Carbon Dots—Plasmonics Coupling Enables Energy Transfer and Provides Unique Chemical Signatures

Lihi Efremushkin,†§ Susanta Kumar Bhunia,‡∥ Raz Jelinek,‡ and Adi Salomon*†

†Department of Chemistry, Institute of Nanotechnology and Advanced Materials (BINA), Bar-Ilan University, Ramat-Gan 5290002, Israel
‡Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 84105, Israel

Supporting Information

ABSTRACT: Plasmonic nanostructures and carbon dots (C-dots) are fascinating optical materials, utilized in imaging, sensing, and color generation. Interaction between plasmonic materials and C-dots may lead to new hybrid materials with controllable optical properties. Herein, we demonstrate for the first time coupling between plasmonic modes and C-dots deposited upon a plasmonic silver hole array. The coupling leads to a remarkable visual attenuation and shifts of the plasmonic wavelengths (i.e., color tuning). In particular, the C-dots—plasmon couplings and pertinent color transformations depend both upon the C-dots’ fluorescence emission wavelengths and functional residues displayed upon the C-dots’ surface. This optical modulation corresponds to energy level alignment and consequent energy transfer between the C-dots and the plasmonic silver hole array. Notably, the energy coupling observed in the C-dot—plasmonic hybrid system allows distinguishing between C-dots species exhibiting similar optical properties, albeit displaying different functional residues.

Photonic modes can interact with emitters to form mixed states with controllable optical properties, leading to development of ultrafast optical switches.7–7 During the past decade, such interactions between the two subsystems were realized also in room-temperature and ambient conditions by using plasmonic systems.1,4,8–11 The advantage of plasmonic systems over conventional photonics is their ability to confine electromagnetic (EM) fields to a deep subwavelength volume, thereby enhancing light–matter interaction.11–13 Various plasmonic systems such as hole arrays, nanoparticles, grooves, and cavities were shown to strongly interact with either dye molecules or quantum dots (Q-dots), following exchange of energy between them, faster than any other competing process present in the emitter.8,10,13–19 Such couplings significantly perturb the emitter systems; new states are consequently formed, separated by the so-called Rabi splitting, leading to new energy relaxation pathways and varying the dynamics of the emitter photochemical processes.1,2,12 Two different regimes of interaction are noted in the literature, namely, the weak and strong coupling regimes. While the latter refers to discrete level systems, the weak coupling regime involves a continuum of states.3,14 In such a case, the states are not mixed, but the emitter lifetime is reduced because of a large density of photonic modes (for more information, see Figure S1). Regardless of the coupling strength, the physical properties of the emitter play a pivotal role, whereas the chemical properties surprisingly are found to have lesser effects. That is, chemical signature of any molecular system is excluded, as is chemical interaction between the molecule and the metallic surface. The molecular system is mostly treated as a two-level system, and the same behavior was observed in the case of both Q-dots and dye molecules, though these systems are not analogous.16,20 Nevertheless, few studies addressed the differences in coupling behavior to these two different subsystems (emitters).12 C-dots are carbon nanoparticles (diameter < 10 nm) which are surface-decorated with functional group and have a broadband photoluminescent emission behavior.21 C-dots exhibit interesting optical, physical, and chemical properties including color tunability, electron-transfer properties, biocompatibility, and low photobleaching.22,23 These features have made C-dots an attractive platform for a wide array of optical applications.24–26 The optical properties of C-dots, in particular, are related to their size as well as surface properties.27 Importantly, the photoluminescence properties of C-dots can be controlled through modification of surface functional groups and doping with heteroatoms such as nitrogen, sulfur, and others. As such, C-dots have been proposed as bioconjugate alternatives for Q-dots and dye molecules in bioimaging and optoelectronic applications.28 Herein we demonstrate, for the first time, interactions between C-dots (fluorescence emitters) and plasmonic modes of silver hole arrays, investigated by linear optical measurements. We focus on two types of C-dots exhibiting similar emission properties (i.e., yellow emission color) and similar transition states, but are different in their chemical properties. That is, one C-dots species displayed electron-donating
functional groups (NH$_2$), while the other C-dots were decorated with electron-withdrawing groups (COCH$_3$ and OR≡OC$_n$H$_{2n+1}$) on the surface. We show that the two subsystems, i.e., plasmonic hole array and C-dots, strongly interacted via energy-transfer processes to form hybrid materials exhibiting enhanced transmission and vivid colors in a broad optical region. Specifically, in longer wavelengths, energy transfer between the two subsystems was dependent upon the alignment of the plasmonic system energy levels with respect to the emission energy levels of the C-dots, whereas in lower wavelengths, the C-dots functional groups (i.e., the chemical signature), were the predominant factor. Importantly, while both C-dots examined had similar photophysical properties, they could be easily distinguished through the distinctive colors of the C-dots/silver hole array hybrid system.

Figure 1. (a) Schematic illustration of plasmonic device (hexagonal hole array) onto which C-dots embedded in a thin PVA film were deposited. Two types of C-dots were used: C-dots displaying NH$_2$ moieties and C-dots functionalized with COOR. The crystalline graphitic core of the C-dots is clearly apparent in the high-resolution transmission electron microscopy (HR-TEM) image. (b) Fluorescence emission spectra (normalized to 1) of the two yellow C-dots, excited at 475 nm: C-dots with electron withdrawing functional group (blue line) and C-dots with electron donating group (red line). Inset: yellow appearance of both C-dots (excited with 450 nm laser). (c) Transmission spectrum of subwavelength hexagonal Ag hole array with periodicity of 390 nm and hole diameter of 160 nm coated with PVA. Two plasmonic modes are observed: a low-energy mode at around 700 nm and a high-mode at about 480 nm.

Figure 2. Energy band diagram describing the interaction between the yellow C-dots and the plasmonic modes of the silver hole array. (a) The C-dots system has a broad absorption band and multiple emissive surface states. The plasmonic system exhibits two photonic modes, in which the high-energy mode can interact with the C-dots absorption band while the lower-energy mode can interact with the C-dots emission states. Energy can be transferred from the C-dots emissive states to the plasmonic system as is indicated by the arrow. The interaction between the two systems is dependent upon the overlap between the modes, as is shown in panel b. Specifically, the upper illustration shows a maximal overlap, whereas the lower drawing shows a very small overlap. (c) The functional groups decorating the C-dots are in proximity to the silver hole array surface; therefore, the silver work function value may increase (left) or decrease (right).
periodicity, $P$, from 330 to 460 nm. An example of a transmission spectrum of a hexagonal hole array with $P = 390$ nm is shown in Figure 1c. Two energy modes are apparent: a lower surface plasmons (SPs) mode at around 700 nm due to plasmonic modes propagating in the first Brillouin zone and a higher SPs mode corresponding to surface plasmon modes propagating at the second Brillouin zone.\textsuperscript{29–31,33}

The C-dots/SPs coupling concept and its implication for color tuning and energy-transfer processes are outlined in Figure 2. Specifically, Figure 2 depicts energy band alignment diagram of the C-dots and the plasmonic hole array, as well as the mode of interaction between them. The broad bands (either absorption or emission) of the C-dots can weakly interact with the confined EM field induced by surface plasmons (SPs) modes (Figure 2a). Potentially, both the absorption and emission levels of the C-dots can interact with the plasmonic system through energy-transfer processes. Explicitly, in our plasmonic system, the high-energy mode of the plasmonic array can be weakly coupled to the continuum C-dots absorption band,\textsuperscript{24} whereas energy transfer is expected from the C-dots’ emission levels to the plasmonic system. Importantly, the degree of interaction and concomitant energy transfer depend upon the overlap between the two subsystems (Figure 2b). By changing the hole array periodicity, the SPs modes can be energetically tuned and thus can be either aligned (resonant) or misaligned (off-resonant) with respect to the C-dots’ energy states. Moreover, the C-dots’ functional groups which are in proximity to the silver surface film may affect its work function value\textsuperscript{34,35} (Figure 2c) and therefore the optical properties of the plasmonic system.\textsuperscript{36,37} In particular, the C-dots’ functional groups can induce dipoles on the silver surface which either reduce or increase the silver work function value (Figure 2c).\textsuperscript{34} Indeed, polar molecules which physically adsorb onto silver (and other metals) surfaces introduce a net electrical dipole perpendicular to the surface. This could result in modification of the metal work function value.\textsuperscript{34,35} In the system depicted here, the C-dots form a dipole layer, which can be perceived as a “parallel plate capacitor” affecting the optical properties of the hole array.\textsuperscript{32} Similar dipole-based tuning was reported in optoelectronic devices, especially in semiconductors, and was found to modify their performances.\textsuperscript{32}

In order to study the nature of the interaction between the C-dots and plasmonic hole arrays, we measured the transmission spectra of the hybrid systems,\textsuperscript{1,12} in which the C-dots/
PVA film was deposited upon silver hole arrays exhibiting three different periodicities (Figure 3). Notably, we used very low concentrations of C-dots in order to keep the same PVA index of refraction. As depicted in Figure 3, two optical wavelength regimes can be distinguished: area A corresponds to the higher-energy regime (interaction with the high SPs mode), and area B reflects the lower-energy regime (interaction with the low SPs mode). The transmission spectra of the hybrid C-dots/SPs systems comprising either the NH2-C-dots or COOR-C-dots are shown in Figure 3 in red or green curves, respectively. The blue curves correspond to the reference plasmonic hole array coated only with PVA (no C-dots). To precisely delineate the mode of interaction between the plasmonic and C-dot systems, we also include in Figure 3d–i the fluorescence spectra of the C-dots with the overlap between the two subsystems marked in blue.

Focusing on the plasmonic mode at about 700 nm (area B), we distinguish three different cases of the hybrid system. The transmission through the hybrid C-dots/SPs arrays is either enhanced (Figure 3a), suppressed (Figure 3c), or does not change (Figure 3b) with respect to the reference plasmonic system, regardless of the type of the yellow C-dots in the hybrid device. These results are consistent with the relationship between the fluorescence emission properties of C-dots and the reference plasmonic system, which are illustrated in Figure 3d–i, area B. Note that the blue transmission spectra in Figure 3d–i correspond to the set of reference plasmonic arrays coated with PVA only. Thus, when the overlap between the C-dots emission states and the plasmonic modes is maximal (i.e., Figure 3d,g), the transmission is enhanced, whereas no change is observed for moderate overlap (Figure 3e,h); suppression is detected when the two subsystems barely overlap (Figure 3f,i). In addition, we note a blue shift of about 30 nm for the hybrid C-dots/SPs system in Figure 3a (see Figure S7). When the two systems exhibit a maximum overlap, the spectrum is shifted toward the yellow C-dots fluorescence emission wavelength. Similar trends in the transmission spectra are presented in Figure S8, which shows a full set of hole array periodicities.

The results depicted in Figure 3 can be ascribed to energy transfer between the C-dots and the plasmonic bands. In particular, the C-dots which are in proximity to the silver hole array surface emit to the near field region leading to excitation of plasmonic modes through energy-transfer processes (see Figure S7). Such energy-transfer processes give rise to enhanced transmission compared to the reference hole array. The transmission is also blue-shifted toward the C-dots emission wavelength. In contrast, when the C-dots emission states and the SPs modes do not (or minimally) overlap energetically, the C-dots behave as multiple scattering particles, leading to damping of light transmitted through the subwavelength plasmonic array.

While the two C-dot species examined here exhibit very similar fluorescence emission (Figures 1b and S6), they are decorated with different functional groups. Thus, an important question is whether the different surface units affect the interaction with the plasmonic system. Indeed, the “chemical signatures” of the C-dots, i.e., the distinct surface functional groups, are nicely observed in area A (Figure 3a–c) in the higher-energy regime (400–550 nm). Clear differences in the spectra are observed between the two types of hybrid systems comprising C-dots with different functional groups (red vs green spectra), in contrast to area B, in which the measured spectra are nearly identical. In this wavelength regime, the plasmonic modes may interact with the C-dots’ continuum absorption bands, yet the absorption spectra of these two yellow type C-dots are very similar, meaning that the observed differences can be related to the different nature of the functional groups.

In general, following interaction of the SPs modes with the C-dots subsystem, the transmission spectra of the plasmonic systems in area A were enhanced and shifted, especially for the hybrid systems containing C-dots with NH2 group (see also Figure S8 for a full set of hexagonal hole arrays). We postulate that the C-dots in proximity to the silver surface can modify its work function, depending upon their surface functional groups, and therefore lead to pronounced shifts of the plasmonic mode. SPs are defined as oscillations of the metal’s free electrons; accordingly, the NH4 moieties can enrich the silver surface with electrons, leading to enhanced transmission through the subwavelength plasmonic hole array. We further note that the plasmonic modes in area A are red-shifted by approximately 20 nm (130 meV) and 50 nm (220 meV) in array periodicity of 410 and 460 nm, respectively. These shifts are ascribed to partial overlap with the emission states of the C-dots, apparent in Figure 3e,f. Indeed, when the overlap between the plasmonic mode and the emissive states are more pronounced, larger shifts are observed. On the other hand, C-dots decorated with COOR functional groups give rise to a different hybrid system at this optical region (area A). In this case, changes in the spectra are less pronounced, but there are few examples (see also Figure S8). In most cases, the SPs modes are enhanced rather than shifted.

The transmission micrographs in Figure 4 underscore the remarkable optical modulation of the plasmonic systems accomplished through coupling with the yellow C-dots. Figure 4a presents transmission micrographs recorded for specific hole array periodicities (the complete hole array series are shown in Figures S8 and S9). Evident changes in the observed
colors were apparent following deposition of yellow C-dots upon the silver hole arrays (Figure 4a). Furthermore, a clear difference is apparent between the transmission colors induced by the two yellow C-dots. Importantly, color changes were recorded even though the C-dots were present in rather low concentrations within the PVA films, indicating that the color modulations were not related to refractive index changes but to the chemical signature of the C-dots subsystems. Notably, in the case of 330 and 350 nm hole array periodicities (Figure 4b), an enhancement of light transmission was recorded rather than color change for both C-dots, reflecting the spectral modulations observed in Figure 3.

The variation in the observed colors shown in Figure 4 between the two C-dots systems and enhanced transmission through the hole array are in agreement with the spectra recorded for those hybrid system (Figure S9). As explained above, we assigned the color changes and the respective spectra to both the fluorescence emissions of the C-dots as well as their surface functional groups. Specifically, while the two yellow C-dots systems exhibit similar photophysical properties, their functional groups induce significantly different dipoles on the silver surface (Figure 2c), leading to changes of the surface polarizability due to interaction with the free surface electrons.

In conclusion, we demonstrate that C-dots can strongly interact with plasmonic systems through energy-transfer processes, affected by band alignment between the two subsystems. Such an interaction forms new hybrid materials with tunable optical properties, affected both by the chemical signatures of the C-dots and the geometrical parameters of the plasmonic system. This work provides a striking example that chemical properties of an emitter in a hybrid plasmonic system play a key role, enabling us to enhance and modulate the optical properties of a given plasmonic system also in the important blue optical regime. Because the functional groups of the emitter can further serve as ligands and capture agents for analytes, such a hybrid system might serve as a sensitive optical detector for molecular targets that lack transition states in the optical regime.

■ EXPERIMENTAL METHODS

Sample Preparation. Subwavelength hexagonal hole arrays were milled by a focused ion beam (FIB, Helios 600, FEI) in sputtered silver films of 250 nm thickness on glass substrates. The diameter of the hole was kept constant at 160 nm as the array period varied from 330 to 460 nm (increments of 10 nm). The 100 nm thick poly(vinyl alcohol) (PVA, 89,000–98,000 Mw, Aldrich) with and without the C-dots was spin-coated on the sample. The C-dots concentration used in PVA was 1.4 mg/mL.

Optical Measurements. Spectral measurements and optical imaging of the hole arrays and molecular layer were conducted using an inverted light microscope in transmission mode (IX83, Olympus). The illumination source was a halogen lamp (100 W, Olympus). The spectrscopic data were obtained using a spectrophotograph (IsoPlane SCT320, Princeton Instruments), the LightField program, and a CCD camera (PIXIS 1024, Princeton Instruments). When using the spectrophotograph, the measurements were taken with the X20 objective (N.A. 0.25) and the 600 and 500 nm blaze gratings (grating density 50 and 300 g/mm respectively) in the spectral range of 200–1000 nm and 380–520 or 580 nm, respectively. The exposure time was 100 ms for the 600 nm blaze grating and 500 ms for the 500 nm blaze grating for all the samples. For NH2 C-dots with periodicity of 450 and 460 nm, the exposure times for the 500 nm blaze grating were 400 and 350 ms, respectively. The spectra were normalized according to the exposure time. The optical images were taken using the FGB35 filter (Thorlabs, United States).

■ ASSOCIATED CONTENT

S Supporting Information

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Coupling between emitter and plasmonic systems, C-dots synthesis and characterization, dispersion relation of plasmons of hole array and their interaction with an emitter, optical measurements of the C-dots/plasmons hybrid system (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: Adi.Salomon@biu.ac.il.

ORCID
Lili Efremushkin: 0000-0002-7472-8921
Raz Jelinek: 0000-0002-0336-1384
Adi Salomon: 0000-0002-5643-0478

Present Address
SK.B.: Schull Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 3200003, Israel.

Author Contributions
LE. and S.K.B. contributed equally to this work.

Notes
The authors declare no competing financial interest.

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