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# "Green" Fluorescent–Plasmonic Carbon-Based Nanocomposites with Controlled Performance for Mild Laser Hyperthermia

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Abstract: Fluorescent carbon nanodots are a promising nanomaterial for different applications in biophotonics, sensing and optical nanothermometry fields due to their strong fluorescence properties. However, their multi-modal applications are considerably limited, requiring the use of several nanoagents that could solve different tasks simultaneously. In this paper, we report the first experimental results on a facile "green" laser-based synthesis of multi-modal carbon-metallic nanocomposites with tuned optical performance. This simple approach leads to the appearance of finely controlled plasmonic properties in carbon-based nanocomposites whose spectral position is adapted by using an appropriate material. Thus, longer laser ablation provokes 29-fold increase in the absorption intensity of carbon-gold nanocomposites due to the increase in the metal content from 13% (30 s) to 53% (600 s). Despite strong plasmonic properties, the metal presence results in the quenching of the carbon nanostructures' fluorescence (2.4-fold for C-Au NCs and 3.6-fold for C-Ag NCs for 600 s ablation time). Plasmonic nanocomposites with variable metal content reveal a ~3-fold increase in the laser-to-heat conversion efficiency of carbon nanodots matching the temperature range for mild hyperthermia applications. The findings presented demonstrate a facile approach to expanding the properties of chemically prepared semiconductor nanostructures due to the formation of novel semiconductor-metallic nanocomposites using a "green" approach. Together with the ease in control of their performance, it can considerably increase the impact of semiconductor nanomaterials in various photonic, plasmonic and biomedical applications.



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** carbon nanodots; photoluminescence; laser ablation; plasmonic nanostructures; nanocomposites; hyperthermia

### 1. Introduction

The rapid development of nanotechnologies has led to the design and fabrication of a wide variety of different nanostructures. Among them, composite nanomaterials attract a high research interest due to their unique specific properties from the merging of different chemical elements. Together with the fine control of their chemical composition and the corresponding performance, it opens up new wide prospects of such nanocomposites (NCs) in various application areas where, undoubtedly, the field of life science is the most promising one [1–4]. However, conventional chemical synthesis methods result in some serious issues, such as complex methodologies and the contamination or use of hazardous chemical precursors, that can lead to critical toxicity effects. Thus, the development of novel, effortless "green" methods is required, which allows for a controllable extension of the performance of existing nanostructures due to the fabrication of composite nanomaterials.

One such environmentally friendly approach is based on the pulsed laser ablation in liquids (PLALs) technique, allowing nanostructure formation at high chemical purity conditions. Its numerous experimental parameters ensure the adaptation of the structural, magnetic and optical properties of single-element nanostructures [5–8]. Moreover, bimetallic nanoparticles (NPs) with tuneable chemical contents can also be easily synthesised by PLALs [9–12]. Nevertheless, there is still a great lack of research devoted to the laser ablation fabrication of semiconductor–metallic nanocomposites and studies of their structural and physicochemical properties. However, a number of recent papers dedicated to the laser-assisted synthesis of semiconductor–metallic nanocomposites convincingly demonstrate their capacity and outlook in biomedical applications. In particular, platforms based on silicon and plasmonic metals, such as Ag-Si or Au-Si prepared via pulsed laser ablation, have been reported recently for optical sensing and light-to-heat conversion applications [13,14]. Furthermore, Si-Au nanocomposites can also be formed without the use of any chemical surfactants via laser ablation of a metallic target immersed in colloidal solutions of semiconductor nanoparticles that were also prepared by PLALs [15–19].

A promising class of materials for nanocomposite fabrication is related to organic and inorganic semiconductor nanostructures that can be widely employed in different photonic applications. Indeed, organic nanostructures exhibit upconversion or multi-band photoluminescence (PL) that is very demanding in sensing, imaging, or nanothermometry applications [20–22]. Various group IV semiconductors, such as silicon nanoparticles, have been successfully demonstrated in the field of life science [23–29], molecule or temperature nanosensing [30–33], nonlinear photonics [34] and hydrogen generation [35–37]. Moreover, germanium nanostructures can be employed for cell imaging [38], memory devices [39] and many other applications [40]. Finally, carbon nanodots (C NDs), exhibiting strong fluorescence in the visible spectral range [41,42], are promising for photonic and life science applications, in particular for optical bioimaging, water cleaning technologies and bimodal fluorescence-photoacoustic imaging [43–45]. Nevertheless, their application areas are still significantly limited due to the absence of other features, such as plasmonic or magnetic properties requiring the development of novel nanomaterials with easily controlled performance.

In this paper, we report for the first time a facile "green" synthesis of novel carbonbased fluorescent–plasmonic nanocomposites with tuneable optical performance. For this purpose, the ultrafast laser ablation of noble metal targets (gold or silver) immersed in colloidal solutions of chemically prepared carbon nanodots was performed. We found a strong time-dependent evolution of both the absorbance and emission properties of C NDs influenced by laser-affected changes in their chemical compositions. These nanocomposites reveal strong plasmonic properties with irradiation time-controlled efficiency whose spectral position depends on the metallic plate used. At the same time, the efficiency of their photoexcitation is found to be considerably decreased, followed by quenching of the nanocomposites' photoluminescence regardless of their strong plasmonic properties. Fluorescent–plasmonic nanocomposites can also reveal perspectives for photothermal therapy applications due to controlled laser-stimulated hyperthermia. Our findings demonstrate a facile route to improve the properties of chemically prepared semiconductor nanostructures by designing novel laser-synthesised nanocomposites with controlled performance that can be used for various photonic and plasmonic applications.

#### 2. Experimental Section/Methods

Carbon nanodots (mean size ~4 nm) were synthesised from a mixture of urea (p.a. grade) and anhydrous citric acid (pharm. grade), taken in a molar ratio of 2 to 1. The total mass of the mixture was 10 g. After mixing, the components were transferred to an open Pyrex glass reactor of 100 mL, which was placed in a shaft furnace, and the furnace temperature was carefully increased to 135 °C for 15 min. The reaction mixture melted and turned a yellow colour. Afterwards, the temperature was raised to 165 °C and held at this value for one hour. At the end of the carbonisation process, no evolution of gases or vapours was observed, and the molten product turned into a black, shiny, fragile mass. Then, the mixture was dissolved in 80 mL of 15% isopropanol with slight heating, acidified with 10 mL of hydrochloric acid, and the precipitate was filtered and dried in air. A loose, black, fine powder was obtained.

To improve the properties of C NDs and to synthesise nanocomposites, a method of direct PLALs was used. For this purpose, various noble metal solid targets (silver and gold) of high purity (>99.99%) immersed in colloidal aqueous solutions of C NDs (concentration 0.1 g/L) were irradiated using an ultrafast laser source (Figure 1a). The solution volume was 15 mL, and the level above the surface was 4 mm. A laser operated at 1030 nm wavelength with a 10,000 Hz repetition rate and 6 ps pulse duration was used. The laser irradiation was focused on a target surface with a galvoscanner (focal distance is 162 mm) into a spot with a size of ~50 µm that also allowed us to scan the irradiation along the surface (10 × 10 mm<sup>2</sup>). The laser energy was controlled using a half-wave plate and was fixed at 20 µJ/pulse in all experiments. The duration of the laser ablation varied from 30 s to 600 s in order to establish its impact on the optical properties of the nanocomposites.



**Figure 1.** A sketch of the laser ablation synthesis of plasmonic carbon–metallic nanocomposites (C—carbon, M—silver or gold metals) (**a**) and their laser-assisted hyperthermia (**b**).

The mass difference of the gold and silver targets was calculated as a difference of their masses before and after laser ablation at different times. For this purpose, an Adam NBL124i scale with  $\pm 0.1$  mg precision was used. Prior to weighting, the ablated targets were washed in order to remove possible contamination by ablation products and then carefully dried in order to avoid a water impact. The ablation speed was estimated by dividing the obtained mass difference by a corresponding ablation time. The metal content in the nanostructures was determined by dividing the mass of metals by the sum of masses of carbon and metals forming nanocomposites. They were obtained with inductively coupled plasma mass spectrometer (ICP-MS) (Agilent 8800, Tokyo, Japan) using carbon-metallic nanoparticles dissolved in the mixture (65% and 35% of nitric and hydrochloric acids) at 190 °C for 600 s prior to the experiments. To detect changes in optical properties of C NDs due to the laser ablation of different metals, their absorbance spectra were measured in the 280-800 nm spectral range with a UV-Vis spectrometer (Shimadzu-2600) using the following parameters: absorbance mode with a single acquisition, slit width—2 nm and accumulation—2 s). Prior to the measurements, colloidal solutions were diluted 10-fold in order to avoid the influence of concentration effects. Moreover, they were also investigated using photoluminescence (PL) spectroscopy using Edinburgh Instruments FLS 1000 spectrofluorometer equipped with double excitation—double emission monochromators, a Xenon lamp (350 W power) as an excitation source and Hamamatsu PMT-R928P detector cooled to -22 °C. Firstly, photoluminescence excitation (PLE) spectra of C ND-based samples were registered in the range 250–460 nm with fixed emission wavelength at 470 nm to find out the best excitation wavelength of the samples. Afterwards, PL spectra were observed in the spectral range from 410 to 750 nm at different (330, 370 and 400 nm) excitation wavelengths. The wavelength at 400 nm was matched to the absorption maximum of silver nanostructures, 370 nm was matched to the best excitation according to the PLE measurements and 330 nm was

located outside of these maxima. The experimental parameters were as follows: excitation bandwidth—1.50 nm, emission bandwidth—0.50 nm, dwell time—0.1 s, step—2 mm and accumulation—1. All detected PL spectra were corrected according to the optics and electronics used. The laser-induced hyperthermia was achieved using a laser operated at 800 nm wavelength, 1000 Hz repetition rate, 35 fs pulse duration and 1.3 W power. The heating was monitored with a Bosch GTC400C thermal camera that observed 1 mL of colloidal solutions placed in a plastic cuvette and irradiated for 10 min (Figure 1b).

#### 3. Results and Discussion

To modify the properties of C NDs, pulsed laser ablation of metallic (silver, gold) targets immersed in colloidal solutions of the fluorescent nanostructures was performed (Figure 1a). The deposition of the used laser energy on the target surface led to the emission of metallic nanoclusters [46–48], which can cover semiconductor nanodots forming the core-shell nanocomposite structure (Figure 1a). At the same time, the high-power ultrafast laser irradiation can also fragment nanoparticles [49], forming, in our case, carbon nanoclusters. They can further interact with nanoparticles emitted from the metallic target, forming an alloy structure. In order to establish an exact structure of the synthesized plasmonic nanocomposites, an additional study by means of electron microscopy (HR-TEM/SEM), Energy-dispersive X-ray (EDX) mapping, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) will be performed and reported separately.

To reveal the amount of ablated material as well as the ablation speed at different irradiation times, the difference in the mass of a metallic target before and after pulsed laser ablation was estimated at different durations (Figure 2). Firstly, one can see the increase in the mass difference for a longer laser ablation process, reaching ~4 mg (in 10 mL volume) at 10 min ablation time of the gold target, which can lead to a higher metallic content in composite carbon-based nanoparticles. It is worth noticing that a larger mass difference was obtained for the ablation of the gold target as compared with the silver one treated at the same experimental conditions (Figure 2a). We hypothesise that the first reason for such behaviour can be associated with the different densities of bulk gold and silver targets (19.32 and 10.50 g cm<sup>-3</sup>, respectively). Moreover, another reason can be related to the different ablation threshold values for the metallic targets used [50,51]. Indeed, it has already been reported that the ablation threshold for silver is ~1.2 times higher than that for gold irradiated at similar conditions [52]. Thus, laser irradiation can lead to a larger number of ablated species of gold as compared with silver due to the lower value of the laser ablation threshold. At the same time, the corresponding ablation speed decreased with the ablation time for both types of metals (Figure 2b). This can happen due to the permanent increase in the nanoparticle concentration leading to additional laser energy losses because of their absorption or scattering. Moreover, the time-dependent ablation speed was found to be higher for the gold target rather than for the silver one due to the larger mass and lower ablation threshold of gold. The mass of the noble metals in fluorescent-plasmonic nanocomposites was estimated by means of the ICP-MS method. It was found that the metallic content was increased with the laser ablation time, reaching  $\sim$ 50% of the mass of C-Ag NCs and  $\sim$ 70% of the mass of C-Au NPs (Figure 2c). One can mention slight time-dependent changes in the chemical composition starting from 300 s of the laser irradiation due to the decrease in the ablation efficiency. The obtained results will help with the preparation of carbon-metallic nanocomposites with the required chemical composition by choosing an appropriate ablation time.

Aiming to reveal the plasmonic properties of the laser-synthesised nanocomposites, their absorbance spectra were measured in the visible spectral range (280–800 nm). In all cases, apart from the carbon absorption band at 350 nm, laser ablation led to the appearance of plasmonic features either at around 400 nm (for silver) or 520 nm (for gold) (Figure 3), thus allowing us to vary the spectral position of the plasmonic maximum [17]. Moreover, their intensity also considerably depended on the duration of the laser treatment. Indeed, a

longer ablation time provoked a stronger plasmonic absorbance of both the C-Ag and C-Au NCs, also providing some enhancement of the carbon absorbance that was more remarkable in the case of C-Au NCs due to the absence of overlap between carbon and metallic bands (Figure 3). Thus, these experimental results show the presence of metallic nanostructures with the content influenced by the duration of the laser treatment. The efficiency of the plasmonic properties (Figure 3) can be associated with the exact chemical composition of each sample defined using inductively coupled plasma mass spectroscopy (Figure 2c). The observed findings indicate a facile possibility of the formation of composite carbon–metallic nanostructures with variable chemical compositions influencing both spectral position and the efficiency of plasmonic properties.



**Figure 2.** The dependencies of the ablated mass of the noble metals (**a**), their ablation speed (**b**) and the mass metal content in nanostructures obtained using the ICP-MS method (**c**) on the laser ablation time during the synthesis of carbon–metallic nanocomposites.



**Figure 3.** Absorbance spectra of plasmonic nanocomposites formed by the laser ablation of silver (**a**) and gold (**b**) targets immersed in colloidal solutions of C NDs.

To check wavelengths, which will provide the most efficient photoluminescence (PL) excitation for carbon-metallic nanostructures with different metallic content, photoluminescence emission (PLE) measurements were carried out. This study discovered a small (~20 nm) redshift of the most efficient excitation wavelength (370 nm) as compared with the maximum absorption of carbon (350 nm). Moreover, the obtained results also indicated a considerable decrease in the excitation efficiency for both C-Ag and C-Au NCs in comparison with the initial C NDs (Figure 4). Indeed, a 2.6-fold decrease in the excitation efficiency was found for C-Au NCs formed at 600 s laser ablation time, and a 3.4-times decrease was observed for C-Ag NCs synthesised in identical experimental conditions (Figure 4). One can hypothesise that it can possibly be associated with stronger light absorption by metallic nanostructures that will reduce the amount of light reaching C NDs and excite the PL of the semiconductor nanostructure. Furthermore, the possible laser-induced structural modification of C NDs did not provoke any spectral shifts in the PLE spectra of carbonmetallic nanocomposites except for some small variation (~4 nm) for C-Ag NCs (Figure 4). It can indicate the absence of any new levels involved in the radiation transitions in the nanocomposites, which can appear because of the interaction between carbon and metallic elements. The obtained results exhibit a strong influence of both metallic elements that appeared as a result of laser ablation on the PL properties of fluorescent carbon nanodots.

To establish the impact of the laser ablation of the metallic targets on the emission properties of C NDs, the corresponding spectra of their PL excited at different wavelengths (330 nm, 370 nm and 400 nm) were studied. These wavelengths were chosen using the following criteria: 400 nm—plasmonic resonance of silver, 370 nm—resonance absorption of C NDs and 330 nm—the wavelength outside these resonances. As indicated in Figure 5, PL spectra were normalised to one using the maximum integral intensity of the PL spectrum of pure C NDs excited at 370 nm (matching maximum excitation efficiency), allowing us to compare the PL intensities of various nanocomposites excited at different wavelengths. Firstly, a similar trend was observed for both C-Ag and C-Au NCs, demonstrating the decrease in their PL intensity with the increase in the laser ablation time, leading to a higher concentration of metallic content (Figure 5). Such a behaviour was observed for all excitation wavelengths used, differing only in the spectra aspect ratio. The results obtained clearly show that the PL quenching of C NDs induced by ablated metallic elements increases with the metallic content.



**Figure 4.** Photoluminescence excitation spectra of plasmonic nanocomposites formed by the laser ablation of silver (**a**) and gold (**b**) targets immersed in colloidal solutions of C NDs. Emission wavelength is fixed at 470 nm.



**Figure 5.** Photoluminescence spectra of plasmonic nanocomposites formed by the laser ablation of silver (**a**–**c**) and gold (**d**–**f**) targets immersed in colloidal solutions of C NDs obtained at different excitation wavelengths.

The plasmonic enhancement of the C NDs' fluorescence, which one could expect here due to the appearance of noble metal elements, did not occur. One speculates that the structure of the nanocomposites formed does not match the conditions favourable for the plasmonic enhancement of the fluorescence via the increase in local electrical fields of noble metal nanostructures. In particular, as suggested above, silver or gold can cover carbon nanodots, shielding them from the excited light that increases with a higher concentration of the metallic elements at longer laser ablation, leading to lower PL intensity. Moreover, it has already been shown that metals can lead to quenching of the PL of semiconductor nanomaterials or other fluorescent emitters [53–55]. Thus, an increased metallic content can lead to more efficient PL quenching of C NDs. To figure out the distribution of the local electric fields possibly provided by plasmonic nanostructures, a computer simulation, e.g., by FTDT, is required. The excitation of the PL of carbon nanocomposites at different excitation wavelengths did not indicate any considerable changes in the aforementioned trends besides some differences in the emission intensity of C NDs due to the change in their absorption (Figure 5). It can indicate the presence of only one mechanism of the radiation transitions in carbon-metallic nanocomposites identical to the initial C NDs without any modifications due to merged metallic elements. The changes in the PL spectra of carbon–metallic nanocomposites observed in Figure 5 are depicted in Figure 6, demonstrating a considerable decrease in the integral PL intensities for all studied nanocomposites excited at different wavelengths. Indeed, in all cases, a stronger reduction in the emission intensity was found for silver-containing nanocomposites as compared with C-Au ones (Figure 6). For instance, a 2.4- and a 3.6-fold decrease occurred for C-Au and C-Ag composite nanoparticles formed during a 600 s laser ablation time, respectively, at a 370 nm excitation wavelength matching the maximum efficiency of carbon (Figure 6b). It can indicate either a larger amount of silver atoms in the C-Ag NCs in comparison with that in C-Au NPs formed in similar conditions or their different distribution in a particle. Thus, the obtained results demonstrate considerable quenching of the PL of C NDs increasing with the laser ablation time, which is higher for C-Ag NCs.

As a further outlook, we assume that the formation of composite C ND-based nanostructures can extend the application range of fluorescent carbon nanodots in the field of life science. As mentioned above, C NDs are employed in fluorescent and photoacoustic bioimaging [43–45]. However, by merging with plasmonic elements in controlled conditions, they can also be employed as optical sensors using surface enhancement of Raman scattering (SERS), infrared absorption (SEIRA) signals or as multi-modal contrast or antibacterial agents [56,57] (Figure 7a). Moreover, this approach can also improve already existing carbon modalities investigated for nanocomposites with a metal content less than 50% of nanostructure mass. As a result, colloidal solutions of bare C NDs showed a slight heating rate (~2 K) when irradiated with an fs laser (800 nm, 35 fs) for 600 s. However, the change in the chemical composition remarkably affected the hyperthermia performance of the semiconductor nanostructures (Figure 7b,c). One can observe a ~3-fold increase in the maximum temperature for both types of fluorescent-plasmonic nanocomposites due to the presence of noble metal elements (Figure 7b,c). It is worth noticing that the plasmonic metals used have a ~3-orders of magnitude higher thermal conductivity than C NDs [58]. Moreover, the concentration of plasmonic metals (Figure 2c) influenced the hyperthermia performance (Figure 7b,c). Indeed, a higher content of silver or gold led to faster heating that may be related to a larger concentration of charge carriers in nanocomposites formed with a longer laser irradiation. Additionally, C-Ag NCs revealed better laser-induced heating as compared with C-Au NCs (Figure 7b,c). The main reasons for such a difference can be associated with (i) the larger thermal conductivity of silver (~430 Wm<sup>-1</sup> K<sup>-1</sup>) in comparison with gold ( $\sim$  320 Wm<sup>-1</sup> K<sup>-1</sup>) as well as (ii) higher silver content in nanocomposites. The heating rate achieved (~6 K), controlled by the laser synthesis conditions, can be very promising for mild hyperthermia in the 39–44 °C temperature range, which can boost the effectiveness of different therapies to kill cancer tumours [59,60]. With an adjustable laser ablation-controlled heating rate, carbon–metallic nanocomposites can be designed

in order to easily achieve the maximum temperature of around 41–43 °C that increases membrane permeability accompanied by the reduction in DNA damage repair that leads to a higher probability of cancer-tumour killing [59]. Fine-tuning of the heating rate of the nanocomposites will allow one (i) to obtain perfect fitting to the temperature, leading to the destruction of cancer tissues, and, at the same time, (ii) to avoid unnecessary overheating of surrounding healthy cells, thus reducing side-effects. The developed method can be a facile route to broaden the functionality of fluorescent carbon nanodots to various applications by choosing the appropriate elements.



**Figure 6.** Dependencies of the PL integral intensities of C-Ag and C-Au nanocomposites at different excitation wavelengths: 330 nm (**a**) 370 nm (**b**) and 400 nm (**c**).





**Figure 7.** Further outlooks of composite carbon nanoparticles with plasmonic properties (**a**). Laser-assisted hyperthermia with C-Ag NCs (**b**) and C-Au NCs (**c**) prepared at different laser ablation times.

## 4. Conclusions

In summary, fluorescent carbon-metallic nanocomposites with tuneable plasmonic properties were synthesised by means of the pulsed laser ablation in liquids technique. Such treatment leads to a larger mass of gold as compared with silver due to (i) its lower ablation threshold, increasing the ablation speed, and (ii) higher gold density. The spectral position of the plasmonic maximum was varied by choosing an appropriate metallic target (400 nm for Ag and 520 nm for Au), while their intensity can easily be controlled by the duration of the laser treatment (from 30 s to 600 s), reaching a 29-fold increase. The efficiency of the photoexcitation at a 370 nm excitation wavelength was considerably decreased for both C-Ag and C-Au NCs prepared at 600 s ablation time (4-times and 3.7-times, respectively) as compared with initial C NDs (0 s ablation time). Various metallic elements decrease the PL intensity of carbon-metallic nanocomposites depending on the metal used and the duration of the laser ablation. In particular, silver provokes stronger quenching of the PL of C NDs than gold, increasing with ablation time in both cases. Moreover, plasmonic metal content increases the laser-induced hyperthermia performance of semiconductor nanostructures, which is promising for cancer theranostic applications. Further prospects of laser-synthesised carbon-metallic nanocomposites are suggested for the extension of their application areas.

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