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PUSHING THE BOUNDARIES OF NANOCRYSTAL OPTOELECTRONICS WITH STRUCTURED PHOTONIC ENVIRONMENTS

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This article discusses the prospect of advanced functionalities in the field of nanocrystal optoelectronics using structured photonic environments, with a particular emphasis on near-infrared light-emitting diodes. The ability to achieve full control of brightness, colour, phase and polarization is highlighted, as well as the importance of determining whether a local or non-local photonic response is required to achieve a given functionality. These developments have implications for various applications, including displays, communication protocols and sensors.

1. Introduction

Colloidal semiconducting nanocrystals surrounded by ligands (NCs) have emerged as attracting materials in optoelectronics [1]. Because their electronic wavefunctions are confined due to their small size, the properties of NCs are not solely related to their chemical composition and that of their ligands, but also to their geometry, dimensions and neighbouring environment. This extended parameter space makes it possible to develop optoelectronic devices in energy ranges that are difficult to access with standard approaches, as is especially the case in a number of infrared windows. NCs are also highly valued in the visible range where they are used in high-end displays as bright secondary sources that reemit light with different colours than the pixels underneath. A number of NCs also favours the excitation of hot electrons which play a key role in the ongoing race to develop solar cells with efficiencies exceeding the Queisser-Shockley limit.

Much of the promises of colloidal NCs have been fulfilled thanks to the staggering progresses in chemical synthesis and processing. This, in turn, has led to tremendous developments in solution-processed optoelectronic devices, in which thin solid films of NCs replace standard semiconducting wafers. Now that the material part has gained maturity, one of the next frontiers is to increase the performances even further and to obtain new functionalities by hybridizing the NC films with tailored photonic environments, such as gratings, metasurfaces or optical antennas. Since NC films are composed of many emitters, two important questions arise: what is the most relevant framework to describe their interactions with their surroundings, and to which extent can we tailor and leverage their properties? In the following, we will tentatively address these questions by reviewing some of our work on ensembles of PbS NCs, one of the most studied colloidal materials and thus considered a model system.

2. Results

We begin this discussion with Figure 1, depicting the experimental behaviour of an LED in which the active medium, a thin (~15-20 nm) layer of PbS NCs, is covering a metasurface made of metallic nanorods [2]. All nanorods have the same subwavelength dimensions and periodicity; however, a part of them is made of Au, to form the character 光, while the rest is made of Pt (Figures 1a-1b). Figure 1c shows the infrared electroluminescence emitted by the device after passing through a linear polarizer aligned along the long axis of the rods. The 光 pattern is clearly visible and its intensity is more than three times higher than the rest of the patterned area made of Pt nanorods. In other words, the Au nanorods locally enhance the brightness of the LED. This behaviour can be attributed to the fact that they act as radiant optical antennas for this polarization, due to their ability to sustain plasmonic resonances resulting from the resonant hybridation of the free electrons of the metal and the photons emitted by the NCs. In this wavelength

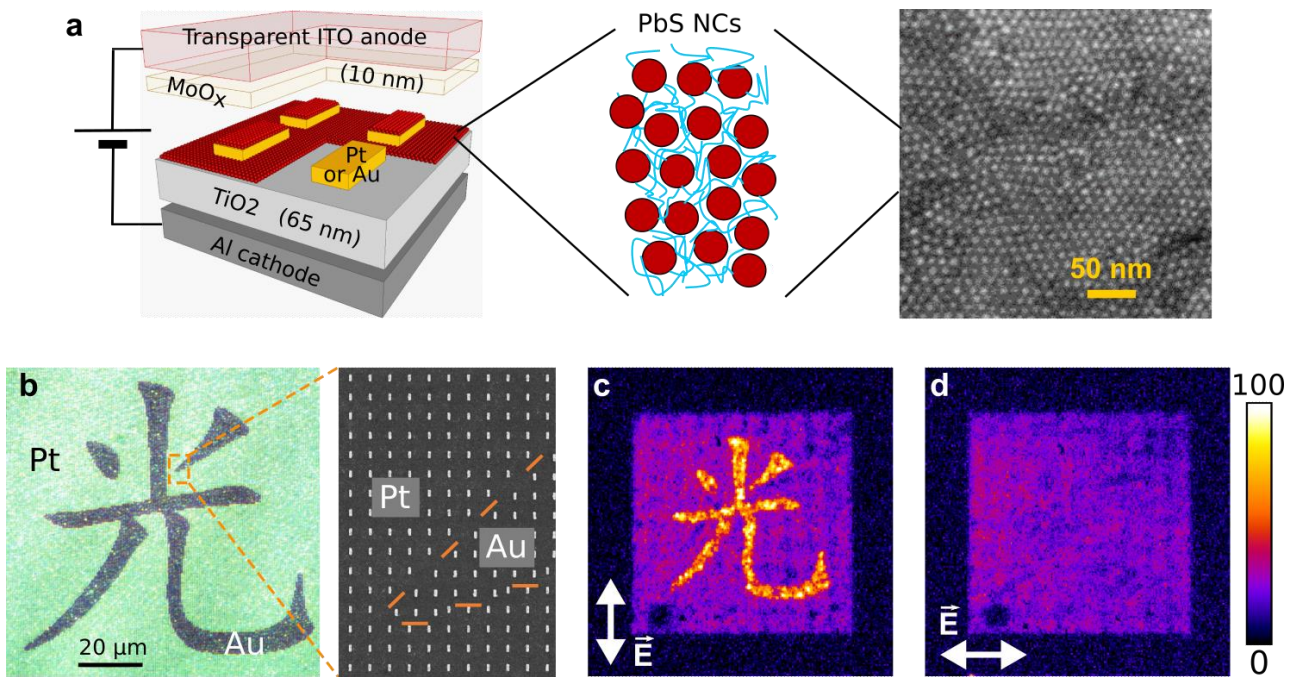


Figure 1. **a.** Schematic of an infrared LED operating with PbS NCs hybridized with arrays of Au and Pt nanorods. The blue lines in the middle sketch represents the organic ligands surrounding the NCs. A scanning electron micrograph (SEM) of a PbS NC film is shown on the right panel. **b.** Optical (left) and SEM (right) images of the Au and Pt nanorod arrays (period: 500 nm). **c.** Infrared electroluminescence of the device seen through a linear polarizer aligned with the long axis of the nanorods. **d.** Electroluminescence of the device when the linear polarizer is rotated by 90°.

Adapted with permission from [2].

range, no plasmon can be excited with Pt nanorods, explaining why a contrast between the two metals is observed. When the same LED is observed through a linear polarizer aligned perpendicularly to the nanorods (Figure 1d), the 光 pattern disappears because no plasmon resonances are sustained by the Au nanorods for this polarization.

This experiment shows that non-trivial light emitting patterns can be engineered by structuring the photonic environment of the PbS NCs at the nanoscale. It also provides key information about the coupling mechanism between the PbS NCs and the metasurface. According to textbook theory describing the interactions of individual emitters and metals, which is based on the Fermi golden rule and the photonic local density of states [3], the electroluminescence should have been quenched for both polarizations because the PbS NCs are in direct contact with the metallic inclusions, favouring non-radiative energy dissipation within Au and Pt over light emission. Figure 1c shows that this model does not apply in our case since the Au nanorods provide a substantial electroluminescence enhancement for one polarization. Perhaps even more strikingly, Figure 1d shows that for the non-resonant polarization, the electroluminescence brightness above Au is undistinguishable from that above the non-resonant Pt inclusions (and still above the levels of the black regions framing the picture, corresponding to the emission of PbS NCs outside the Pt/Au metasurface). **This result is spectacular because Pt is a metal with ten times more material losses than Au, yet, the electroluminescence is not affected by this additional loss.**

To understand these results, we note that the emitters do not only interact with the metal inclusions, but also with each other (via electronic and/or dipole-dipole coupling) and with the phonon population of the PbS NCs. Said otherwise, radiative and non-radiative coupling to the metasurface is but one of the many possible channels through which each PbS NC exchange or dissipate energy. To take these mutual interactions into account, it is useful to draw an analogy with bulk semiconductors in which excited carriers also mutually interact and also exchange energy with phonons, leading, after sub-picosecond processes, to the formation of thermalized populations of electrons and holes characterized by Fermi-Dirac distributions (in this context, “thermalized” means that the carrier populations are in thermal equilibrium with the semiconducting host). The luminescence $I(\lambda)$ of such a medium is related to its absorption cross-section $A(\lambda, \Delta\mu)$ via a non-thermal form of the Kirchhoff law [4]:

$$I(\lambda) = A(\lambda, \Delta\mu) \cdot \frac{2hc^2}{\lambda^5} \frac{1}{\exp\left[\frac{hc/\lambda - \Delta\mu}{k_B T}\right] - 1} \quad (1)$$

In this expression, λ is the wavelength of emission, $\Delta\mu$ is the chemical potential of radiation (i.e. the difference between the quasi Fermi levels), k_B the Boltzmann constant and T the carrier temperature. Under weak pumping, $\Delta\mu$ is small and Equation (1) can be further reduced to:

$$I(\lambda) \approx A(\lambda) W(\lambda, T) \exp\left[\frac{\Delta\mu}{k_B T}\right], \quad (2)$$

where $A(\lambda)$ is independent of $\Delta\mu$ and $W(\lambda, T) = 2hc^2\lambda^{-5}\exp[-hc/(\lambda k_B T)]$ is the Wien approximation of Planck's law.

Figure 2a demonstrates that the luminescence of our devices follows Equation (2). The sample under consideration is similar to the first example, except that the metasurface is solely made of Au inclusions. The left panel of Figure 2a reveals that the luminescence spectrum greatly varies with the excitation conditions. Yet, the right panel shows that it is possible to superimpose all the traces by renormalizing them with the ratio $W(\lambda, T_i)/W(\lambda, T_1)$, where $T_{i=1,2,3,4}$ are carrier temperatures that have been adjusted to obtain this result. The fitted temperatures, which range from 300 K to 387 K, are reasonable because they increase with the power used to excite the device.

Figure 2a shows that the spectra are modulated by the Wien radiance $W(\lambda, T)$, in accordance with Equation (2). **This result leads to two key conclusions.** The first is that an assembly of interacting NCs acts as an effective semiconducting medium in which the excited carriers are thermalized, albeit at a temperature that can be higher than that of the host matrix. The second is that the metasurface's ability to induce changes in the luminescence properties stems from its ability to modify the absorption cross-section of the coupled emitters *at the wavelength of emission*. Figure 2b confirms this latter point by showing that the photoluminescence boost obtained by hybridizing a layer of PbS NCs with a Au metasurface specially designed to take full advantage of the Kirchhoff regime occurs at the same wavelengths for which an enhancement of photocurrent, and thus absorption, is observed [6].

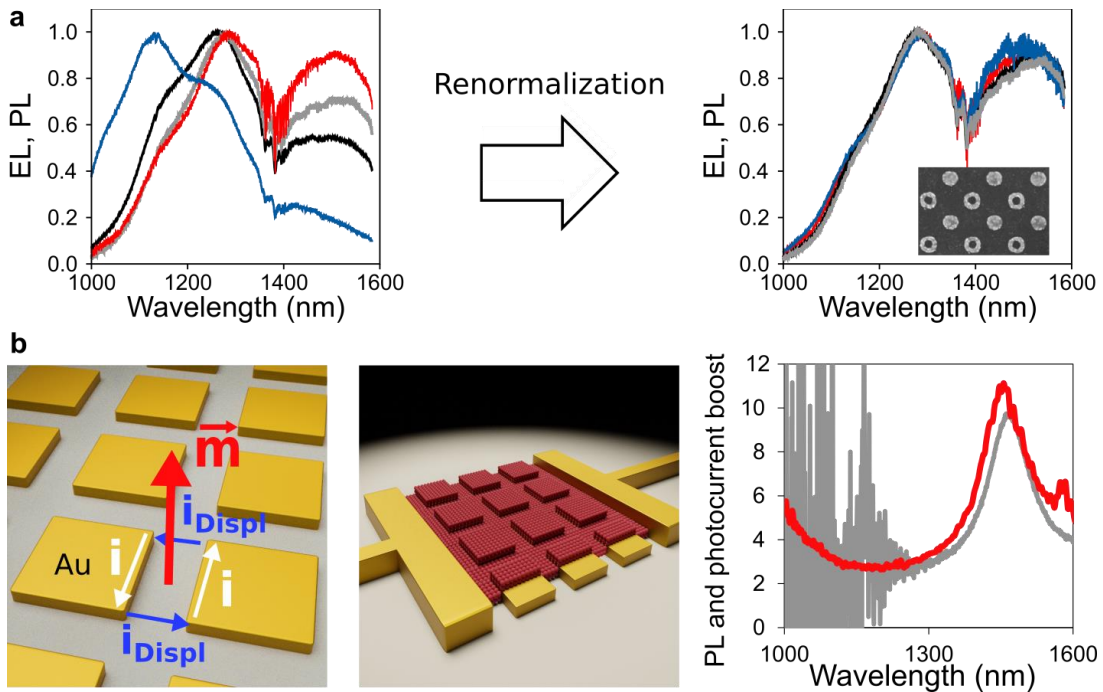


Figure 2. a. The left panel shows the electro- and photoluminescence spectra of an LED operating with PbS NCs hybridized with a Au metasurface under various pumping conditions. The right panel shows the result of the renormalization described in the text. Inset: SEM image of the Au metasurface (period 450 nm). Adapted with permission from [5]. **b.** When square Au inclusions are closely spaced, a family of magnetic resonances develops between them (left panel). These resonances interact with the usual dipolar plasmons of the Au inclusions, generating an optical analog of electromagnetically induced absorption (EIA). This EIA can be transferred to a thin film of PbS NCs coated onto the Au patterns (middle panel), resulting in both enhanced emission and photocurrent (i.e. absorption) at the same wavelengths (right panel). Adapted with permission from [6].

The fact that an assembly of interacting NCs acts as an effective semiconductor is not new, especially in the photovoltaics community where their properties are analysed with the Kirchhoff law just as any other semiconducting medium. However, it is surprising that this model can be extended to the heterogeneous photonic environment and extremely thin layers that are considered here because the hypotheses upon which Equations (1) and (2) are derived are extremely restrictive and solely apply to bulk semiconductors that are sufficiently thick to absorb any incoming radiation. A few years ago, an extension of the theory that precisely tackles this problem was proposed [7]. This theory shows that the Kirchhoff law is still formally valid for our devices, except that the thermodynamic parameters characterizing the system (the temperature T and the chemical potential $\Delta\mu$) must be understood as local (i.e. out-of-equilibrium) quantities that vary in space. Moreover, the out-of-equilibrium temperature of the thermalized carriers needs not be the same as that of the host matrix.

Now that a general framework has been established to understand the (weak) coupling of an ensemble of interacting NCs to their environment, it is possible to assess to which extent their optoelectronic properties can be transformed by design. As shown through the examples of Figures 1 and 2, it is possible to control the polarization, colour and brightness of NC LEDs by integration of a network of subwavelength inclusions. In addition, one can show that the metasurface considered in Figure 2b also changes the radiation pattern of the PbS NC layer [6]. Inversely, the same approach can be used in photodetection because of the equivalence between emission and absorption (Figure 2b). In these examples, the response of the different patterns was purely local, at the level of the individual metallic inclusions (or between them for the metasurface of Figure 2b).

While significant, the results achieved in terms of light emission are far from the degree of complexity that can be obtained with lasers, which can be designed to emit highly directional beams with a variety of non-trivial polarization and phase textures. The reason is that contrarily to lasers, LEDs operate in the regime of spontaneous emission, producing spatially incoherent light with randomly varying phase, which is at odds to the precise phase conditions that are required to construct even the simplest directional beams. There is, however, a well-known route to improve the spatial coherence of spontaneous emission, which consists in forcing the emission of light into the propagating modes of a waveguiding structure. Such modes possess a spatial coherence length that extends over many wavelengths and, as such, can be manipulated in more ways than photons directly emitted in free space or photons coupled to local resonators such as those examined above.

To illustrate this point, let us consider the structure displayed in Figure 3a, made of a continuous Au film with periodic corrugations and covered by a thin layer of PbS NCs. By pumping the NCs optically, the resulting photoluminescence predominantly feeds the propagating surface plasmon modes that exist at any metal/dielectric interface. It becomes then possible to leak them into free space in a controlled way, using the periodic grating to diffract the energy away from the metal surface. We have developed a simple yet powerful holographic method to design gratings capable of shaping complex beams. In Figure 3, we have applied this approach to demonstrate the spontaneous emission of a vector vortex beam, that is, a swirl of light with helical wavefronts that possesses a phase singularity and a polarization singularity at its centre [8]. The singularity in phase is imparted by the grating, which consists of an Archimedean spiral (Figure 3b), while the singularity in polarization stems from the electromagnetic field structure of the diffracted plasmons. The directionality is manifest in the dispersion relation of the emission (Figure 3c), the singular (in this case radial) polarization can be appreciated by examining the beam through a linear polarizer (Figure 3d), while the helical structure and phase singularity are revealed with interferometric structures (Figure 3e).

While Figure 3 demonstrates that it is possible to control the spontaneous emission of an incoherent source with the same degree of complexity as lasing light, these results represent a special case because the samples were excited with a focused laser spot at the centre of the holographic gratings. Such a selective pumping plays the role of spatial filtering, simplifying the design of the structures since the problem is reduced to controlling the phase and polarization of a point-like emission source. Achieving a full control of the spontaneous emission over an extended area is even more challenging because each point of an incoherent source emits light with a different phase that

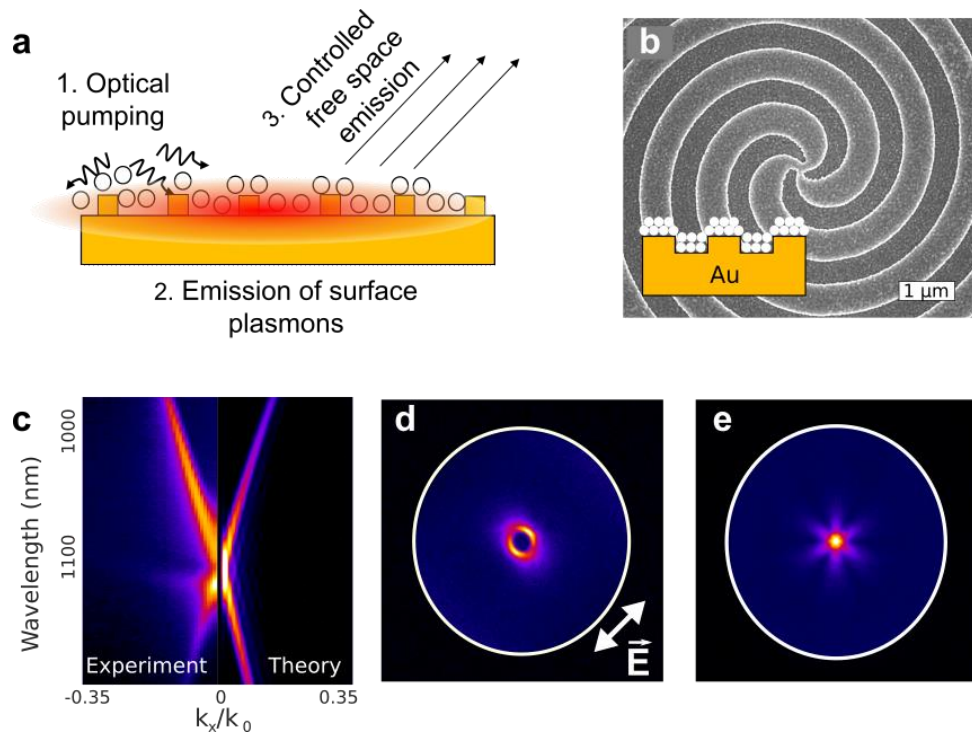


Figure 3. **a.** Schematic illustrating how to extend the spatial coherence of the photoluminescence of PbS NCs (white circles) and shape their emission into a directional beam. **b.** SEM image of the holographic grating used to produce vector vortex beams. This grating is covered by a thin layer of PbS NCs, as sketched in the inset. **c.** Dispersion relation of the infrared photoluminescence. **d.** Polarization measurement showing the radial distribution of the electric field. **e.** Interference measurements to probe the phase singularity. Adapted with permission from [8].

randomly varies over time. As theoretically proposed for thermal radiation [9], which represents another system obeying a Kirchhoff law, such a feat is possible by simultaneously leveraging local effects (such as those discussed on Figures 1 and 2) as well as non-local interactions (such as those discussed on Figure 3). It is one of the great challenges of the community nowadays, not only for thermalized nanocrystal assemblies, but also for any other source of incoherent light that can be described by a Kirchhoff law (thermal radiation, photo- and electroluminescence from epitaxial quantum wells, homogeneous semiconductors...).

3. Conclusion

As the field of NC optoelectronics is gaining technological maturity, there is a push toward advanced functionalities that requires their hybridization with photonic environments at the subwavelength scale. The few examples reviewed here, such as the control of the polarization, brightness and colour at the nanoscale, or the emission of singular vector beams, herald more profound advances in terms of light emission, with the arbitrary (and eventually dynamical) control of the phase and polarization of extended incoherent sources soon at hand. This quest is not restricted to NCs and concerns any other material for photoluminescence, electroluminescence or thermal radiation applications, such as displays for augmented reality, ultra-broadband optical and/or wireless communication protocols, or active sensing.

While not discussed in this short perspective, similar ideas can be applied to engineer sensors capable of reacting to complex forms of light, or to develop high-efficiency solar cells, for example by enhancing the generation of photocarriers, or by slowing down their thermalization rate to harness their excess kinetic energy before it is lost as heat. Last, it is noteworthy that we have solely focused on the weak coupling regime, where the energy flows one way from the emitters to the photonic environment or vice-versa. The field of NC optoelectronics will probably witness new exciting breakthroughs with the demonstration of devices operating in the strong coupling regime, with hybrid light-matter states that possess entirely new energy landscapes, coherence properties and transport characteristics.

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