Photoluminescence properties of silk–carbon quantum dots composites

Elena Colusso¹ · Luca Cicerchia¹ · Michele Rigon¹ · Vincent Gomes² · Alessandro Martucci¹

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Abstract
In this paper, we report silk fibroin (SF) and carbon quantum dots (CQDs) nanocomposites obtained through a facile solution casting approach. The optical properties of the nanocomposites have been characterised by UV–vis absorption and photoluminescence spectroscopy. Crosslinking of SF and chemical interactions with the CQDs have been investigated by FTIR spectroscopy. In addition, water stability and degradability of the prepared composites have been investigated in terms of mass loss, important for applications in a real scenario. We observed that for a concentration of CQDs above 1%wt aggregation of nanoparticles occurs, affecting the photoluminescence of the material. The results show that the best composition in terms of photoluminescence intensity and water stability is 0.5%wt CQDs.

Graphical abstract

Keywords  Fluorescent polymer composites · Carbon quantum dots · Silk fibroin · Methanol annealing

Highlights
- Silk–carbon quantum dot composites were formed via a solution casting method.
- Carbon quantum dots and silk fibroin were physically mixed, and no chemical bonds were detected.
- Luminescence quenching and loss in transparency were observed for concentrations of CQDs > 1%.

¹ Industrial Engineering Department and INSTM, University of Padova, Padova, Italy
² School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, NSW 2006, Australia
1 Introduction

Carbon quantum dots (CQDs) have attracted increasing attention in the last 10 years because of their photoluminescence properties, inherent biocompatibility, solubility in water, easy, low-cost, and green synthesis procedures, and surface modification [1, 2]. They have promising applications in optoelectronic devices, solar cells, ion sensing, bioimaging, and implantable devices [3–8]. Most of these applications require the fabrication of a thin film to utilise the high fluorescence of CQDs. A typical approach is the fabrication of a polymer matrix composite. The incorporation of CQDs in a suitable polymer matrix has undoubted advantages. Polymers offer mechanical support and chemical resistance. On the other hand, CQDs provide new capabilities such as self-healing, shape memory, stimuli responsive, and electrochemical characteristics.

Several strategies have been investigated for the fabrication of the composites, involving one or two-steps synthesis, as recently reviewed by Du et al. [9]. The polymer matrix is selected based on the application. CQDs can be either covalently attached to the polymer or physically blended depending on the type of polymer and the adopted approach. Typical polymers are polymethyl methacrylate (PMMA), polydimethylsiloxane (PDMS), and polystyrene (PS). However, the stabilisation of CQDs inside those polymers remains a challenge. Aggregation and phase separation could occur, thereby compromising the photoluminescence properties of CQDs. In addition, those polymers are not degradable nor biocompatible. Due to their high solubility in water, the combination of CQDs with hydrophilic polymers, such as poly(vinyl alcohol) (PVA) [10, 11] and gel-forming biopolymers such as agar [12], has also been investigated.

Feng et al. [13] have recently reviewed CQDs/polymer composites for energy, environmental and biomedical applications. In energy applications, conducting polymers have been adopted, such as polypyrrole or polyaniline. Cellulose, PVA, and alginate have been instead investigated for the fabrication of fluorescent probes, as adsorbents for the removal of contaminants or for biomedical scaffolds. However, most of the polymers considered are still obtained from fossil-based sources, and the approaches adopted for the fabrication of the composites are not sustainable. Researchers are looking for new materials obtained using green processing and renewable resources to face the global challenge for a more sustainable ecosystem.

Silk fibroin (SF) is a natural biopolymer, derived from silkworm cocoons, that is water-soluble, biodegradable, and biocompatible. It could be processed in a variety of shapes, including films, membranes, hydrogels, sponges, and fibres [14]. Compared to other biopolymers, SF is superior in terms of mechanical properties, biocompatibility, optical properties, and tuneable degradability. In addition, green methods can be applied to process SF from raw fibres into the final material format [15].

SF molecules self-assemble in a gel during water evaporation, which is converted into a dense polymer after drying. Gelation is achieved by physical crosslinking resulting in 3D polymerisation in solution. Irreversible gelation is obtained through the formation of thermodynamically stable β-sheets [16]. The arrangement of polymer chains into β-sheets involves the breakage of hydrogen bonds between water and silk and the formation of intra-/inter-chain hydrogen bonds [17]. Crosslinking of SF could be promoted by treatments with alcohols, such as ethanol or methanol. Annealing of SF materials with methanol is used to promote the water stability of the devices and tune the degradability [18].

Fluorescent SF composites materials have been developed with inorganic QDs (CdSe, ZnSe) as a suitable platform for optical sensing or white-light-emitted devices [19–21]. However, the use of these materials in bio-applications is limited because of the inherent toxicity of those nanoparticles.

In this paper, we combined SF and edge-enriched CQDs [22, 23] to obtain transparent luminescent film composites. Since both silk and CQDs are biocompatible [23, 24] and the process is all water-based, this study represents a starting point for the fabrication of green and biocompatible SF–CQDs composites.

We investigated the optical properties of thick self-standing films with different CQDs content by UV–vis spectroscopy and photoluminescence (PL) spectroscopy. Formation of CQDs–protein interaction and β-sheets were detected by Fourier transform infrared (FTIR) spectroscopy. Since the environmental and biomedical application of hydrophilic polymers is affected by water stability, we also investigated the effect of methanol treatment on the PL and its degradability in terms of mass loss. Similar composites were recently reported by combining SF with graphene QDs [25], however, no studies of the crosslinking effect of the methanol treatment and the water stability of the nanocomposites were previously conducted.

2 Experimental

2.1 Materials

Details on the synthesis and physicochemical characterisation of CQDs were previously reported in [22, 23]. SF solution was prepared according to a standard protocol starting from raw silk cocoon fibres. The process involved different steps: degumming, dissolving, dialysis, and purification through centrifugation. All the details are reported
The final concentration of the as-prepared SF solution in water was set to 60 mg/ml.

2.2 Fabrication of SF-CQDs composite films

SF water solution and CQDs (10 mg/ml) water solution were gently mixed to form SF-CQDs solution. Specifically, different amounts of CQDs solution were added to 3 ml SF solution (60 mg/ml) to tune the CQDs content in respect of the fibroin as follows: 0, 0.05, 0.5, 1, 2, 3, 5%wt. The mixed solution was cast on a polydimethylsiloxane (PDMS) substrate and left to dry (40% RH, 25 °C). Methanol annealing was used to induce a structural transition from the random coil (silk I) to β-sheet (silk II) [28]. Dried films were immersed in methanol (Sigma-Aldrich) for 4 h and then dried under a hood before measurements.

2.3 Characterisations

ATR FTIR spectra were recorded with a Jasco FTIR6200 spectrometer with ATR pro ONE, in the 4000–600 cm⁻¹ range (4 cm⁻¹, 64 scans). UV–vis absorption spectra of both solutions and solid-state composite films were recorded in the 300–800 nm range (Jasco V650). The spectra of the solutions were collected using a quartz cuvette (1 cm length path). Absorption spectra of the freestanding films were collected with the same instruments using a data pitch of 1 nm. The films were fixed on a framework and inserted in the measuring chamber normal to the incident beam. PL spectra of CQDs in solution were collected in a cuvette by using a spectrofluorometer (Jasco FP630). PL of the composite films was measured at room temperature with a custom-made set-up consisting of a 380 nm LED source (Ocean Optics LS-450), a detector (Ocean Optics HR400), two optical fibres (Ocean Optics QP400-1-VIS-NIR) and a sample holder. The excitation beam was normal with respect to the sample surface and the signal collected at 60° in respect of the sample. A bandpass optical filter was used to reduce the collection of the exciting light below 400 nm. The spectra reported are raw data. The structural characteristics of the SF-CQDs nanocomposites were examined by TEM (JEOL 1400) operating at 200 kV. Measurements of the mean diameter of nanoparticles agglomerates were conducted by using ImageJ. A set of about 30/40 aggregates was analysed, and the results were reported as an average dimension with standard deviation.

2.4 Stability in water

Stability tests were performed by dipping the methanol-treated samples in water for 5 min and then letting them dry under a fume hood for 48 h. Samples were weighed before the immersion and after drying to calculate the mass loss. Mass loss was calculated according to the following formula:

\[ \Delta m(\%) = \frac{m_0 - m_1}{m_0} \times 100 \]

where \( m_0 \) is the initial weight of the sample and \( m_1 \) the weight after the treatment.

Residual water solutions were analysed by UV–vis spectroscopy to detect the presence of CQDs.

3 Results and discussion

3.1 Preliminary characterisations

CQDs show a characteristic absorption in the range 300–500 nm, with two peaks at 335 and 405 nm (Fig. 1) corresponding to surface functionalities (n–π* transitions) [8, 29]. These absorption peaks are still evident when CQDs are in silk solution (blue line). We reported for comparison the spectrum of the silk solution. Absorption of the SF throughout the visible range is mainly due to the scattering effect caused by the high concentration of the analysed solution, while the increase in absorption in the UV range (<300 nm) is ascribable to the contribution of the amino acid residues [30].

We verified the emission properties of CQDs in water and SF solution by using a spectrophotometer. CQDs show tuneable emission by changing the excitation wavelength, as shown in Fig. 2. The emission shifts from 450 nm to 527 nm for an excitation wavelength, respectively, of 355 and 420 nm. At 380 nm excitation (LED wavelength used to test the composites), the emission peak is broader, and the maximum intensity is at 505 nm. Changes in the emission colour with the excitation wavelength is a common feature.
of CQDs and is caused by structure inhomogeneities that introduce different surface traps with different energy levels in the dots. Variation in emission shape is likely related to the presence of two absorption peaks (Fig. 2). Only for some excitation wavelengths both the absorption centres are active, causing variation in emission spectra [23]. When the CQDs are mixed with SF in solution, the emission intensity decreases by about 50%, probably due to the interaction of CQDs with the polymer chains or aggregation. In the case of 380 nm excitation, there is an effect also on the emission peak broadening, indicating a possible modification of the surface-active sites due to interaction with the protein.

### 3.2 Pristine composite films

Transparent and flexible films with different CQDs content were obtained for RH < 50% at room temperature. As the CQDs mass increases, the colour of the sample shifts from colourless to deep orange, as shown in Fig. 3.

The thickness of the samples is about 40–60 µm, measured with a micrometre. Variation of the thickness has been observed from sample-to-sample.

Compared to SF-CQDs solution, the UV–vis absorption spectra of the composite films show the typical absorbance peaks of the CQDs in the 300–500 nm range (Fig. 4). The main peaks are slightly redshifted at 340 and 408 nm with respect to the CQDs in water.

When illuminated with UV light, SF films exhibit blue emission (400–500 nm) due to the contribution of endogenous fluorescence groups of the protein. In the composite films, the emission is stronger and shifts toward the green spectral region (500–600 nm), indicating that the CQDs give the main

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**Fig. 2** a PL emission spectra of CQDs in water (16 mg/ml) for different excitation wavelengths. Inset: photograph of the solution under 365 nm UV light excitation. b PL emission spectra of CQDs in SF solution (CQDs concentration 16 mg/ml) for different excitation wavelengths

**Fig. 3** Photographs of SF-CQDs composites with different CQDs content under visible (a) and 365 nm UV-lamp irradiation (b)

**Fig. 4** UV–vis absorption spectra of SF-CQDs composites with different CQDs amounts (wt%)
contribution to the PL. Figure 5 shows the emission spectra of SF-CQDs composite films excited at 380 nm. The emission intensity increases by about 150% with increasing CQDs concentration from 0.05 to 0.5%wt, and then decreases for higher concentrations.

The quenching of the PL peak for high CQDs loading can be attributed to the interaction between the SF moieties and the surface functionalities of CQDs, or to the aggregation of nanoparticles inside the matrix [10]. As the CQDs concentration increases, they tend to agglomerate, and the particle size increases. The redshift and the broadening of the PL peaks due to the increase of CQDs size has been already reported in the literature. This effect has been related to the variation of the aromatic sp2 nano-domains and the band-edge overlap between the intrinsic and extrinsic bands of CQDs [31].

Further confirmation of agglomeration phenomena is given in Fig. 6a by the drop-in transparency to 40% for a concentration of 5%wt and by TEM images (see Fig. 6b).

As already observed in the literature, a drop-in transmittance is most likely due to the scattering of the light by agglomerated nanoparticles [10]. To better visualise the decrease in transmission, we report in Fig. 6a the transmittance as a function of the particle content at a representative wavelength of 550 nm, where the human eye has the highest sensitivity [32].

As seen in Fig. 6b, samples with a high concentration of CQDs show agglomerates of hundreds of nanometres in diameter, compared to the size of the as synthesised CQDs of about 4 nm [23]. From the image analysis, we determined a mean diameter of 170 ± 47 nm in the case of 5%wt concentration, while the value for a lower concentration (0.5% wt) was about 15 ± 5 nm, confirming that the observed transmittance decrease is due to the aggregation of the CQDs.

We performed FTIR measurements to investigate the possible interaction occurring between the polymer chains and the CQDs during the formation of the dense films (Fig. 7). All the films show an infrared spectrum similar to that of silk (black line, 0%wt CQDs). The characteristic amide bands exhibit maxima at 1637 cm$^{-1}$ (amide I), 1513 cm$^{-1}$ (amide II) and 1234 cm$^{-1}$ (amide III).

These bands are sensitive to the variation in the secondary structure of the fibroin, in particular to the formation of $\beta$-sheets. According to the literature, bands at 1650 and 1530 cm$^{-1}$ are assigned to a disordered structure (helices and random coils), and bands at 1624 and 1510 cm$^{-1}$ to $\beta$-sheets [16, 33]. This suggests that the secondary structure of our silk contains both disordered structural elements, together with $\beta$-sheets. No changes are detected by increasing the CQDs content, indicating that no chemical bonds are formed between SF and CQDs during the sol-gel transition, and the particles are only physically mixed with the matrix, as already reported for similar composites with lower particles loading [12, 25].

### 3.3 Post-crosslinking composite films

The stability and degradation of SF materials depend on the protein secondary structure. An increase in the $\beta$-sheet content
enhances the water stability of SF films and reduce the biodegradation rate. Crosslinking of SF-CQDs composites induced by a methanol annealing was conducted to improve the water resistance of the materials. Methanol is often used to promote a conformational transition from random coils to β-sheets [34]. Figure 8 shows the FTIR spectra of treated nanocomposites films. After methanol annealing, the peak of the amide I band shifts from 1637 to 1622 cm\(^{-1}\). This shift reflects an increased fraction of the peak components between 1625 and 1620 cm\(^{-1}\) attributable to the β-sheets structure. Similarly, the shift of the amide III band from 1234 to 1230 cm\(^{-1}\) is ascribable to an increase of the β-sheets conformation [35, 36]. As for the pristine samples, no variations between the different compositions were detected.

We measured the mass loss after the treatment (Table 1). Mass loss is related to the dehydration of SF and partial dissolution of the material [18]. UV–vis absorption spectra of the residual methanol solutions showed the typical absorbance peak of quantum dots (data not reported), indicating that the treatments affect the stability of the nanocomposites causing leaching of the NPs.

We finally tested the stability of the methanol-treated composites in water. As reported in Table 2, we observed a mass loss for all the compositions, with a minimum for a CQDs concentration between 0.5 and 1% wt. By analysing the residual solution, we observed the presence of the characteristic absorbance peaks of SF (275 nm) and CQDs (408 nm) in the UV–vis absorption spectra (see Table 2). For CQDs < 0.5%wt, the mass loss is primarily ascribable to SF degradation, while for CQDs > 2%wt there is also a strong signal related to CQDs.

The results suggest that the presence of high content of CQDs affects the water stability of SF composites. Since no chemical bonds are formed between CQDs and SF, CQDs can be easily leached when immersed in solvents (such as methanol and water). In addition, water affects the surface planarity of the films by wrinkling, thereby compromising the applicability of such composites in practical applications such as sensing devices or displays. Future studies will investigate alternative strategies to improve the stability of such composites, for example by chemical crosslinking or water vapour

![Fig. 7 FTIR spectra of pristine SF-CQDs composite films. Positions of principal amide bands are reported](image)

![Fig. 8 FTIR spectra of pristine SF-CQDs composite films after methanol treatment. Positions of the principal amide bands are reported](image)

### Table 1 Mass loss (Δm) of SF-CQDs composites after methanol annealing

| Sample CQDs wt% | Δm after MeOH treatment (%) |
|-----------------|-----------------------------|
| 0               | 8.8                         |
| 0.05            | 4.3                         |
| 0.5             | 1.1                         |
| 1               | 3.9                         |
| 2               | 2.0                         |
| 3               | 4.5                         |
| 5               | 9.8                         |

### Table 2 Mass loss (Δm) after immersion in water and absorbance (Abs) at 275 nm (corresponding to the SF characteristic absorption) and at 408 nm (corresponding to the CQDs absorption)

| Sample CQDs wt% | Δm after water immersion (%) | Abs @ 275 nm | Abs @ 408 nm |
|-----------------|-----------------------------|--------------|--------------|
| 0               | 4.44                        | 0.09         | /            |
| 0.05            | 13.3                        | 0.24         | 0.01         |
| 0.5             | 1.45                        | 0.06         | 0.04         |
| 1               | 1.37                        | 0.16         | 0.09         |
| 2               | 8.25                        | 0.75         | 0.33         |
| 3               | 2.60                        | 0.61         | 0.38         |
| 5               | 4.05                        | 0.84         | 0.57         |
annealing [37], and the investigations of biocompatibility for application in biomedical devices.

4 Conclusions

In this work, we investigated the PL properties of SF-CQDs composites with different CQDs content. The best results were achieved for 0.5 wt% CQDs, while quenching of PL intensity and loss in transparency was observed for higher concentrations, due to aggregation phenomena. FTIR analysis showed that the CQDs and the SF matrix were physically mixed, and no chemical bonds were detected. Treatment of the samples with methanol promoted physical crosslinking of SF through the formation of β-sheets, but it reduced the PL of the materials because of leaching and quenching of CQDs especially for CQDs > 1%wt. Finally, we investigated the stability of the nano-composite in water, and observed a mass loss for CQDs > 1%wt. We found that the best composition in terms of PL intensity and water stability is 0.5%wt CQDs. These preliminary results offer a first understanding of the interaction between CQDs and the SF matrix and a starting point for the fabrication of green and biocompatible SF-CQDs composites with tuneable degradability and PL emission.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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