve spatial confinement in these highly topographic networks at a broad range of frequencies.45,46,48

On the other hand, electron microscopy techniques such as electron energy loss spectroscopy (EELS) and CL can meet those challenges because in these techniques the excitation results from an interaction with a highly localized (subnanometer) electron beam.29,45,46,48–54 Additionally, the beam is considered as a “white source” comprising a broad range of frequencies and is therefore able to excite all available modes in the sample.

In a raster-scanning geometry, it is possible to retrieve the full spectrum from each pixel of the entire scanned sample with nanometer resolution. In EELS, one measures the energy transfer from electrons to plasmons by calculating the energy loss of electrons that have passed through the sample. In CL, on the other hand, photons scattered by the sample are directly collected, reflecting the efficiency of the decay of plasmons into radiation. Thus, in either technique it is possible to map the local electric fields with nanoscale resolution (for further information, see the Supporting Information)29,40,52,55,56. As EELS is measured in transmission, it is not suitable for thick 3D samples such as those studied here (with a thickness of a few micrometers).

In this work, we used CL to map the local electric fields of a nanoporous silver network over a broad spectral range spanning the ultraviolet (UV), visible (VIS), and near-infrared (NIR) regions. A multitude of hotspots at different frequencies and intensities were observed at subwavelength scales. In contrast to well-defined plasmonic structures, the hotspots do
not necessarily correlate with the network morphology, reflecting the complexity of the network and possible interactions between the building blocks as well as energy dissipation through the network. However, accidental large cracks in the studied network could be distinguished by collecting CL emission in the NIR. In addition, we show that silver ligaments that are multiply connected ("hubs") permit energy flow through the network and therefore show different optical behavior compared with ligaments that are linked to the network presumably via a single string.

### RESULTS AND DISCUSSION

The polychromatic optical response of the nanoporous silver network and its corresponding scanning electron microscopy (SEM) image are shown in Figure 1a,b, respectively. The CL emission is due to excitation of surface plasmon (SP) modes of the 3D silver network. The emission pattern is rich in localized spots spanning the VIS–NIR regime (Figure 1c) demonstrating the functional potential of the network and in agreement with its reported transmission spectrum. The observed hotspots are mixed modes of different frequencies, reflecting energy dissipation as well as coupling through the 3D network. Furthermore, modes with different energies and intensities over subwavelength distances are observed, a possible indication of light localization.

Modes appear from both metal ligaments and hole regions (see Figure 1b,c), and no clear correspondence between the network morphology and hotspot locations is observed (see Figure 1d for the panchromatic CL image and Movie S1). This observation is in agreement with previous studies on 2D metallic networks, wherein it was attributed to the topological complexity of the 2D network. The network topography is revealed by the selection of a spectral range of 330 ± 10 nm, the silver bulk plasmon wavelength (Figure 1e). Additional interesting features are detectable in Figure 1a. For example, the rim of a large crack (see the white curved contour line) is characterized by red-shifted emission that can be distinguished upon selection of the 775 ± 10 nm band from the hyperspectral CL map (see Figure 1f). Plasmon coupling between nearby ligaments and particles along the crack lowers the mode energy and is therefore expressed as a red-shifted CL emission area.
inherent property of this type of solid interconnected 3D network that contributes to the complex multimodal CL emission observed from the studied network.

To better understand the optical outcome of the inherent structural connectivity of the network and its optical robustness, we studied in detail the CL emission from two prototypical network structural elements (see Figure 2). One structural element is characterized by single connectivity, as it is linked at its bottom to the rest of the network (Figure 2a). Contrarily, the second prototypical element is an octopus-like fragment that is characterized by high-connectivity, with at least seven connection points to the whole 3D network structure (Figure 2b). The SEM image in Figure 2c shows such prototypical network features at the same scan.

Differences between the two prototypical optical elements are demonstrated by their overlaid polychromatic CL images at $\lambda_{CL} = 460 \pm 15$, $500 \pm 15$, and $620 \pm 15$ nm. Whereas localized modes can be assigned at the low-connectivity ligament (Figure 2d), the CL emission detected from the octopus-like fragment is relatively weak and diffuse (Figure 2e).

CL spectra extracted from the low-connectivity ligament quantitatively reflect the ample number of localized modes owned by this single network ligament (Figure 2d); intense CL emissions at different wavelengths (e.g., 400, 420, and 500 nm) are observed from three spots located at subwavelength distances from each other on the ligament. On the other hand, similar spectra are observed from spots located on the octopus-like ligament with about a half order of magnitude less intensity (Figure 2g).

Next, we studied the spatial distribution of plasmonic modes of the two prototype ligaments mentioned above. Six monochromatic CL emission maps over the range of 400–650 nm are presented in Figure 3 for both the singly connected ligament and the octopus-like ligament.

For the singly connected ligament, a clear spatial confinement of the modes located on the ligament is revealed within the range of 400–500 nm, indicating energy localization. At relatively high mode energies (400–500 nm), the CL emission patterns are spatially localized, and the localized modes fluctuate in energy and intensity. At lower mode energies (600 and 650 nm), the CL emission is delocalized along the ligament and is less intense. In all of the maps, the emission is lowest at the ligament center, where the metallic morphology is narrower and thinner. Such ligaments of low-connectivity support high-intensity modes that are spatially confined to steep subwavelength volumes. In addition, intense CL emission is observed from the gap between the upper neighboring tip and the low-connectivity ligament (Figure 3). The emission peak is observed at about 500 nm and is probably related to coupling of this neighboring tip to the ligament coming into expression by green light emission (see Figure 2d).

Figure 3d maps the CL emission of the octopus-like ligament. Here, unlike the low-connectivity ligament, little emission is observed, and it is diffused around the “hub” (also see Figure S3).

Hotspot Fluctuations. Enhancements of local fields at different frequencies are observed, as shown in Figure 4. Monochromatic CL maps extracted from two different locations are presented in Figure 4a,b. The observed hotspots (high CL intensities) are wavelength-dependent, and their intensities fluctuate, in agreement with our former studies on nonlinear responses of nanoporous 3D metallic networks.16 Figure 4c shows three sets of point CL spectra from proximate network locations (~150 nm). The observed spectra of the plasmonic modes fluctuate in both energy and intensity at

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Figure 2. Effects of the network’s building block connectivity on the CL response. (a, b) Illustration of (a) low- and (b) high-connectivity network ligaments (marked in yellow). The low-connectivity ligament in (a) possesses one bottom connection point to rest of the network and has two disconnected ~250 nm wings. Contrarily, the high-connectivity ligament in (b) is a nodal ligament with an octopus-like shape having at least seven connection points to the whole 3D network structure. (c) SEM image in which both low- and high-connectivity network ligaments appear (see Figure 2f). The polychromatic CL images are made of overlapped monochromatic CL maps at the upper and lower dotted-line squares, respectively, as illustrated in (a) and (b), respectively. (d, e) Polychromatic CL images of the ligaments marked in (c). The polychromatic CL images are of overlapped monochromatic CL maps at $\lambda_{CL} = 460 \pm 10$, $500 \pm 15$, and $620 \pm 15$ nm. The discrete monochromatic CL maps color-coded according to the emitted color (blue, green, and red, respectively) are shown in Figure S2. (f, g) Local CL spectra corresponding to the probe positions indicated in (c) and in the insets in (f) and (g). The difference in the CL intensity scale bars in (f) and (g) should be noted.
subwavelength distances. Modes fluctuate from about 420 to 580 nm at a distance of about 100 nm. Figure S4 shows three additional sets of point CL spectra from locations on the network in Figure 1b that are distanced by ∼50 nm. However, at far field the different resonances are averaged out, giving rise to a very broad spectrum as was reported previously.15,16

In the context of strong coupling photochemistry, molecules deposited in and on such a metallic network will experience very strong fields, which may alter their emission rates and directionality as well as their physical and chemical properties.58–63 Such localized hotspots can lead to modification of the surface potential energy along a given reaction coordinate and open new pathways for energy redistribution that are not accessible through homogeneous catalysis, for example. In addition, the excited plasmonic modes of the network may induce crosstalk between remote molecules deposited on and inside the network, resulting in a supramolecular hybrid system with outstanding optical and chemical properties. We think that the metallic network offers a broadband spectral range for strong interactions and the possibility to host molecules in the large pores, forming a large-scale 3D molecular plasmonic network. Strong coupling between molecules and the network plasmonic modes should result in hybrid states with longer dephasing times and therefore should lead to enhancement of nonlinear optical phenomena such as Raman and second harmonic generation.15,16 Raman spectra of C60 deposited on the 3D silver network and their reduction process with up to five or six electrons have been shown previously.15

### CONCLUSION

We have experimentally mapped local fields of a 3D silver network by CL nanoscopy. The disorder in such materials is characterized by mixed eigenmodes with fluctuating frequencies and intensities at subwavelength distances, reflecting the topological complexity of the network. A correspondence between the network morphology and the hotspots was found only in the presence of a large crack, where the observed hotspots at the rim of the crack are intense and in the IR regime. The network connectivity prominently affects the LDOS, such that high-connectivity leads to energy propagation through the network. To the best of our knowledge, this is the first experimental demonstration of CL properties of a 3D metallic networked system with a thickness of a few micrometers.

The large-scale lateral dimensions of the networks together with the random localized hotspots suggest that 3D plasmonic networks can exhibit superior performance in a range of technological fields including photonics, optoelectronic devices, photocatalysis, sensing, bioimaging, and quantum information. They can as well be used as fruitful systems for fundamental science endeavors.

### EXPERIMENTAL METHODS

**3D Silver Network Preparation.** Samples of 3D nanoporous silver networks were prepared by sputtering on a silica aerogel substrate as detailed elsewhere.15 In brief, sample
preparation comprises two steps: (1) aerogel substrate synthesis and (2) physical vapor deposition. Silica aerogels were synthesized by a one-step base-catalyzed sol−gel process followed by drying with supercritical CO2 (K850, Quorum). Metals were sputtered (682, Gatan) from pure targets (99.99%, Kurt J. Lesker).

CL Measurements. CL studies were performed on an Attolight Rosa 4634 CL microscope (Attolight AG, Switzerland), which tightly integrates a high numerical aperture (N.A. = 0.72) achromatic reflective lens within the objective lens of a field-emission-gun scanning electron microscope (FEG-SEM). The focal plane of the light lens matches the FEG-SEM optimum working distance. CL was spectrally resolved with a Czerny−Turner spectrometer (320 mm focal length, 150 grooves/mm grating) and measured with a high quantum-efficiency CCD camera (Andor Newton 920) suitable for UV−VIS and NIR spectroscopy. The acceleration voltage and emission current of the electron beam were 7 kV and 20 nA, respectively. The CL data were analyzed using Mountains v.8 (Digital Surf) and MATLAB.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c03317.

Monochromatic components of the polychromatic CL image in Figure 1a (Figure S1); monochromatic components of the polychromatic CL images in Figure 2d,e shown at a higher magnification and presenting both low- and high-connectivity structural elements of the 3D silver network (Figure S2); CL response of a highly connected nodal network ligament (Figure S3); demonstration of hotspot fluctuations at an additional 3D silver network scan (Figure 1b) by point CL spectra extracted from proximal probe positions (~50 nm apart) (Figure S4); panchromatic CL map of the network in Figure 4b over the range of 250−790 nm (Figure S5); resolution of CL imaging (PDF) Monochromatic CL images (250−790 nm) of the network in Figure 1b (MP4).

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ACKNOWLEDGMENTS

R.R. thanks the Charles Clore Foundation for a fellowship for Ph.D students. This work was supported by the Energy and Water Resources Ministry of Israel (Grant 016-11-216) and the Israel Science Foundation (ISF) (Grant 1231/19).

ABBREVIATIONS

CL, cathodoluminescence; 2D, two-dimensional; LDOS, local density of optical states; EELS, energy electron loss spectroscopy; UV, ultraviolet; VIS, visible; NIR, near-infrared; SEM, scanning electron microscope; SP, surface plasmon; PanCL, Panchromatic CL; FEG-SEM, field-emission-gun scanning electron microscope

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