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ABSTRACT: Fluorescence based on quantum confinement is a property restricted to the nanoscopic range. The incorporation of nanoparticles in a three-dimensional polymeric network could afford macroscopic scaffolds that show nanoscopic properties. Moreover, if these scaffolds are based on strong bonds, the stability of the resulting materials can be preserved, thus enhancing their final applications. We report for the first time the preparation of a graphene
quantum dot (GQD)-composite based on a cationic covalent network. This new material has unusual features: (i) the final composite remains stable after several swelling-deswelling cycles, thus demonstrating the strong interactions between GQDs and the polymeric material, and therefore it could be used as a portable system. (ii) Fluorescence emission in the composite and in solution is quasi-independent to the excitation wavelength. (iii) However, and in contrast to the behavior observed in GQD solutions, the fluorescence of the composite remains unaltered over a wide pH range and in the presence of the different ions commonly found in tap water. (iv) Fluorescence quenching is only observed as a consequence of molecules that bear aromatic systems and this could be applied to the preparation of in situ water sensors.

INTRODUCTION

Quantum confinement is the origin of the fluorescence of quantum dots. Among the quantum dots reported to date, carbon (CQDs) and graphene (GQDs) quantum dots have received a great deal of attention due to their chemical inertness, low toxicity, hydrophilicity and photostability. In recent studies, the fluorescence properties of these nanoparticles have been exploited, e.g., materials for solar cells, analytical science and a biosensing toolkit, and biomedical applications. However, the tendency for aggregation of these fluorescent nanoparticles in dry states is considered to be a limiting factor that can affect the photoluminescence behavior. In an effort to prevent this agglomeration, nanoparticles can be incorporated into appropriate matrices.

Soft matrices such as hydrogels have been extensively used and have shown great potential for a wide range of relevant applications. In particular, the incorporation of nanoparticles within three-dimensional hydrogel structures to form nanocomposites is a useful strategy to enhance the mechanical properties or the response to certain stimuli. Taking advantage of this synergistic
effect, hydrogel nanocomposites have found applications in diverse fields and, in this respect, it is worth highlighting the biomedical applications.\textsuperscript{18,19}

Several research groups have incorporated QDs into hydrogels to preserve the nanoparticle and impart photoluminescence on the resulting nanocomposite.\textsuperscript{20,21} However, there are fewer examples of hydrogels in which carbon or graphene quantum dots are embedded. Recently, low molecular weight gelators (LMWG) have been used to prepare hybrid carbon dot-hydrogels. These nanocomposites are fluorescent probes for mono-\textsuperscript{22} and divalent cations.\textsuperscript{23} Silane derivatives of carbon dots have also been entrapped in organically modified silicate thin film xerogels and the intrinsic fluorescence of C-dots is maintained.\textsuperscript{24} In addition, carbon-dot-loaded alginate gels have been described as a copper(II) probe.\textsuperscript{25} In a very recent example, a GQD-amino acid supramolecular hydrogel composite has been described that shows electron transfer and self-healing properties.\textsuperscript{26} All of these approaches lead to hydrogels and organogels based on electrostatic interactions, hydrogen bonds, van der Waals forces or π−π interactions, amongst other interactions (physical gels). Furthermore, chemically crosslinked hydrogels based on carbon dots have been described in the literature.\textsuperscript{27,28} For instance, a chemically crosslinked hydrogel based on acrylamide and acrylic acid incorporating graphene quantum dots has been recently prepared as a white-light-emitting hydrogel.\textsuperscript{29} This material has been used as a sensor of pH, vapors or temperature.

In general physical gels are prepared using reversible interactions while covalently bonded hydrogels are more robust materials and can afford reversible swelling-deswelling cycles without compromising the mechanical properties. This property can be very useful, for example in the preparation of 3D aerogels starting from polymer hydrogels.\textsuperscript{30}
The preparation of a macroscopic, three-dimensional and stable material that has fluorescence properties associated with the quantum confinement of graphene quantum dots remains a challenge. We envisioned these materials as easily handled sensors, in the form of dry portable ‘stones’ that could be transported outside the laboratory and swelled \textit{in situ} for the detection of water contaminants.

We report here the preparation of macroscopic fluorescent scaffolds consisting of GQD-based hydrogels that can be easily transformed into aerogels. GQDs were prepared by a completely green protocol. The hydrogel is a cationic network prepared by radical polymerization of [2-(acyloyloxy)ethyl]trimethyl-ammonium chloride (AETA) and N,N'-methylenebisacrylamide (MBA) as a cross-linker. The positively charged nitrogen was used as an anchor for the GQDs. The fluorescence properties of the materials were studied. The macroscopic structure retains the quasi-independent emission ($\lambda_{\text{em}}$) from the excitation wavelength ($\lambda_{\text{ex}}$) observed for the GQDs. The possibility of using these nanocomposites as sensors for the detection of polyaromatic molecules in water was also studied.

\textbf{RESULTS AND DISCUSSION}

\textbf{Preparation and characterization of GQDs and their photoluminescence and sensing properties}

The application of the Principles of Green Chemistry\textsuperscript{31} to nanotechnology has been a frequent theme in recent years.\textsuperscript{32} Efforts are currently focused on the assessment of environmental and safety risks associated with the materials themselves, rather than the risks related to their synthesis and/or modification. Synthetic routes are generally not optimized to satisfy green nanoscience objectives, such as energy saving or waste minimization, and this approach is transferred to industrial processes. This situation encouraged us to develop a new, easy and green
method for the preparation of these materials based on mechanochemistry.\textsuperscript{33–37} GQDs were prepared by ball-milling graphite in the presence of sodium percarbonate (SPC) as a solid oxidant. Sodium percarbonate is a cheap, non-toxic, stable and easily handled oxidant.\textsuperscript{38} This oxidant is a green source of hydrogen peroxide and carbon dioxide is the only by-product.\textsuperscript{39} In addition, mechanically induced oxidation preserves the crystallinity of natural graphite\textsuperscript{40} and guarantees a large number of edge-located oxygenated functional groups, which provide good water solubility and can also be used for further functionalization.

This approach is related to the mechanochemical method reported previously by our group for the preparation of few-layered graphene from graphite\textsuperscript{41} and from carbon fibers.\textsuperscript{42} The scale-up of this green methodology has been demonstrated for the production of few-layer graphene.\textsuperscript{43} In contrast to the conventional techniques used for the synthesis of graphene, and now for graphene quantum dots, the ball-milling process avoids the use of strong mineral acids, high temperatures, reduction processes and high vacuum chambers, while the solvents, if used, can be recovered and recycled. A mechanochemical approach to prepare carbon quantum dots has recently been reported,\textsuperscript{44} but the method requires milling for 50 hours and has a tedious work-up procedure: ultrasonication (10 min), centrifugation (10 min), reduction with sodium borohydride (6 h), further centrifugation and, finally, dialysis.

The amount of SPC and the ball milling parameters were varied in order to optimise the preparation of GQDs (See SI Table S1). The use and the quantity of SPC as an oxidant were studied. Ball milling in the absence of SPC gave a non-reproducible process and heterogeneity in the GQD size. It was thus confirmed that the presence of SPC is required to obtain GQDs reproducibly with a high degree of homogeneity. Moreover, different amounts of the initial powder and different graphite/SPC ratios were evaluated. The milling time and speed were also
modified. A milling speed of 400 rpm and at least 2 hours were needed for the SPC to react. We also varied the total quantity of the initial powder. The optimized conditions are as follows: 300 mg of initial powder (a graphite/SPC ratio of 2 is used) were ball milled for 12 hours at a speed of 400 rpm (see experimental section for a detailed description).

The resulting GQDs were characterized by Raman, X-ray photoelectron spectroscopy (XPS) and Fourier-Transform Infrared (FTIR) spectroscopy. Thermogravimetric analysis (TGA), Zeta potential and Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) also proved to be useful techniques.

Figure 1. Raman spectra of prepared GQDs and graphite

A Raman microspectrometer equipped with a 532 nm point-based laser was employed to characterize the GQDs. The Raman spectra of the starting graphite and the resulting GQDs are shown in Figure 1. The D band can be observed at ~1350 cm\(^{-1}\) and this is associated with the
symmetry breaking of the sp\(^2\) carbon ring,\(^{45}\) thus indicating the presence of sp\(^3\) hybridized carbon atoms. The G band is originated from the E\(_{2g}\) phonon at the Brillouin zone center.\(^{46}\) The intensity ratio ID/IG was 0.6 and, to our knowledge, this is the lowest ratio reported in the literature to date for GQDs.\(^{47,48}\) The absence of the 2D band indicates disruption of the stacking order due to the presence of oxidized functional groups.\(^{49}\)

![Figure 2. C1s and O1s core-level spectra of a GQD sample purified by dialysis](image)

X-ray photoelectron spectroscopy was used to verify the presence of oxygenated functional groups (Figure 2). The C1s peak can be deconvoluted into five different components and this shows the existence of different bonds: C–O (286.2 eV), C=O (287.3 eV), COOH (288.6 eV) and COO– (290.4 eV) and the most intense peak at 284.8 eV, corresponding to carbon atoms of GQDs. The O1s peak is centered at 531.7 and can be deconvoluted into two different components: O=C (531.6 eV) and O–C (533.2 eV). A surface atomic O/C ratio of 0.66 was estimated. Thus, the presence of hydroxy, epoxy, carbonyl, carboxylic acid and carboxylate groups is expected.
The FTIR spectrum (Figure S1) shows clear stretching vibrations for O–H at 3300 cm\(^{-1}\), C=O at 1723 and 1645 cm\(^{-1}\) and C–O at 1419, 1146 and 892 cm\(^{-1}\). In addition, the skeletal in-plane vibration of C=C is observed at 1591 cm\(^{-1}\).

Thermogravimetric analysis shows a weight loss of 22% at 600 °C. This result confirms the presence of the functional groups. The thermal stability of the GQDs obtained is unusually high when compared with some literature examples.\(^{50}\) TGA (Figure S2) and XPS (Figure S3) data verify the effective purification of our graphene quantum dots after dialysis.

The Zeta potential was found to be –21.2 eV in water, owing to the carboxylic acid and carboxylate groups on the surface, and this corroborates the stability in aqueous solution.

![Figure 3. A) Lateral size distribution and B) representative TEM/HRTEM images of the GQDs.](image)
Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) provide evidence of the shape and size of the GQDs. The lateral size distribution (Figure 3A) shows that more than 50% of the GQDs are smaller than 5 nm and more than 75% are under 10 nm. These values are consistent with the observed quasi-independent PL emission from the excitation wavelength. However, some aggregates are also observed in TEM images which may be formed during the drying process used for the preparation of TEM grids. TEM and HRTEM images (Figure 3B) reveal that the interlayer distance, 0.38 nm, is slightly higher than the interlayer spacing of bulk graphite (0.335 nm). This finding is consistent with the presence of functional groups. Furthermore, HRTEM indicates the high crystallinity of the GQDs, with a lattice parameter of 0.21 nm corresponding to the lattice fringes of graphene.

Figure 4. 3D-PL spectra of an aqueous solution (2 g/L) of the GQDs. Intensity units are arbitrary.

Photoluminescence (PL) is the most attractive property of graphene quantum dots. The emission wavelength ($\lambda_{em}$) is strongly related to the size and edge structure of the GQDs. The PL spectrum of a solution of the graphene quantum dots obtained in this study is shown in Figure
4. The PL was recorded on a solution at 2 g/L as this is the concentration of the maximum PL intensity.

It is worth highlighting the sharp distribution of the emission maximum as one of the main characteristics of our derivatives. The quasi-independent emission from the excitation wavelength and a full width at half maximum (FWHM) of less than 100 nm suggests that the size, edge and surface state of the sp\textsuperscript{2} domains in GQDs are uniform.\textsuperscript{56,57} In addition, a large Stokes displacement of 125 nm (λ\textsubscript{ex} = 315; λ\textsubscript{em} = 430) was observed. Aqueous solutions of the GQDs (2 g/L) were stable and the photoluminescence remained for more than 15 days (Figure S4).

The photoluminescent quantum yield of the prepared GQDs is 4.4%. This value is in the range of those described in the literature.\textsuperscript{58,59}

The aqueous solution of GQDs was pH sensitive and significant changes in emission intensity were observed when the pH was varied. As shown in Figure 5A, the fluorescence intensity was studied from pH 2.8 to 10.6, with PL quenching observed in acidic media. This result is consistent with others reported in the literature.\textsuperscript{60,61} However, it is relevant to note that even at pH 2.8 the GQDs are highly fluorescent, which makes these GQDs useful for sensing over a wide pH range. To evaluate the reversibility of the PL properties at different pH values, a GQD solution of 0.2 g/L was subjected to pH cycling between pH 3 and pH 10. HCl (2 M) and NaOH (2 M) were used to adjust the pH. It can be seen from Figure 5B that the process can be repeated for at least ten cycles with more than 50% of the initial intensity retained at 430 nm.
As indicated above, there are already numerous reports that describe the ability of GQDs to be used as sensors for cations. We also studied the photoluminescence behavior of GQD aqueous solutions (0.2 g/L) when Li(I) and Hg(II) were added. Both cations partially quench the GQD fluorescence, even at $10^{-10}$ M (Figure 6A, 6B). The use of other cations such as Co(II), Pt(II) and Fe(III) led to a similar photoluminescence response (see SI Figure S5). Furthermore, the PL properties were also studied for GQDs dissolved in tap water, which was used as an indicative
example of a wide variety of ions (see SI Table S2). In this case, a similar quenching of the GQD fluorescence was observed (Figure 6C).

Figure 6. PL intensity of the GQD solution (0.2 g/L) in the presence of A) Hg$^{2+}$ and B) Li$^+$ at different concentrations. C) PL intensity of the GQD solution (0.2 g/L) in tap water. In all cases $\lambda_{ex} = 315$ nm.
It is also known that graphene quantum dots have the ability to interact with \( \pi \)-systems.\(^6\)\(^6\)\(^2\) In this respect, the influence of rhodamine 101 (R101), 2-methoxynaphthalene (2-MN) and sodium 1-naphthalenesulfonate (NA) on the PL properties of GQDs was studied. These compounds represent cationic, neutral and anionic aromatic molecules, respectively, and these were selected as examples to determine if there is any effect on the GQD PL properties considering the combined presence of charge and aromatic systems. It can be seen from Figure 7 that concentrations of \( 10^{-4} \) M of R101 (Figure 7A), \( 10^{-3} \) M of 2-MN (Figure 7B) and \( 10^{-3} \) M NA (Figure 7C) caused changes in the fluorescence of the GQDs. A concentration of \( 10^{-4} \) M of R101 quenches completely the GQDs fluorescence. Moreover, a concentration of \( 10^{-3} \) M of 2-MN or NA caused more than 50% fluorescence quenching. In all cases, the fluorescence of the \( \pi \)-compound was modified in the presence of GQDs (Figure 7D, 7E and 7F), thus revealing an effective \( \pi-\pi \) interaction between the aromatic compounds and the GQDs.
Figure 7. Figures A, B and C are spectra for comparison between a solution of GQDs, a solution of the aromatic compound and a mixture of the two. The compound and its concentration in each case are: A) rhodamine 101 at 10^{-4} M, B) 2-methoxynaphthalene at 10^{-5} M and C) sodium 1-naphthalenesulfonate at 10^{-3} M. Figures D, E and F are the PL spectra of a GQD solution (0.2 g/L) in the presence of different concentrations of D) rhodamine 101, E) 2-methoxynaphthalene and F) sodium 1-naphthalenesulfonate. In all cases \lambda_{ex} = 315 \text{ nm}.
**GQD-Aerogel: preparation, stability, characterization and sensing properties**

A chemically cross-linked hydrogel (CN) was synthesized by radical polymerization of AETA in the presence of MBA as a crosslinker (see Scheme 1 and the experimental section). The appearance of the freshly prepared material is shown in Figure 8A. AETA was chosen because it generates a positively charged polymer in which GQDs could remain anchored due to electrostatic interactions. In order to verify this hypothesis and prepare the nanocomposite material, the already prepared CN was dried and loaded with GQDs by immersion of the material in a GQD solution (see Scheme 1 and the experimental section). The as-prepared hydrogel (CNGQDs) was then washed by immersion in 10 mL of water for 24 hours. After this time, the water was replaced by another 10 mL of fresh water and the fluorescence of the initial water was analyzed by fluorescence spectroscopy. The process was repeated for 5 days. Fluorescence was not observed in this washing water on any day, which confirms that the GQDs are anchored to the polymeric network. The lyophilization of the as-prepared hydrogels affords the GQD-aerogels (Figure 8B).
Scheme 1. Preparation process and chemical structure of the GQD-aerogel.

The typical microscopic morphology of the hydrogels was confirmed by Cryo-Scanning Electron Microscopy (Cryo-SEM) (Figure 8C). The pore sizes of these materials were analyzed by Cryo-SEM. As shown in Figures 8D and 8E, both the CN and CNGQDs have a pore size distribution that ranges from 10 to 60 \( \mu m \), with an average of around 25 \( \mu m \). It can be concluded that the small size of GQDs does not modify the structure of the polymer network.
Figure 8. A) Digital image of the freshly prepared hydrogel; B) Digital image of the cylindrical-shape aerogel; C) Representative porous morphology of the materials (scale bar: 10 µm); D) Pore size distribution of CN and E) Pore size distribution of CNGQDs.

The photoluminescence properties of both hydrogels were studied. Cylindrical-shaped hydrogels (0.75 cm diameter, 2.5 cm of size and 1 mL of solution inside) were prepared. It can be observed from Figure 9A that only the hydrogel prepared using GQDs is fluorescent and its emission intensity is unaltered after the washing treatments. The PL properties of CNGQDs were studied at different excitation wavelengths. As shown in Figure 9B, a quasi-independent emission from the excitation wavelength is observed, as in the case of the GQD solution. Thus, the nanocomposite incorporates the PL properties of the GQDs in a macroscopic scaffold. The nanoscopic property is now expressed at the macroscopic scale.
Swelling experiments were performed by immersing the dried materials in doubly deionized water at room temperature. The weights of the swollen samples were recorded at different time intervals until they reached a constant weight. The final swelling degree was calculated after one day, when the weight of the samples was found to be constant. Significant changes were not observed in the swelling degree (SW) of CN when compared with CNGQDs, which confirms that the GQDs do not modify the structure of the polymer network (Figure S6).

The reinforcement and improvement of the mechanical properties of materials is normally one of the principal reasons for creating composites based on nanomaterials. Compressive tests were performed on CN and CNGQD materials. The compressive Young’s modulus (E) of the CN and CNGQD materials were $27.81 \pm 3.14$ and $55.12 \pm 7.87$ kPa, respectively (Figure S7). This result is relevant regarding the application of these nanocomposites as in situ sensors, since stiff scaffolds are needed to withstand swelling-deswelling cycles.
In this sense, and in order to test the stability of the fluorescence properties of the nanocomposite gels after swelling-deswelling cycles, cylindrical-shaped CNGQD aerogel samples were re-swollen with 1 mL of water. The fluorescence response was studied and the process was repeated 5 times (Figure S8). Significant changes in PL intensity were not observed, which shows that this material can be dried, transported and re-swollen without losing its properties.

Moreover, pH variation in water could also influence the photoluminescence of the GQDs inside the gels. To study the influence of pH on the photoluminescence of CNGQDs, cylindrical-shaped aerogels were re-swollen successively with acidified water. The results are represented in Figure 10A. Surprisingly – and in contrast to the behavior observed with GQD solutions – there was no significant effect on the intensity or on the emission wavelength of CNGQDs. In this case protonation of the carboxylate groups, which is the cause of the quenching, should not be possible due to the strong interaction between the GQD carboxylate groups and the ammonium cations in the network. A similar effect on the fluorescence was observed when aerogels were re-swollen with 1 mL of aqueous Li(I) or Hg(II) solutions at $10^{-4}$ M, and even with tap water. The fluorescence response remained quasi-constant in the presence of several ions (Figure 10A). Under a UV light, there was no differences between CNGQDs in deionized and in tap water (Figure 10B).
Figure 10. A) PL intensity of CNGQDs in deionized water (black), at pH 2 (red), in the presence of Hg$^{2+}$ at $10^{-4}$ M (blue), in the presence of Li$^+$ at $10^{-4}$ M (green) and in tap water (pink). In all cases $\lambda_{ex} = 315$ nm. B) Photo under UV light (365 nm) of CNGQDs in deionized water (left) and in tap water (right).

Once the stability of our GQD hydrogel had been confirmed in a wide range of pH conditions and with different ions, along with the consistency and fluorescence invariability after swelling-deswelling cycles, we considered the possibility of using the new nanocomposite as a sensor for polyaromatic molecules in water. For this purpose, rhodamine 101, 2-methoxynaphthalene and sodium 1-naphthalenesulfonate were selected. Cylindrical-shaped CNGQD aerogels were refilled with 1 mL of solutions of the aromatic molecules. The result obtained are shown in Figure 11A. The fluorescence of the CNGQDs was quenched by both aromatic compounds. $\pi-\pi$ interactions between the GQDs and the aromatic compounds may be responsible of this quenching. Furthermore, this quenching was also observed under a UV light (Figure 11B).
this way, our nanocomposite can be used as a sensor for molecules that are able to establish π–π interactions.

The sensitivity of the CNGQD-aerogel was studied by adding different concentrations of the polyaromatic compound solutions (see SI Figure S9). Non-significant quenching effects were observed at lower concentrations, which is consistent with the results obtained for the GQD solution.

It was also determined whether the π–π interaction occurs in the presence of different ions. With this aim in mind, the PL intensity of CNGQD aerogel when re-swollen with a solution of sodium 1-naphthalenesulfonate in tap water was studied. It can be seen from Figure 11A that the quenching does not depend on the media, as the interaction also occurs in the presence of several ions. This effect was also observed under a UV light (Figure 11C).
Figure 11. A) PL intensity spectra of CNGQDs (black) and CNGQDs in the presence of R101 at $10^{-4}$ M (red), 2-NM at $10^{-3}$ M (blue) in deionized water and NA ($10^{-3}$ M) in both deionized (green) and tap water (pink). In all cases $\lambda_{ex} = 315$ nm. B) Photo under UV light (365 nm) of CNGQDs in deionized water (left) and in the presence of $10^{-3}$ M NA (right). C) Comparison of CNGQDs aerogel, CNGQDs in tap water and CNGQDs in tap water in the presence of $10^{-3}$ M NA under UV light (365 nm).
In order to confirm that the quenching was caused by a \( \pi-\pi \) interaction with GQDs and not by an anionic interchange between the polymeric network and the aromatic molecules, a blank aerogel (CN) was loaded with 1 mL of NA \( (10^{-3} \text{ M}) \). Once loaded, the hydrogel was washed by immersion in 10 mL of water for 24 hours. After this time, the water was changed for other 10 mL of fresh water. The process was repeated for 5 days and the fluorescence of the washing water was analyzed. The PL band at 330 nm corresponding to NA was observed in the washings, which confirms that NA had been released from the cationic network. When the same process was performed with CNGQDs, the washing water did not show the GQD PL signal at 430 nm or the NA PL band at 330 nm (Figure S10). It can be concluded that NA is not retained within the blank hydrogel by electrostatic interactions, which confirms the \( \pi-\pi \) interaction between GQDs and NA in CNGQDs.

**CONCLUSIONS**

A three-dimensional scaffold with nanoscopic-based properties has been prepared by anchoring GQDs in a cationic polymeric network. The quasi-independent emission from the excitation wavelength associated with the GQDs was maintained in the final macroscopic scaffold. The polymer network was based on a chemical hydrogel and the graphene quantum dots were fixed by means of electrostatic interactions between the carboxylate groups of GQDs and the ammonium groups of the network.

In contrast to the observations on GQDs in aqueous solutions, the fluorescence of the composite material was not affected by the presence of ions. The electrostatic interactions between anionic GQDs and the cationic network avoid fluorescence quenching. Furthermore, the prepared material remained unaltered after several cycles of swelling-deswelling and could be
stored as an aerogel without changes in the properties. However, in aqueous solutions of polyaromatic molecules, the GQD-aerogel composites did suffer fluorescence quenching, which makes these materials be potential candidates for \textit{in situ} portable sensors for polyaromatic molecules as contaminants in water in the presence of different ions and over a wide pH range.

Improvements in sensor sensitivity and selectivity can be envisaged.

**EXPERIMENTAL SECTION**

**Materials.** All reagents were used without further purification as purchased from commercial sources. Graphite SP-1 powder was purchased from Bay Carbon, Inc. Sodium percarbonate, \[2-\text{(acryloyloxy)ethyl}\]trimethyl-ammonium chloride, N,N'-methylenbisacrylamide and potassium persulfate were purchased from Sigma Aldrich. Regarding the reagents used for the photoluminescence study, 2-methoxynaphthalene was purchased from TCI Chemicals and rhodamine 101, 1-naphthalenesulfonate, NaOH, HCl and lithium and mercury chlorides were purchased from Sigma Aldrich.

**Preparation of graphene quantum dots.** 200 mg of graphite (Bay Carbon, Inc. SP-1 graphite powder) and 100 mg of sodium percarbonate were placed in a Retsch PM 100 ball mill and the sample was milled for 12 hours. A 50 mL stainless steel flask was used and this contained 10 stainless steel balls (1 cm diameter). The milling speed was 400 rpm. The resulting powder and the balls were placed in an appropriate receptacle with 20 mL of water and the sample was sonicated in an ultrasonic bath for 2 minutes. The flask and grinding balls were thoroughly washed with distilled water. The aqueous extracts were combined (2 L approximately) and filtered using a 0.2 µm pore filter (Millipore). The filtrate, which contained the graphene quantum dots, was concentrated and 20 mL of GQD solution was dialysed against deionized water through a dialysis membrane (MWCO: 3500 Da), using 120 mL of deionized water as
solvent. The permeate was replaced every 2 hours during the day and dialysis was continued overnight to give a total dialysis time of 24 hours. The final product was obtained by removing the solvent under reduced pressure.

**Characterization of graphene quantum dots.** Fluorescence spectra were recorded with a Photon Technology International, Inc. spectrofluorometer, using a slit width of 1 nm. For fluorescence experiments quartz cuvettes with a 10 mm path length were used. The photoluminescent quantum yield was determined by using quinine sulfate in 0.5 M H$_2$SO$_4$ as the standard and at an excitation wavelength of 315 nm. In the case of the $\pi-\pi$ interaction studies, the maximum concentration of each polyaromatic compound depended on its solubility in deionized water. The samples were then diluted until no changes in PL intensity were observed. Raman spectra were recorded on an Invia Renishaw microspectrometer equipped with a 532 nm point-based laser. Raman samples were prepared by dropping the GQD solutions (0.2 g/L) onto silicon oxide surfaces (silicon wafers, WRS materials). Photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer with a pass energy of 50 eV and a Mg K $\alpha$ (hv = 1254.6 eV) X-ray source, powered at 120 W. Binding energies were calibrated relative to the C 1s peak at 284.8 eV. High-resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software ‘XPS peak’. Symmetric Gaussian–Lorentzian curves were used to approximate the line shapes of the fitting components. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors. FTIR spectra were recorded with a Shimadzu IRAffinity-1S system. Thermogravimetric analyses were performed with a TGA Q50 (TA Instruments) at 10 °C/min under a nitrogen atmosphere. TEM and HRTEM samples were prepared by inmersion of the nickel grid (LC200-NI Lacey carbon grid from Electron
Microscopy Sciences) into the GQD solution (0.05 g/L). After drying under vacuum, the samples were investigated by TEM/HRTEM (Jeol 2100).

**Aerogel preparation.** Pure [2-(acryloyloxy)ethyl]trimethylammonium chloride hydrogel (CN) was prepared using N,N'-methylenebisacrylamide (MBA) as cross-linker and potassium peroxydisulfate (KPS) as initiator. In a typical experiment, 5.66 mL of [2-(acryloyloxy)ethyl]trimethylammonium chloride (AETA) (26.4 mmol) and 0.01 g of MBA (0.06 mmol) were added to 5 mL of deionized water. Finally, KPS (0.017 g, 0.06 mmol) was added to the blend of monomers. The mixture was homogenized by stirring with mild sonication for 5 minutes and then placed in an oven at 80 °C for 9 hours. The resulting material was immersed in pure water for 5 days, with the water changed every day in order to remove any unreacted monomer and initiator. A similar process as previously described for the preparation of CN was followed to synthesize the hydrogel in the presence of GQDs (CNGQDs). Previously washed polymer network CN was dried by heating in an oven at 45 ºC for 12 hours and submerged in 1 mL of the GQDs solution (0.2 g/L). At this point, dried CN swells and the GQDs enter into the polymer network to form the CNGQDs. The volume of the GQD solution was equal to the volume of deionized water used to form the CN. Therefore, the swelling degree of the freshly prepared samples was the same in both cases. To verify that GQDs remain inside CNGQDs, the nanocomposite was washed as described before and the washing water fractions were concentrated on a rotary evaporator and analyzed by PL. Finally, the GQD-aerogels were prepared by lyophilization of the initial hydrogel.

**Hydrogel characterization.** A GeminiSEM 500 from Zeiss coupled with Cryo-SEM QUORUM was used to visualize the porous structures. Cryo-SEM experiments were carried out on previously swollen samples. The samples were frozen in slush N2, fractured and the
condensed surface water was sublimed by controlling the temperature at –90 °C for 8 minutes. The samples were then sputtered with gold. Finally, the samples were introduced into the microscope sample stage for examination at an accelerating voltage of 5 kV. Swelling studies were performed on dried hydrogel samples after washing. The hydrogels were dried in an oven. These samples were immersed in excess ultrapure deionized water at room temperature. Excess water on the hydrogel surfaces was removed using a filter paper prior to weighing. The weights of the swollen hydrogels were recorded at regular time intervals until they reached a constant weight. The non-absorbed water on the surface of the gels was removed with a filter paper before weighing. The swelling degree was then calculated. Compressive tests were performed on samples at 25 °C using a Mecmesin Multitest 2.5-i dynamic mechanical analyzer. Cylindrical disks of gels (∼6) were molded. The dimensions of each hydrogel sample were measured before each analysis in order to normalize the results. Hydrogel disks were then mono-axially compressed between two plates at a rate of 6 mm/min (cell load = 50 N). The hydrogel behavior was represented in stress-strain curves, from which Young’s modulus was obtained (15–20% strain). Photoluminescence studies were performed using a Photon Technology International, Inc. spectrofluorimeter. Cylindrical-shaped hydrogels (0.75 cm diameter, 2.5 cm size and 1 mL of solution inside) were prepared using a 1 mL syringe (Novico ICOplus3) as a mold. Quartz cuvettes with a 10 mm path-length and a slit width of 1 nm were used.

ASSOCIATED CONTENT

Supporting Information.

Table of the ball milling parameters studied; FTIR spectrum of GQDs; TGA comparison between SPC and the GQDs, both before and after dialysis; C1s core-level spectra from XPS of
GQDs before dialysis; study by fluorescence spectroscopy of the stability of the GQDs solution; study of fluorescence of the GQDs in the presence of different ions; table of the ions that exist in the used tap water; swelling behavior curve of CN and CNGQD hydrogels; stress-strain curve obtained from the compressive study and the Young’s Modulus comparison between CN and CNGQDs; fluorescence study after the swelling-deswelling study; PL spectra of the composite in the presence of different concentrations of the polyaromatic compounds; PL spectra of the washing water of CN and CNGQDs in the presence of NA.

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Notes

The authors declare no competing financial interest.

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