

Engineering the Surface of Carbon Dots for Enhanced Photoluminescence and Controlled Plasmonic Interactions

Interactions

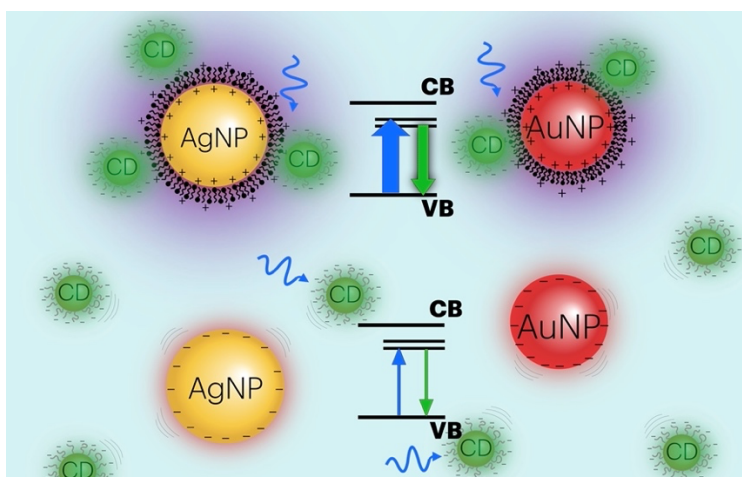
M. Reale¹, Z. Moussadjy¹, G. Buscarino^{1,2}, U. De Giovannini¹, A. Emanuele¹, M. Cannas¹, R. Cillari³, N. Mauro³, A. Sciortino^{1,2*}, F. Messina^{1,2*}

¹*Dipartimento di Fisica e Chimica “Emilio Segrè”, Università degli Studi di Palermo, Via Archirafi 36, Palermo 90123, Italy.*

²*ATeN Center, Università degli Studi di Palermo, Palermo, Italy.*

³*Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università degli Studi di Palermo, via Archirafi 32, Palermo 90123, Italy*

**Corresponding author E-mail: fabrizio.messina@unipa.it, alice.sciortino02@unipa.it*



Abstract

The design of hybrid nanosystems that integrate distinct optical and electronic properties in a synergistic way represents a key challenge in modern photonics. While a few works have proposed to exploit the interactions with plasmonic nanoparticles to enhance the photoluminescence of carbon dots, achieving satisfactory and consistent results remains a demanding challenge. In this work, nitrogen-doped Carbon Dots (CDs) are functionalized with polyethylene glycol (PEG) through a hydrothermal route to form a polymeric shell, enabling an improvement of their photophysical properties and allowing to control the plasmonic interactions with silver (AgNP) and gold nanoparticles (AuNP). The interaction between PEGylated CDs and metal nanoparticles, driven by electrostatic forces, resulted in a photoluminescence enhancement depending on the interaction distance provided by the different PEG chain length. These findings demonstrate that PEGylation

stabilizes CDs, improves their optical properties, and facilitates the control on interactions with plasmonic nanoparticles, opening new possibilities for the development of advanced hybrid nanomaterials.

Introduction

Coupling various nanomaterials with distinct optical and electronic properties to create hybrid nanosystems is an emerging frontier in nanoscience, enabling the design of novel nanostructures with tailored functionalities. When building blocks with orthogonal physical properties - luminescent, magnetic, plasmonic, chiral, etc. - are synergistically integrated, their combined optoelectronic characteristics can modulate existing properties or introduce entirely new features, with several implications for optically driven applications [1,2].

Carbon Dots (CDs) are particularly promising as building blocks for functional hybrid and composite nanosystems in photonics. As a well-established class of carbon-based nanoparticles, CDs exhibit strong and tunable light absorption-emission properties in the visible range, combined with high photostability as well as low-cost and easy synthetic routes [3,4]. These combined features make CDs promising alternatives to semiconductor quantum dots, in which the presence of toxic heavy metals represents a limiting factor for everyday applications, due to their cost and severe environmental and human health impact. Instead, CDs are widely recognized as non-toxic, highly biocompatible and water-soluble, these representing enormous benefits with respect to their inorganic analogues [5]. Furthermore, not less importantly, CDs offer unique advantages given by the peculiar chemistry of carbon, which makes them easy to functionalize for potential coupling with other suitable systems. Indeed, CDs are characterized by a passivated surface shell rich of organic functional groups which can be finely tailored in view of specific couplings [6–8]. In the last years, researchers have begun exploring hybrid materials that aim to combine the tunable optoelectronic properties of CDs with the specific characteristics of other carefully chosen systems [7,9–13].

Among these hybrid systems, coupling CDs with metallic nanoparticles (MNPs) has attracted considerable attention due to the Localized Surface Plasmon Resonances (LSPRs) characterizing the MNPs. LSPRs are collective oscillations of conduction electrons localized at metallic surfaces that can be optically excited at a resonant frequency dependent on the chemical identity of the MNP, its size and shape, with typical extinction cross-sections which can be up to 100 times with respect to their geometrical cross section [14–16]. Since such charge density oscillations occur on a scale smaller than the wavelength of incident light, this allows to confine light into volumes well below the diffraction limit. Such a significant sub-wavelength confinement enables plasmonic nanoparticles to

behave as nanoantennas [17], producing a confined and strongly enhanced field compared to the excitation field [14], thus paving the way to a new range of specific light-matter interactions.

Distance-dependent coupling between fluorophores and plasmonic nanoparticles has been extensively studied, including systems based on organic dyes [18] and semiconductor quantum dots [19]. In general, these studies have established two fundamental mechanisms driving photoluminescence plasmonic enhancement [14,20]. First, LSPR excitation amplifies local electric fields, increasing the excitation rate of nearby fluorophores, which leads in turn to an enhancement of the photoluminescence produced by the fluorophore. This phenomenon, often referred to as *lightning rod effect*, is particularly efficient when the absorption band of the chromophore perfectly overlaps with the plasmonic band of MNP [14]. Second, LSPR can modify the radiative and nonradiative decay rate of the nearby fluorophores. Thereby, the photoexcited fluorophore can decay through increased radiative decay rate, according to the so-called Purcell effect [21], ultimately determining an enhanced emission intensity. However, systematic studies addressing the interplay between distance-dependent photoluminescence enhancement and quenching in CD-MNP systems remain limited. Indeed, regardless of the specific PL enhancement mechanism, these effects require precise control of the physical separation between the fluorophore and the plasmonic system to avoid quenching effects from photoinduced electron or energy transfer processes, which dominate at very short distances [22,23]. Considering that these transfer processes are extremely short-range phenomena, described by exponential decay laws with an effective range of a few angstroms [24], the inclusion of a physical spacer between interacting systems can effectively prevent emission quenching and harness plasmonic interactions [25]. Studies involving CDs and plasmonic nanoparticles frequently employ particle/shell configurations, where an insulating shell (e.g. SiO₂) around the plasmonic nanoparticles acts as a spacer [23,26–28]. Additionally, CDs functionalized with spacer molecules have also been explored for plasmonic coupling, as we demonstrated in a previous study on a particular type of red-emitting CDs [29]. However, existing literature often focuses on specific spacer types or single-case studies without systematically investigating how spacer length influences the dynamic and static PL behavior of CDs in plasmonic systems. Furthermore, a comprehensive comparison of CD-plasmonic interactions in silver versus gold nanoparticle systems under equivalent conditions are extremely sparse [27].

In this work, we aim to address these gaps by presenting a systematic investigation of the interactions between green-emitting CDs and plasmonic silver and gold nanoparticles. Specifically, we functionalize the surface of CDs with polyethylene glycol molecules of varying lengths, creating a polymeric shell that prevents quenching effects and allows controlled modulation of the interaction distance. By carefully tuning the surface charge of both silver and gold nanoparticles, we achieve spontaneous coupling with CDs in aqueous phase, driven by electrostatic interactions.

Comprehensive optical characterization, including time-resolved photoluminescence measurements, reveals that the surface functionalization of CDs effectively creates a polymeric shell which prevents emission quenching when interacting with plasmonic nanoparticles, and enables the plasmonic enhancement of CD emission intensity, mostly due to a lightning rod mechanism, as also corroborated by theoretical calculations. These systematic comparisons provide new insights into interaction pathways between photoluminescent and plasmonic nanoparticles, highlighting the potential of CDs as versatile building blocks for functional nanocomposites with tailored optoelectronic properties.

Materials and Methods

Synthesis and purification of CDs. The microwave synthesis method reported in [30] was modified into a hydrothermal decomposition route to synthesize the CDs used in the current study. Specifically, 3 g of citric acid monohydrate and 3 g of urea (Sigma Aldrich) were dissolved in 10 mL of Milli-Q water. The resulting aqueous solution was heated on a hotplate set at 200 °C until complete evaporation, yielding a strongly hygroscopic black material. This material was ground with a mortar and pestle to obtain a fine black powder consisting of CD aggregates. 15 mg of the resulting powder were dissolved in 5 mL of Milli-Q water and subjected to a separation/purification via size exclusion chromatography (SEC). The separation was performed using a glass column (2.5 cm diameter) packed with a stationary phase composed of three resins – Sephadex G25 (15g), G15 (15g) and G10 (15g) – with increasing cutoff values, using Milli-Q water as the eluent. From the multiple fractions of eluates (each ~4 mL), the fraction containing the CDs with the highest quantum yield was selected.

PEGylation of CDs. The as obtained CDs underwent surface functionalization utilizing polyethylene glycol (PEG) molecules with molecular weights of either 400 or 3000 Da (purchased from Sigma Aldrich). This process resulted in the creation of two CD families with different surface shell thicknesses. The PEGylation was carried out using a hydrothermal route conducted in an autoclave. Initially, 1 mL of a ~22 μ M aqueous solution of purified CDs was mixed with 1 mL of pure PEG400 (or PEG3000). The resulting mixture underwent a 24-hour reaction in the autoclave at 120°C. Following cooling, SEC separation was employed to purify the sample, aiming to isolate the fraction predominantly composed of PEGylated CDs from unreacted CDs and free PEG molecules. The SEC purification was conducted using a glass column with a 2.5 cm diameter, wherein 2 mL of the sample obtained after hydrothermal reaction was inserted as an eluant. The stationary phase comprised three resins – sephadex G25 (15g), G15 (15g), G10 (15g) – each with increasing cutoff values for optimal

separation. The relevant fraction is recognized by the modification in the absorption spectrum induced by surface PEGylation.

Synthesis of AgNPs. Silver Nanoparticles (AgNPs) of approximately 30 nm diameter were synthesized using a Turkevich-inspired route [31]. A 50 mL volume of a 5 mM aqueous solution of sodium citrate (Sigma Aldrich) was heated on a hotplate under vigorous stirring and continuous refluxing, covered to prevent evaporation. About 2 minutes after boiling began, 1 mL of 25 mM AgNO₃ solution was quickly introduced. Within approximately ten minutes, the initially transparent solution started showing a yellowish hue, indicating the formation of silver nanoparticles, as also confirmed by a real-time monitoring of the UV-Vis spectrum of the solution during synthesis (see Figure S1). The solution was maintained at the boiling point for about 40 minutes until the color stabilized, signifying complete nanoparticle formation. To remove any residual reagents, the solution underwent two rounds of centrifugation (8000 rpm, 15 min), and the sediment was resuspended in ultrapure water after removing the supernatant.

Synthesis of AuNPs. Gold nanoparticles (AuNPs) of approximately 15 nm diameter were synthesized using a seeded growth approach inspired by previous studies [32]. In a 75 mL aqueous solution of 2 mM sodium citrate (Sigma Aldrich), heated on a hotplate under vigorous stirring and continuous refluxing, gold nanoparticle seeds were formed by swiftly injecting 1 mL of 12.5 mM HAuCl₄ (Sigma Aldrich) when the solution reached the boiling point. The color of the solution changed instantaneously from transparent to bluish-gray, quickly followed by dark brownish-red, indicating the formation of gold nanoparticle seeds. After seed formation, the solution was cooled to 90 °C, and 0.5 mL of sodium citrate (60 mM) was added, followed by 1 mL of HAuCl₄ (12.5 mM) after 2 minutes. This process was repeated up to five times to obtain the 5th generation of gold nanoparticles. To remove any residual reagents, the solution underwent two rounds of centrifugation (8000 rpm, 15 min), and the sediment was resuspended in ultrapure water after removing the supernatant.

Estimation of metallic nanoparticles concentration. We estimated the concentration of metallic nanoparticles using a widely accepted protocol from the literature [33], combining theoretically calculated extinction cross-sections and experimental data. For both AuNPs and AgNPs, the mean size was determined through AFM and DLS, with results in agreement with each other. Using this size estimate, we simulate the molar extinction coefficient of the nanoparticles with MiePlot Software. The concentration was then calculated by applying the Lambert-Beer law to the

experimentally measured extinction spectra in correspondence to the maximum of their plasmonic resonance peak.

Ligand exchange of metallic nanoparticles. AgNPs and AuNPs obtained through the described routes exhibit a negative surface charge in water due to the presence of citrate ions. To obtain positively charged counterparts, a ligand exchange procedure inspired by previous works was employed [34,35]. For both AgNPs and AuNPs, 1 mL of the final purified dispersion was added dropwise into 1 mL of 5 mM cetyltrimethylammonium bromide (CTAB) solution, and the mixture was gently stirred for 24 hours. In each case, centrifugation (8000 rpm, 20 min) was employed to remove free CTAB molecules.

Atomic Force Microscopy. Atomic Force Microscopy (AFM) images were acquired using a Bruker FAST-SCAN microscope equipped with a closed-loop piezo-scanner, offering a maximum X-Y scan range of 35 μm and a Z range of 3 μm . The scans were collected in tapping mode in air, employing a FastScan A probe, with a nominal tip radius of 5 nm, selecting a pixel resolution comparable to the tip radius. The measured samples were prepared by drop-casting the solution on a mica substrate, followed by drying under vacuum. The size of the studied nanoparticles was estimated by analyzing their height profiles over multiple scans conducted on the various points of the mica substrate to get statistical significance.

Dynamic Light Scattering. Dynamic Light Scattering (DLS) measurements were conducted using a Brookhaven BI-200SM goniometer with a fixed 90° scattering angle, equipped with a PerkinElmer Optoelectronics APD (SPCM-AQR-14) and a Flex-01 1088 channel multitaup correlator. As light source, a 671 nm laser line was employed. The sample was opportunely diluted before the measurements to work under optimal scattering conditions. By the analysis of the intensity autocorrelation functions, these measurements allowed to estimate the diffusion coefficient of particles in solution and therefore calculate the particle radius .

Zeta-potential. Zeta-potential measurements were performed in 1 mL of aqueous samples, using a Malvern Zetasizer NanoZS instrument equipped with a 532 nm laser line with a fixed scattering angle of 173° and Dispersion Technology Software 7.02 (Malvern Panalytical Ltd) The zeta-potential values (mV) were obtained from the electrophoretic mobility using the Smoluchowski equation.

ATR Infrared Spectroscopy. Attenuated Total Reflectance (ATR) Infrared Spectroscopy measurements were conducted on a Bruker Platinum ATR spectrometer equipped with a single-

reflection diamond crystal. The collection of the spectra in the 500-3500 cm^{-1} spectral range was carried out by drop-casting an aqueous solution of the sample on the crystal waiting for a complete evaporation of the solvent before data collection.

Steady-State Optical Characterization. Absorption spectra in the UV-Vis range were collected on aqueous solution of sample in a 1 cm quartz cuvette using an optical fiber spectrophotometer (Avantes, AvaSpec-ULS2048CLEVO) providing 1 nm spectral resolution, coupled to a dual halogen-xenon lamp used as light source. Steady-state Photoluminescence (PL) measurements were conducted in 1 mm quartz cuvette using a modular spectrofluorometer consisting of a Xenon lamp, two monochromators (Acton, SpectraPro 2150i and 2300i used in to disperse the excitation and the emission, respectively) and a CCD camera (Princeton Instruments, Pixis 400). A spectral resolution of 3 nm was used for the acquisition of all PL spectra. All the measurements were performed at room temperature.

Time-resolved emission. Time-resolved emission measurements were performed by using a tunable laser (Vibrant OPOTEK) pumped by a Q-switched ND-YAG laser, providing 5 ns pulses at 10 Hz repetition rate. The emission of the sample was detected by an intensified CCD camera (Princeton instruments, PI-MAX), after passing through a monochromator (Acton, SpectraPro 2300i). By gating the emission spectrum over a certain temporal window at different programmable delays from excitation, the kinetics of the whole decaying emission band was reconstructed.

Results and Discussion

In a preliminary experiment, nitrogen-doped CDs synthesized and fully characterized in a previous paper from our group [30], were tentatively coupled to either Ag or Au nanoparticles in solution phase to study the resulting effects on the photoluminescence. In both cases, the CDs resulted to undergo emission quenching after complexation in aqueous phase with plasmonic nanoparticles, due to the direct contact favoring photoinduced electron and/or energy transfer [22]. Thus, we functionalized CDs with PEG molecules to produce two families of CDs characterized by a polymeric shell of different thickness on their surface, acting as a physical spacer capable of preventing electron transfer quenching. Specifically, the surface functional groups of the pristine CDs, mainly consisting of carboxyl and hydroxyl groups (see Figure S2), were reacted with PEG molecules with a molecular weight of either 400 or 3000 Da. Here, we firstly focus on the results obtained with CDs functionalized with PEG molecules of 400 Da. The PEGylation reaction was conducted at 120° C for 24 hours using a hydrothermal route, fully described in the Materials and Methods. After the

PEGylation procedure, the sample was purified by column chromatography technique to isolate the fraction primarily composed of PEGylated CDs, and get rid of unreacted PEG and CDs. In Figure S3, we report the absorption spectra of eight fractions extracted by SEC after PEGylation, which can be grouped into three distinct subsets (A, B and C) based on their different spectral features. Due to its early elution, subset A is expected to contain the bigger particles, corresponding to the PEGylated CD, referred to as P400-CDs in the following text.

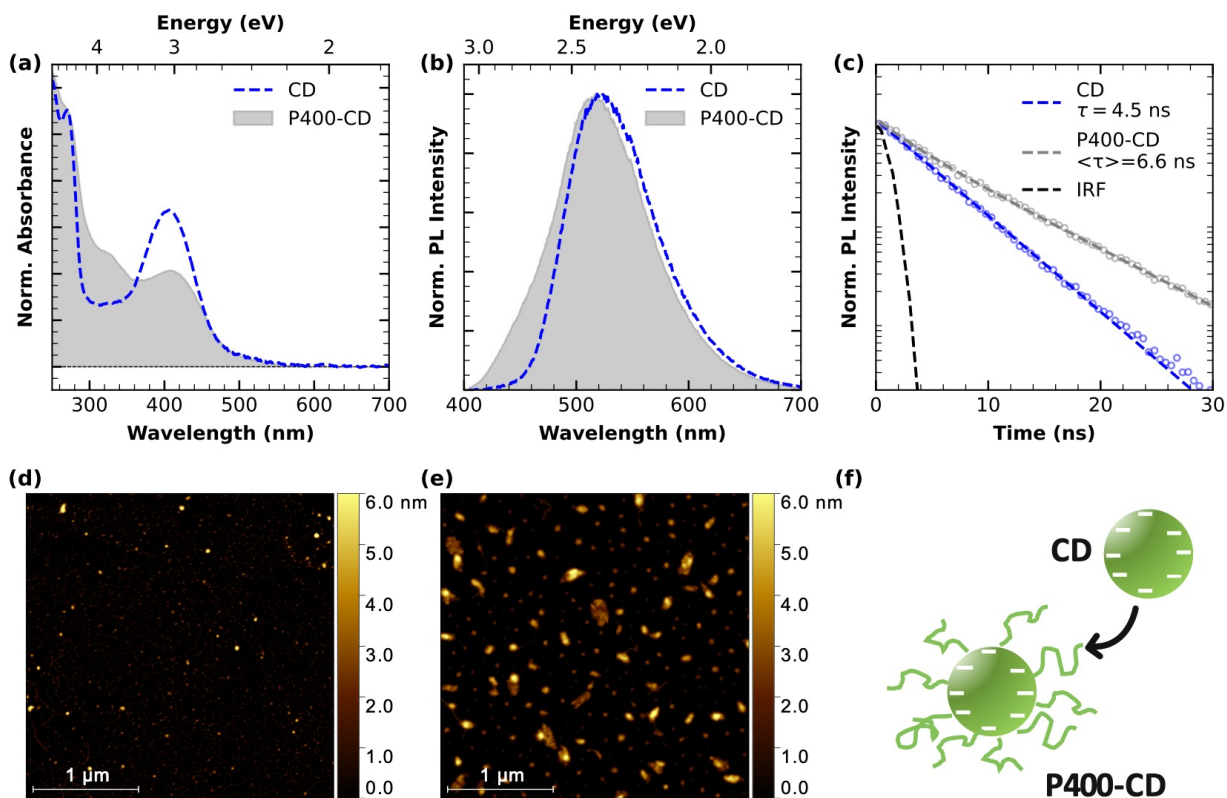


Figure 1: (a) Absorption and (b) PL spectra of pristine CDs (dashed blue curves) and P400-CDs (colored grey curves). (c) PL decay kinetics and corresponding least-square fitting curves of pristine CDs (blue) and P400-CDs (grey). AFM images of (d) pristine CDs and (e) P400-CDs. (f) Schematic of PEGylation of CDs, with PEG400 molecules arranged in a mushroom configuration.

Figure 1 highlights the effects of CD functionalization with 400 Da PEG molecules (P400-CD). These effects are first examined by a purely spectroscopic standpoint, analyzing the impact of PEGylation on the optical characteristics of CDs. Specifically, Figure 1(a) shows the comparison between the UV-Vis absorption spectrum of P400-CD (colored grey curve) and that of pristine CDs (dashed blue curve). Notably, we observe a decrease in the relative intensity and a broadening of the characteristic band located around 410 nm, associated with a sub-gap transition of the nitrogen-rich CDs [36]. Similarly, in Figure 1(b) we explore the impact of PEGylation on the normalized PL emission of CDs. PEGylation leads to a slight blueshift of the peak, and to a more symmetric spectral shape, resulting from an increase in the relative signal in the bluer part of the spectrum. By measuring the QY of CDs and P400-CDs, we also found that PEGylation with PEG 400 leads to an increase from

QY=20 % to 30 %. This increase can be directly linked to the changes detected in the PL decay kinetics shown in Figure 1(c). Specifically, we observed an increase in the average emission lifetime of CDs after PEGylation $\langle\tau\rangle = 6.6$ ns, compared to that of pristine CDs ($\tau = 4.5$ ns), likely due to the improved surface passivation, enabling a more effective screening effect from water molecules, which are directly involved in the non-radiative excited-state decay [37].

Overall, the results in Figure 1 clearly demonstrate the success of the PEGylation procedure and its effects on the optical response of CDs. As a blank comparison, Figure S4 shows that the effects of PEGylation on the UV/Vis spectrum of P400-CD are strongly different from those resulting solely from adding PEG at room temperature or subjecting CDs to high-temperature treatment without PEG.

The effectiveness of surface passivation in CDs was also confirmed from a morphological point of view using AFM measurements, as reported in Figure 1(d) and Figure 1(e), which refer to pristine CDs and P400-CDs, respectively. As can be appreciated, the average size of P400-CDs is larger than that of the starting CDs, while the former are also less regular in shape, confirming that a surface coverage of their surfaces occurred. More quantitatively, zeta profile analysis of images allowed estimation of a mean diameter of $d = 4.1 \pm 0.3$ nm for the starting CDs and $d = 5.2 \pm 0.8$ nm for P400-CDs, indicating a mean PEG layer thickness of $(5.2 - 4.1)/2 \approx 0.6$ nm. This value is less than the expected fully extended length of PEG400 [38], suggesting that the PEG adopts a mushroom-like configuration, as schematically illustrated in Figure 1(f). Moreover, the surface of P400-CDs remains negatively charged ($\zeta = -12$ mV), although the absolute value is significantly decreased compared to pristine CDs ($\zeta = -28$ mV).

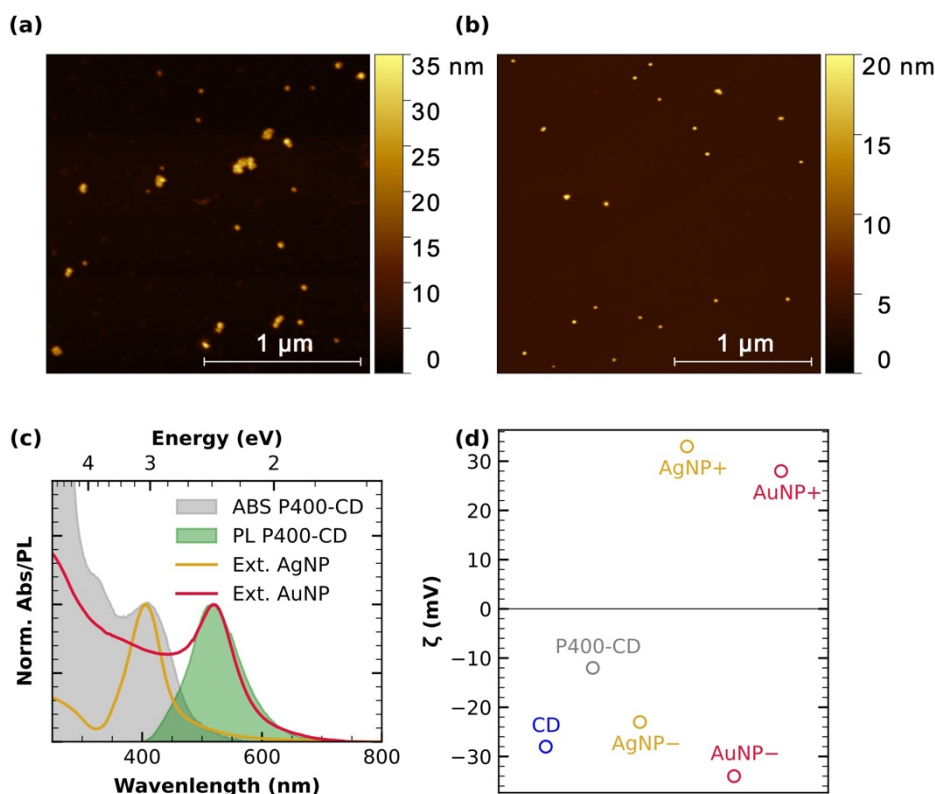


Figure 2: AFM images of (a) AgNPs and (b) AuNPs. (c) Normalized absorption (colored grey curve) and emission at $\lambda_{exc} = 410$ nm (colored green curve) spectra of P400-CD. Normalized extinction spectra of AgNPs (continuous yellow curve) and AuNPs (continuous red curve). (d) Zeta potential values of aqueous solutions of the different species involved in the study.

With the aim to evaluate how the emission characteristics of CDs are affected by plasmonic coupling, we synthesized silver and gold nanoparticles according to the synthetic routes reported in Materials and Methods. AFM measurements revealed that the AgNPs (Figure 2(a)) and AuNPs (Figure 2(b)) have average diameters of 25 ± 4 nm and 13 ± 2 nm, respectively. These size estimations were obtained by analyzing horizontal cross-sections of isolated nanoparticles in the AFM images (see representative examples in Figure S5). The diameter of each isolated nanoparticle was estimated by taking the z-value corresponding to the maximum height in the cross-section profile. We obtained compatible values by DLS measurements, which provided $d = 27 \pm 3$ nm for AgNPs and $d = 13 \pm 1$ nm for AuNPs. Indeed, since the plasmonic properties of metallic nanoparticles strongly depend on their morphological characteristics, their size was carefully chosen to reach an adequate spectral overlap with respect the spectral features of CDs. More specifically, as can be appreciated from Figure 2(c), the plasmonic band observed in the extinction spectrum of AgNPs (yellow curve) falls in correspondence of the lowest-energy transition observed in the absorption spectrum of P400-CDs (grey colored spectrum). Instead, the plasmonic band of the obtained AuNPs (red curve) shows a good overlap with the emission band of the P400-CDs (green colored spectrum). These completely distinct overlaps may potentially disclose the door for different types of photophysical interactions

between PEGylated CDs and the specific nature of metallic nanoparticles involved, since in the case of AgNPs the LSPR should play a role in the excitation stage of CDs, while in the case of AuNP any LSPR are expected to couple to the emissive transition [39,40]

The metallic nanoparticles as obtained after synthesis are characterized by a negative surface charge due to the presence of citrate ions, so in the following they will be referenced to as AgNP[−] and AuNP[−]. Specifically, from zeta potential measurements we get $\zeta = -23$ mV and $\zeta = -34$ mV for AgNP[−] and AuNP[−] (Figure 2(d)), respectively. Starting from these, we obtained also a second type of metallic nanoparticles with identical morphologies but oppositely charged surface, by performing a ligand exchange procedure with CTAB surfactant described in Materials and Methods. In this way we get AgNP⁺ and AuNP⁺, characterized by a ζ potential of +33 mV and +28 mV (Figure 2(d)), respectively. As expected [41,42], replacement of citrate ions by CTAB on the surface of MNPs also causes a small redshift (see Figure S6) of the plasmonic peak maximum from 520 to 523 nm from AuNP[−] to AuNP⁺, and an even more marked redshift from 405 to 413 nm from AgNP[−] to AgNP⁺. Besides, particularly for AuNPs, a small broadening in the redder part of the plasmonic band is detected, associable with minor aggregation effects during the ligand exchange-procedure [35,43]. Based on the ζ potential values reported in Figure 2(d), and considering the negative surface charge of P400-CDs, we expect for AgNP⁺ and AuNP⁺ a stronger tendency to interact with CDs, as facilitated by electrostatic attractions.

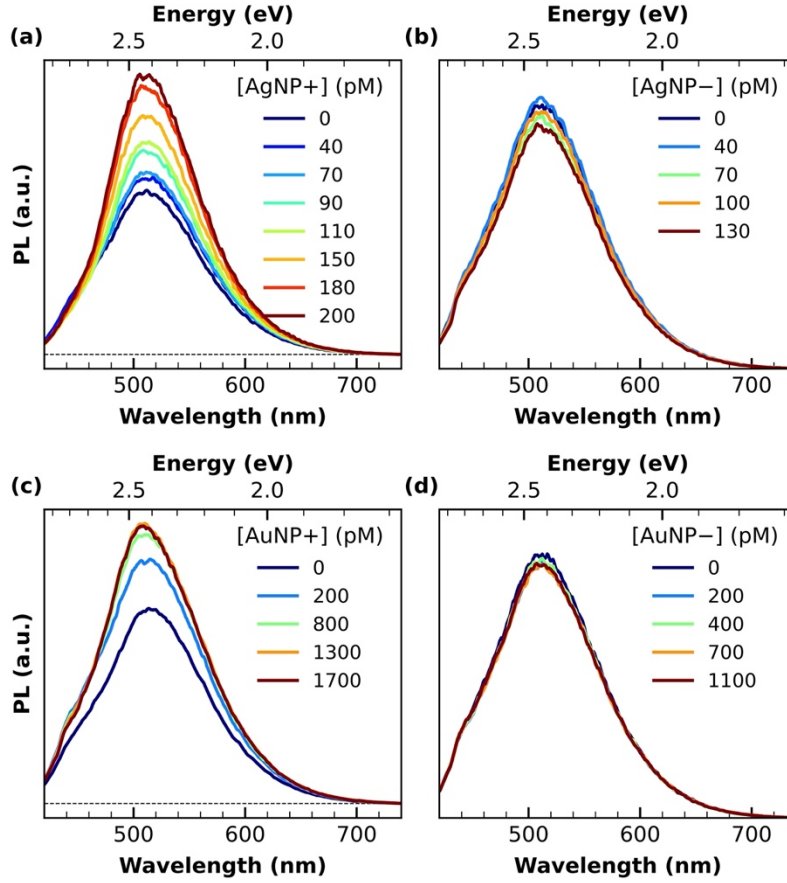


Figure 3: PL spectra of P400-CD aqueous solution under $\lambda_{exc} = 410$ nm upon increasing concentrations of (a) AgNP+, (b) AgNP-, (c) AuNP+ and (d) AuNP-.

On these grounds, we assessed the interactions in aqueous phase between PEGylated CDs and the distinct typologies of MNPs through fluorescence measurements. Figure 3 displays the effects observed on the emission of P400-CDs ($\lambda_{exc} = 410$ nm) upon increasing addition of MNPs. More specifically, Figure 3(a) and Figure 3(b) show the results related to AgNP+ and AgNP- additions, respectively, while Figure 3(c) and Figure 3(d) refer to the effects of increasing amounts of AuNP+ and AuNP-, respectively. We corrected all the data reported in Figure 3 to account for filter effects on excitation [44] which, particularly for AgNPs, cannot be entirely disregarded. Notably, we observe a significant enhancement in PL intensity of P400-CDs induced by the addition of increasing AgNP+ concentration (Figure 3a). Specifically, within the investigated range of AgNP+ concentration (up to 200 pM), the emission increases by a factor of about 1.8. Interestingly, as shown in Figure 3(b), when negatively surface-charged AgNP- are introduced, no significant changes in the emission characteristics of P400-CDs are observed. Similar findings are observed in the case of gold nanoparticles. The PL intensity undergoes an appreciable enhancement upon addition of AuNP+ (Figure 3c) approaching a saturation regime after reaching a AuNP+ concentration of about 800 pM, determining an overall enhancement of approximately a factor 1.5 (Figure 3(c)). As can be appreciated from Figure 3(d), almost no effect is detected when using negatively-charged AuNP-

nanoparticles. These results clearly show that both silver and gold nanoparticles can cause a fluorescence enhancement in PEGylated CDs, achieved via the spontaneous coupling of the two systems upon simple mixing. At the same time, this kind of plasmonic interactions are possible only in presence of an opportune electrostatic attraction, since the only interactions found are between precursors with oppositely charged surfaces. This suggests that P400-CDs do not bind to the surface of AgNP[−] and AuNP[−] due to the mutual electrostatic repulsion. In contrast, AuNP⁺ and AgNP⁺ exhibit strong interactions with P400-CDs, as evidenced by a significant change in the emission intensity. Also, DLS measurements revealed a mean relative size increase of 1.20 and 1.17 for AuNP⁺ and AgNP⁺, respectively, in the presence of P400-CDs, further confirming the effectiveness of their complexation.

For comparison, Figure S7 shows the significantly different behavior found in the case of the pristine CDs which, as anticipated, undergo a quenching of their emission upon addition of positively charged silver and gold nanoparticles. This also confirms the essential role of surface PEGylation of CDs in preventing the emission quenching of CDs which is widely accepted to occur in cases involving direct contact between photoexcited CDs and metallic nanoparticles [22,23,27,29,45].

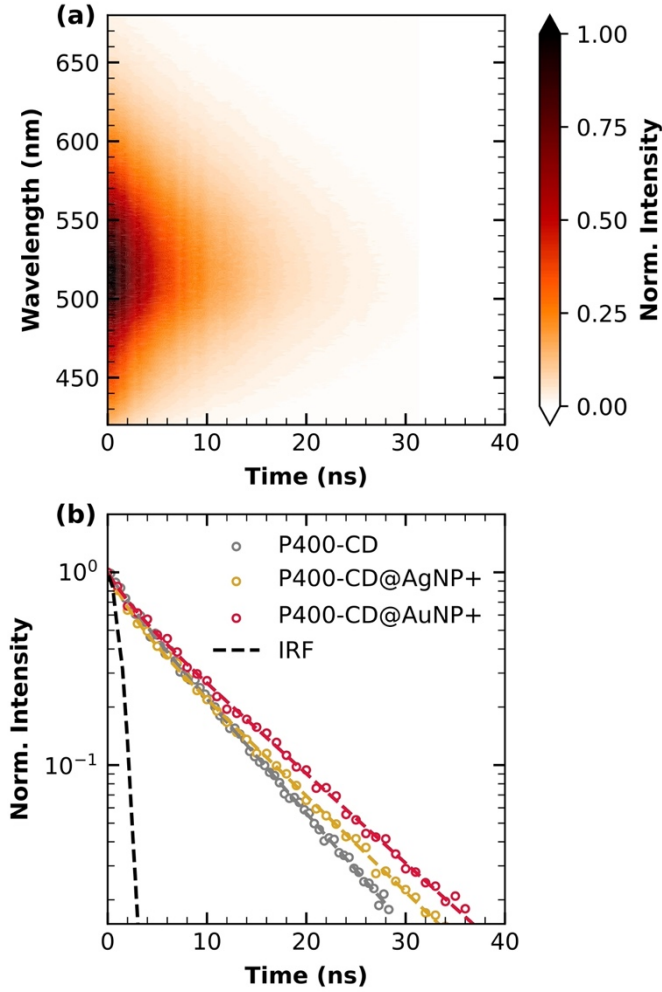


Figure 4: (a) Time-wavelength PL plot of P400-CDs aqueous solution upon 410 nm excitation. (b) PL decay kinetic traces ($\lambda_{exc} = 410$ nm, $\lambda_{em} = 520$ nm) of aqueous solution of bare P400-CDs (grey), P400-CDs in the presence of AgNP+ (yellow) and P400-CDs in the presence of AuNP+ (red).

To get more insights into the specific mechanism behind the PL enhancement of P400-CDs in the presence of AgNP+ and AuNP+, as shown in Figure 3(a) and Figure 3(c), we conducted time-resolved PL measurements. Figure 4(a) shows the time-wavelength PL plot of P400-CDs aqueous solution upon 410 nm excitation. In Figure 4(b) we provide a comparison of the normalized kinetic traces of PL decay of naked P400-CDs (in grey) with those of P400-CDs in presence of AgNP+ (in yellow) and AuNP+ (in red). For naked P400-CD, a biexponential decay fit reveals two decay constants: $\tau_1 = (2.3 \pm 0.6)$ ns and $\tau_2 = (7.4 \pm 0.2)$ ns, with a weighted mean decay time constant of $\langle \tau \rangle = 6.6$ ns. When AgNP+ are introduced, the first time constant remains unchanged within experimental uncertainty, being $\tau_1 = (2.0 \pm 0.5)$ ns, while $\tau_2 = (8.7 \pm 0.2)$ ns. This slight increase in τ_2 suggests a reduction in the non-radiative decay rate of P400-CDs upon binding to AgNP+, likely attributed to an electrostatic screening effect [37]. This effect can arise from specific interactions between cationic CTAB molecules on the surface of AgNP+ and the negatively-charged surface of P400-CDs, potentially reducing solvation effects at the surfaces of P400-CDs near AgNP+ and

decreasing the non-radiative decay rate in the second decay component. Despite these small changes in the decay components, the average lifetime for P400-CD in presence of AgNP+ remains essentially unaffected (6.6 ns), suggesting that the fluorescence enhancement achieved with AgNP+ is predominantly due to a near-field enhancement effect [46], commonly known as *lightning rod* phenomenon [14]. This occurs because the electronic transition stimulated at $\lambda_{exc} = 410$ nm in P400-CDs spectrally overlaps with the plasmonic band of the silver nanoparticles (see Figure 2(c)), effectively behaving as “nanoantennas”. In this scenario, AgNPs optically concentrate the local electric field, thereby enhancing the excitation rate of nearby P400-CDs and resulting in an increased emission without altering the excited state lifetime [47], analogously to what reported for CDs-Silica hybrid systems [10.1039/C4TC02599G].

On the other hand, in the presence of AuNP+ the biexponential fit yields $\tau_1 = (2.4 \pm 0.5)$ ns and $\tau_2 = (9.4 \pm 0.2)$ ns, with a mean timescale of 7.8 ns. The slightly increased τ_2 suggests that the effect of reduced solvation at the surfaces of P400-CDs near AuNP+ is even more pronounced compared to AgNP+. However, it is worth noting that the increase in PL lifetime alone (by a factor ~ 1.18) cannot fully account for the PL enhancement (by a factor ~ 1.44) observed in Figure 3(c), indicating the involvement of plasmonic-mediated interactions, rather than a situation where PL enhancement exclusively stems from a reduction in non-radiative decay rates. Given the spectral overlap between the PL spectrum of P400-CDs and the plasmonic band of AuNP+ (see Figure 2(c)), we would expect a Purcell-like mechanism for the metal enhanced fluorescence, leading to a shortened emission lifetime due to increased radiative decay rate [27,48–50]. Nevertheless, since we did not observe a shortened emission lifetime, it is plausible that either this occurs on a timescale faster than our temporal resolution or, similar to AgNP+, also in the case of AuNP+ a *lightning rod* effect contributes to the PL enhancement of P400-CDs. Furthermore, plasmonic interactions between AuNPs and CDs with emission overlapping the plasmonic band of the former have been shown to depend on the type of bond established between them [28]. For complexes with covalent bonds, more significant PL enhancements are typically observed. In contrast, the electrostatic interactions, as present in our systems, determines PL enhancement.

In Figure S8, we show simulations of near-field enhancement obtained from Mie theory for a 30 nm AgNP (panel a) and a 15 nm AuNP (panel b), both calculated at $\lambda = 410$ nm (see SI for more details). The near-field enhancement is defined as the ratio of the scattered electric field amplitude to the incident electric field amplitude. Our simulations reveal a higher field enhancement for AgNPs. Specifically, at a distance of 1 nm from the surface, the calculated field enhancement is 4.0 for AgNPs and 1.5 for AuNPs, along the incident field polarization. These findings align with the more efficient

PL enhancement observed in the presence of AgNPs and confirm that AuNPs can also contribute to near-field enhancement, albeit to a lesser extent.

Additionally, a second batch of CDs was functionalized with longer PEG chains, characterized by a molecular weight of 3000 Da, to obtain P3000-CD. This PEGylation procedure, detailed in the Material and Methods, followed the same approach used to obtain P400-CD. After the hydrothermal reaction, the resulting solution was similarly separated via SEC to isolate the P3000-CDs. AFM measurements (see Figure S9) revealed a broader size distribution, with a mean diameter of 15 ± 6 nm, suggesting a mean PEG layer thickness of approximately $(15.9 - 4.1)/2 \approx 6$ nm, which is consistent with previously reported thicknesses of PEG coatings [51]. In Figure S10 we compare the absorption spectrum of P3000-CDs with that of pristine CDs. The modifications observed in this case are more pronounced than for P400-CDs (compare with Figure 1), as highlighted by the significant broadening of the absorption peak at 410 nm. Moreover, the PEGylation with PEG3000 led to a less negative surface charge ($\zeta = -6$ mV), consistent with successful polymeric functionalization.

The plasmonic interactions with positively charged metallic nanoparticles were also briefly assessed for P3000-CDs. As shown in Figure S11(a), the addition of AuNP⁺ results in an enhancement in the PL intensity for P3000-CDs, similar to the effect observed for P400-CDs. In contrast, as shown in Figure S11(b), no noticeable effect on the emission was observed with the addition of AgNP⁺, even at 70 pM concentration of added MNPs. This contrasts with the remarkable PL enhancement seen in P400-CD under similar conditions. This lack of PL change in P3000-CDs with AgNPs can be attributed to the absence of significant complexation between the two systems, as suggested by DLS measurements. Indeed, while a mean size increase of 1.70 was observed with AuNP⁺, the addition of P3000-CDs to AgNP⁺ resulted in no appreciable change in hydrodynamic radius. Further studies comparing polymeric spacers of several lengths will be required for a more complete understanding and modeling of these effects.

Conclusions

In conclusion, taking advantage of the chemical versatility of nitrogen-containing CDs, we introduced a polymeric shell on their surface via a simple hydrothermal PEGylation reaction, to explore its impact on their photophysical properties and interactions with plasmonic silver and gold nanoparticles. Functionalizing CDs with PEG molecules allows to enhance their emission properties, increasing quantum yield and fluorescence lifetime, resulting from an effective surface passivation which reduces the non-radiative decay due to hindered interactions with water molecules. More

importantly, we demonstrated that careful manipulation of the surface charge on silver and gold nanoparticles enables their self-assembly with PEGylated CDs, primarily driven by electrostatic interactions. Shorter PEG chains enabled an appreciable photoluminescence enhancement of PEGylated CDs when coupled with both silver and gold nanoparticles, mostly due to a lightning rod effects in both cases, as also confirmed by theoretical calculations. However, longer chains increased the interaction distance, leading to reduced plasmonic coupling and almost no interaction with silver nanoparticles, confirming that interaction distance is a key factor in determining coupling strength. Overall, our investigation of plasmonic coupling of green emitting CDs with both gold and silver nanoparticles under controlled conditions provides deeper insights into plasmonic modulation of PL in hybrid systems. These findings open up new possibilities for tailoring nanomaterial characteristics for advanced optoelectronic applications through the strategic modulation of surface passivation, charge modulation and interaction distance. For example, this approach could pave the way for high-performance fluorescence-based sensors leveraging plasmonic coupling for signal enhancement or energy-efficient optoelectronic devices benefiting from improved photoluminescence and stability.

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