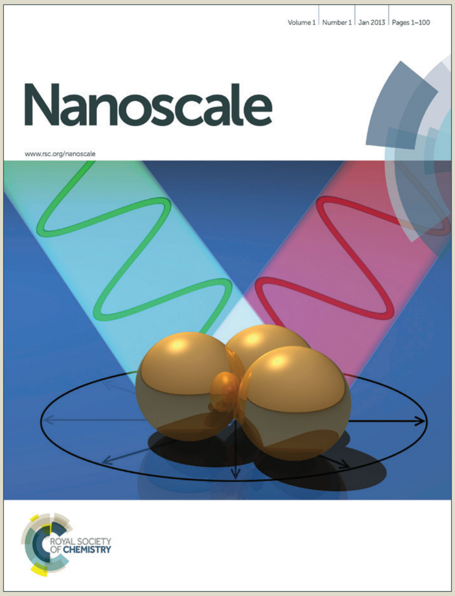
Nanoscale

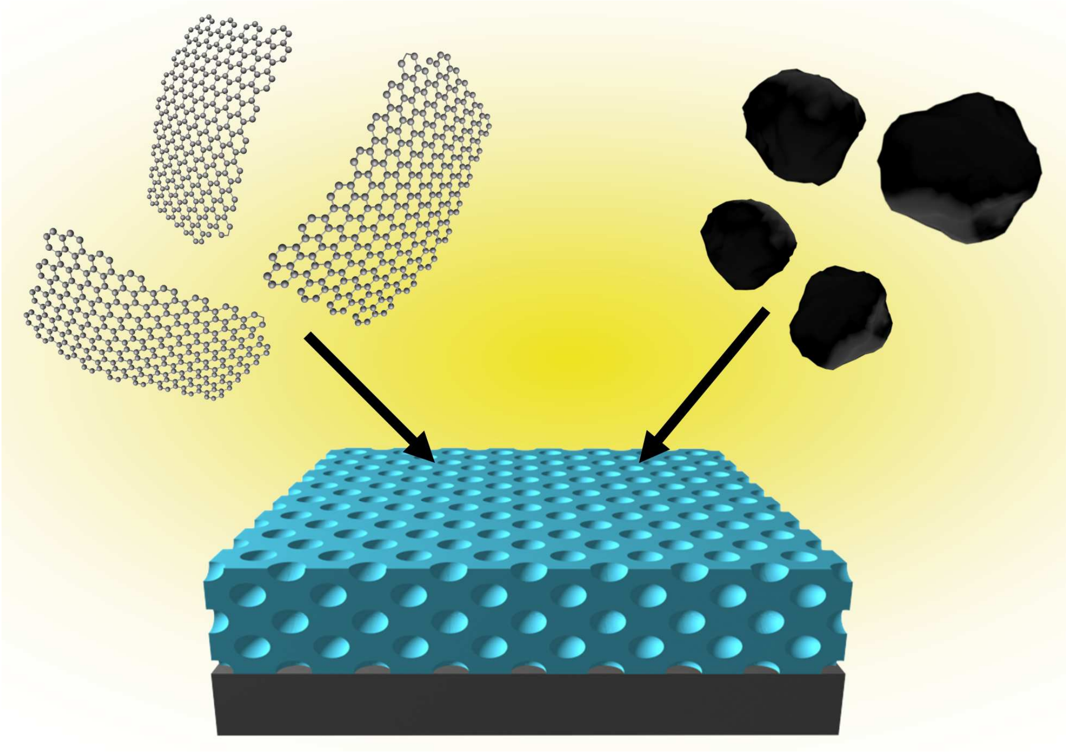
Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/nanoscale

Table of Content



The review is focused on a specific class of nanocomposites obtained through a combined assembly of graphene, or carbon-based nanomaterials, and mesoporous inorganic or hybrid materials.

Graphene and carbon nanodots in mesoporous materials: an interactive platform for functional applications

Plinio Innocenzi[a]*, Luca Malfatti[a], Davide Carboni[a]

[a]Laboratorio di Scienza dei Materiali e Nanotecnologie, CR-INSTM, DADU, Università di Sassari, Palazzo Pou Salid, Piazza Duomo 6, 07041 Alghero (SS), Italy

Abstract

The present review is focused on a specific class of nanocomposites obtained through integration of graphene, or carbon-based nanomaterials (such as carbon nanodots), with mesoporous inorganic or hybrid materials, obtained via template assisted self-assembly. The task of integrating graphene and carbon nanodots with a self-assembly process is still very challenging and this review shows some of the solutions which have been envisaged up to now. These nanocomposite materials are an ideal interactive platform for developing innovative functional applications; they have a high capability of integration in advanced devices which well exploits the advantage of tuning the wide properties and the flexibility of the soft-chemistry route. A wide range of applications has been developed so far which spans from sensing, to electronics up to optics and biomedicine. Even if a large number of proof-of-concepts have been reported to date, an even greater expansion of applications in the field is expected to come in the near future.

* Corresponding author: plinio@uniss.it

Keywords: mesoporous materials, graphene, carbon nanodots, carbon quantum dots, graphene quantum dots, nanocomposites.

1. Introduction

Mesoporous ordered materials obtained through a template assisted self-assembly process [1] have been widely used and tested for many applications, especially in form of particles. These materials show several peculiar properties such as the high surface area, provided by the monodisperse porosity, the possibility of functionalizing the pores surface, and their use as a platform for host-guest nanocomposites. Although a large variety of systems has been obtained through the integration of mesoporous materials with guest nanomaterials and/or functional molecules, one of the most promising platform is represented by graphene and carbon dots mesoporous nanocomposites.

Graphene [2] is a two-dimensional carbon-based structure which has somehow changed our way of thinking about nanomaterials. It has striking properties, but it could be modified and combined with other nanostructures following both chemical and physical routes, which is opening amazing windows on the future of nanoscience.

Besides graphene, other carbon-based nanostructures have recently risen to the attention of the scientific community: the carbon nanodots.

The chemistry of graphene is now quite well developed and synthesis and control of surface can now be mastered at good level, however important challenges are still waiting the scientific community, such as integrating graphene chemistry with other soft synthesis routes. In particular, graphene and its derivatives have to be well combined with sol-gel chemistry and self-assembly processes at low temperature. When this goal will be achieved, the oxide and hybrid organic-inorganic materials will become an ideal host for such functional carbon structures. This is particularly true in the case of mesoporous materials that are an open and interactive platform for graphene, where the combination of the host-guest system is the most interesting property of such type of nanocomposites.

Mesoporous materials have pores typically ranging between 2 and 50 nm and the pores can be organized in different ordered structures, for instance specific arrangements are, for instance, possible for bidimensional mesopores by aligning the pores vertically or horizontally with respect to the substrate. Other features can be easily designed via the chemical approach, such as the pore surface functionalizatin; different functional molecules can be grafted on the surface through one-pot or post-grafting synthesis. The scaffold of the mesopores also plays an important role; in fact its chemical composition can be tuned depending on the prospected application. It can be an oxide, a combination of oxides or an organic-inorganic hybrid network, and, within some limits, additional features such as crystallinity and crystal phase dimension, can be also adjusted.

When mesoporous materials are used as a host for functional nanostructures, such as graphene, the combination of the two nanomaterials provides a set of new synergic properties. The main advantage, in fact, is not given by the porosity of the matrix itself, but rather by the mutual interaction between the two materials; when a functional oxide, such as nanocrystalline titania, is used as a scaffold of the porous network, for instance, different types of interactions arise between host and guest species, enabling improved properties and innovative applications. Embedding graphene or other carbon-based nanostructures into a mesoporous oxide matrix provides an improved mechanical and thermal stability that makes the nanocomposites suitable for a wide range of applications. Moreover, the platform could simultaneously host other responsive nanostructures, such as metallic and semiconductor nanoparticles, or functional organic molecules, allowing the design of complex "*nanodevices*".

Despite the huge potential of carbon-based/mesoporous nanocomposites, there are still a lot of challenges that are actually hampering a full integration of graphene in the chemistry of mesoporous precursors. Several creative solutions have been adopted so far, but further studies are necessary before self-assembly of mesoporous materials could become an easy and flexible method for fabricating graphene-based nanocomposites. Things are much simpler in the case of carbon dots, but still very few works have fully explored all the potential of such materials. This review is therefore dedicated at providing the reader with an overview of the current state of the art as a starting point for future explorations.

2. Graphene and graphene oxide in mesoporous materials

2.1 Sandwich mesoporous structures

The idea of combining mesoporous materials with graphene is clearly attractive with the added value being the open and controlled porosity. Handling the chemistry of self-assembly is however a critical task, especially because of the low solubility of not-oxidized and pristine graphene (graphene oxide is much more friendly for sol-gel chemistry) [3]. On the other hand, is also easy to think about graphene as an interactive functional platform where growing or bonding nanoparticles or other different nanostructures. One of the simplest approaches in building a graphene - mesoporous material composite is therefore using graphene or graphene oxide as a substrate for mesoporous layers of controlled properties. Graphene oxide sheets, in particular, can be produced as a high surface single layer by the Hummers method [4]. Thanks to the presence of oxygen atoms, the sheets can be functionalized with hydroxyl groups or different types of functional moieties, such as epoxy, carbonyl and carboxyl units at the sheet edges [5]. This makes the graphene oxide sheets negatively charged; this property is quite important for the chemistry of self-assembly in presence of an organic template, such as the positively ionic surfactant cethyltrimethylammonium bromide (CTAB). CTAB is absorbed on the highly negative charged graphene oxide surface and drives the nucleation and growth of mesoporous layers on the GO substrate. The graphene oxide substrate immersed in the proper precursor solution is able to seed the growth of mesoporous layers on both surfaces allowing the formation of sandwich mesoporous structures $mSiO_2$-GO-$mSiO_2$ (m = mesoporous) [6]. These structures show the possibility of reducing graphene oxide through a pyrolysis process without aggregation of the sheets because of the presence of the silica layer ending up in $mSiO_2$-G-$mSiO_2$ structures. It is interesting that such materials can be also used as a template for other mesoporous oxides materials which can be tailored for specific applications. A simple nanocasting route has been chosen, using sucrose as carbon source and cobalt nitrate as cobalt source, to obtain graphene-based mesoporous carbon (mC-G-mC) and Co_3O_4 (mCo_3O_4-G-mCo_3O_4) structures. The sandwich mesoporous carbon graphene structures have shown interesting electrochemical properties as an anode material for lithium ion batteries [7].

The method for fabricating mesoporous silica graphene or graphene oxide sandwich structures has been also extended to mesoporous titania graphene sandwich layers (**Figure 1**) [8].

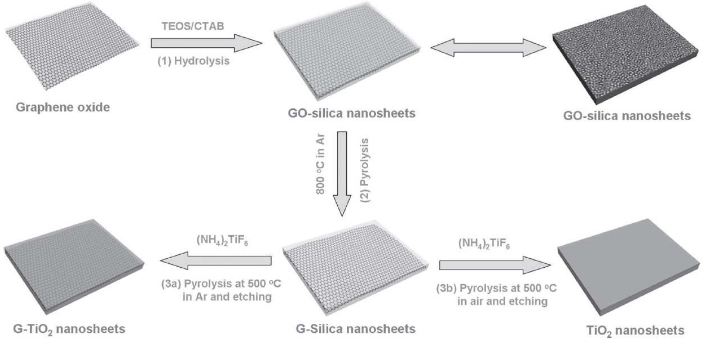


Figure 1. Fabrication of graphene-based titania (mTiO_2-G-mTiO_2) nanosheets and mTiO_2 nanosheets without graphene. Reproduced with permission from ref. 8.

Similar protocols have been successfully applied also if a non-ionic triblock copolymer was used instead of an ionic surfactant [9]. In fact, by using Pluronic P123 as a template, highly ordered mesoporous cubic silica sandwich structures, $Ia\bar{3}d$, have been fabricated [10].

The oxide on the graphene sheet can be changed to titania by impregnating the silica mesoporous layers with an aqueous solution of $(NH_4)_2TiF_6$ and H_3BO_3, followed by pyrolysis at 500°C in argon and silica etching; this has allowed obtaining mTiO_2-G-mTiO_2 sandwich structures (**Figure 1**). Noticeable if the pyrolysis is done in air, a pure titania mesoporous layer is obtained. These layers have been successfully tested as anode materials for lithium storage, in particular the mTiO_2-G-mTiO_2 have shown a higher lithium insertion coefficient with respect to pure titania suggesting the existence of additional lithium storage sites in the graphene mesoporous titania structures [11].

A similar method has been also employed for producing mSnO_2-G-mSnO_2 sandwich structures for lithium ion batteries even if SnO_2 seems to grow forming nanoparticles in the graphene sheets more than homogeneous layers, this in order to accommodate the possible volume expansion of SnO_2 [12].

A nice example of sandwich structures has been also reported by Ozin et al. who have fabricated a graphene oxide-silica mesoporous sandwich with vertically oriented channels [13]. A single platelet of graphene oxide, whose surface has been reduced in a basic solution, has been used as a template for growing silica mesoporous layers.

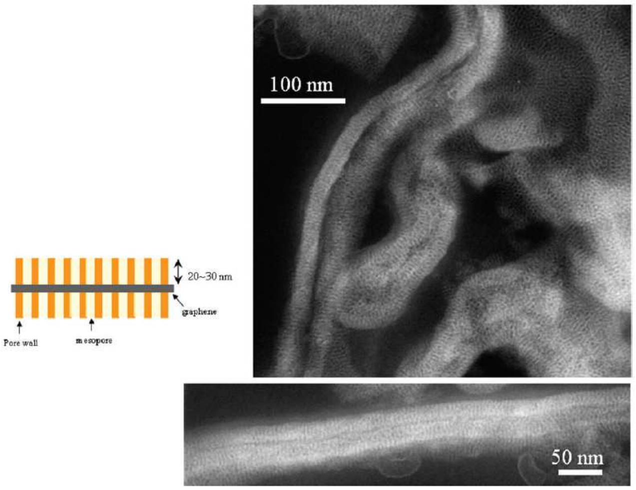


Figure 2. Microtome STEM pictures of rGO-PMS(0.27) prepared at pH 11.7, which clearly shows rGO sheets sandwiched by arrays of vertically aligned mesopores having heights of 20-30 nm. Repoduced with permission from ref. 13

The pores, which are 20-30 nm in length, result vertically well oriented with respect to the GO substrate (**Figure 2**). The formation of such kind of intriguing mesostructures has been explained on the basis of an admicelle-initiated growth model. The cationic admicelles, cethyltrimethylammonium choride, CTACl, strongly adhere close to each other to the GO surface and in this way they are able to direct the self-assembly of the mesoporous layer with vertically aligned mesoporous with respect to the surface of GO platelet surface (**Figure 3**).

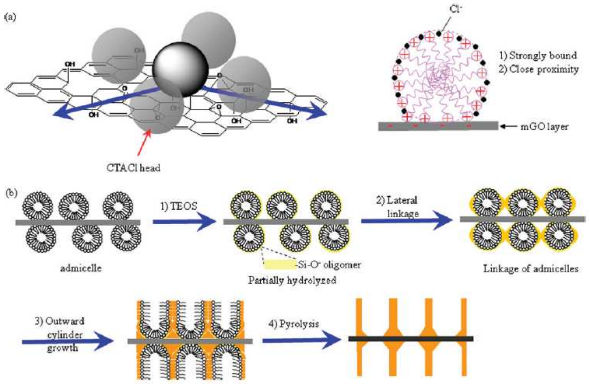


Figure 3. (a) Schematic representations of a CTACl headgroup (left) and an admicelle (right) on a mGO surface and (b) proposed mode of formation of rGO-PMS. Reprinted with permission from ref.13

The sandwich method can be also exploited to encapsulate very small metal nanoparticles in between the graphene nanosheets and the mesoporous silica layer. This system has proved to be an extremely robust catalyst for promoting both oxidation and reduction reactions [14]. Interestingly, the enhanced catalytic activity of this nanomaterials is not only attributed to the large surface area of graphene, but also to the synergic effect of the mesoporous silica layers which simultaneously stabilize the Pd nanoparticles and prevent the aggregation of the graphene nanosheets.

Besides energy storage and catalysis, the sandwich structures have shown other promising applications, such as in nanoproteomics [15,16]. The well defined porosity of mesoporous ordered materials is in fact a good tool for extraction of endogenous peptides and exclusion of larger molecules. A mesoporous silica graphene sandwich structure has been prepared using a graphene sheet whose surface has been hydrophilized in nitric acid. This sheet has been employed for growing sandwich mesoporous layers whose pore walls have been functionalized with n-octyltriethoxysilane that should allow adsorption of hydrophilic guest molecules. Tests of the system to extract endogenous peptides from a mouse brain tissue have shown that the material has excellent performances in size selectivity and specifically enriching peptides from both standard peptide mixtures and real biological samples [15] The same group has also realized another improved sandwich structure using graphene onto whose surface magnetic Fe_3O_4 particles have been bonded. The magnetic graphene layers have been then coated with silica mesoporous films (**Figure 4**).

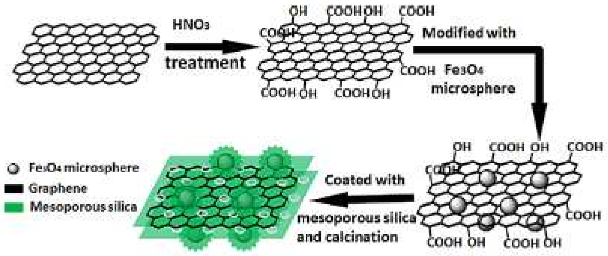


Figure 4. Scheme of synthesis of double-sided graphene magnetic layers and mesoporous silica. Reprinted with permission from ref. 14

The material has shown high selective enrichment capability of endogenous peptides in biological samples. A similar sandwich silica-graphene material with Fe_3O_4 magnetic particles has been prepared for the enrichment of phthalates in environmental water [17] while a further development of a similar platform, that is a polydopamine-coated magnetic graphene/mesoporous silica composites with titanium(IV)-immobilized in the pore walls, has shown to enable the selective capture of low-abundant endogenous phosphorylated peptides for peptidome analysis [18]. A variation on the theme of sandwich structures has been done by Maji et al. [19] which have grafted gold nanoparticles (~3 nm) onto a $mSiO_2$-RGO-$mSiO_2$ surface. This system has been used for developing a sensor for the electrochemical detection and quantification of H_2O_2, which is a potential marker for cancer, in aqueous medium under physiological conditions [20]. The detection of H_2O_2 has been sensitive and selective with a wide linear detection range, low detection limit, and high sensitivity. The sensor has been applied to measure glucose and H_2O_2 in human urine. The sandwich structure formed by graphene-mesoporous silica and gold nanoparticle has been also used in different types of biodetection. Nice examples of this application are the fabrication of an integrated sensing platform for the ultra-sensitive and selective detection of DNA [21] and the development of an electrochemical label free aptasensor as an enhanced element for ATP detection [22].

After a suitable chemical modification, the sandwich-like graphene-mesoporous silica systems can be converted into an effective carrier for the delivery of anticancer drugs [23]. After a modification with a targeting peptide, in fact, mesoporous silica-coated graphene nanosheets have been successfully loaded with doxorubicin and then tested as drug delivery nanodevices in the chemo-photothermal synergistic therapy of Glioma. The peptide modification allows enhancing significantly the accumulation of the nanocomposite within the cancer cells while the release of the drug resulted to be triggered both by thermal and pH changes.

2.2 Mesoporous particles and graphene sheets

Graphene sheets have shown to be a good platform for growing s*andwich* mesoporous layers through self-assembly, however other structures can be also obtained, such as mesoporous particles on graphene [24]. Different types of metallic and semiconductor nanoparticles have successfully grafted on graphene surface which has shown a high versatility as platform for functional nanoparticles. This possibility has been also exploited for oxide nanoparticles and this has been extended to the case of mesoporous particles [25]. Anatase titania nanoparticles, for instance, have been grown on graphene sheets without employing any template [26]. The mesopores within the particles are not organized but have a worm-like structure with an average size of 4 nm and pore walls of 3 nm; the particles have a size of 100 nm and are well dispersed and bonded onto the graphene sheets (**Figure 5**). The titania particles have also shown a single crystal-like structure, which indeed should expect to decrease the electron trapping phenomenon generated by the polycrystals boundaries. In general, the functional groups on the graphene and graphene oxide sheets act as heterogeneous nucleation sites for the growth of mesoporous oxide structures, this process is favoured by the presence of surfactants both ionic and non-ionic (block copolymers). If the graphene surface and the oxide chemistry is properly designed growth of homogeneous oxides on graphene are also observed in the absence of templates.

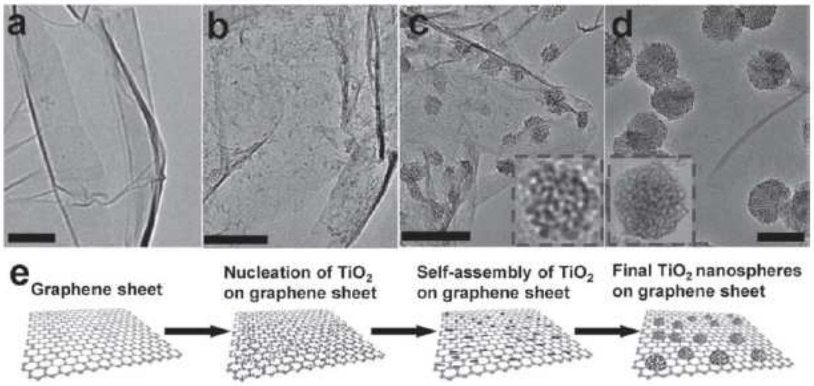


Figure 5. a–d) Representative TEM images of a) pristine graphene sheets, treated graphene sheets in the sulfuric acid reaction solution containing titanium sulfate at 100 °C for b) 1 h, c) 4 h, and d) 6 h. e) Schematic of growing TiO_2 nanospheres on a graphene sheet. Scale bar in (a–d), 100 nm. Reprinted with permission from ref. 26

The performances of the graphene-mTiO_2 nanoparticle system for lithium batteries [27,28] and photocatalysis [29,30,31] have resulted highly improved in comparison to a reference TiO_2. In particular, anatase titania and graphene used in photocatalysis show improved properties because the Fermi level of graphene is higher than the minimum of conduction band of anatase TiO_2 [32,33]. This favours the transfer of photoexcited electrons from anatase titania to the electronic states of graphene.

Another example of mesoporous particles graphene composite is obtained by self-assembly of colloidal titania crystals on graphene oxide sheets. The method is quite versatile and also Cu_2S and CeO_2 graphene systems have been produced although the porosity is not organized. Other examples of preparing similar composites *via* different methods, in any case without getting ordered porosity and not via template self-assembly routes, have been also reported [34,35,36]. A hydrothermal treatment has been also used to prepare sheet-belt hybrid nanostructures from one-dimensional mesoporous TiO_2 nanobelts and graphene sheets to be used in lithium-ion batteries [37]. Mixing of titania mesoporous particles with graphene to prepare a paste electrode is another possibility which has been explored for developing an electrochemical sensor [38].

Graphene oxide has been also used to support mesoporous silica spheres containing magnetic nanoparticles. In this case the precise design of the material enables its use as bifunctionalized adsorbents, capable of simultaneous removal of two kinds of environmental pollutants such as heavy metals and humic acid [39].

Another another example of mesoporous materials combined with graphene is given by In_2O_3-G mesoporous particles that have been encapsulated with graphene. The graphene wrapped system has, in fact, shown an improved electrochemical response, in fact, and in comparison to unwrapped particles the mIn_2O_3-G exhibited better performances for lithium storage [40]. The wrapping of mesoporous silica nanoparticles with ultrathin graphene oxide sheets allows designing an ideal nano-container for fluorescent dyes typically used for cellular imaging [41]. The graphene oxide layer prevents both dye leakage and nucleophilic attack on the dye due to the biological environment. Moreover, the system is fully biocompatible and exhibits a remarkable stability in aqueous solution.

The careful engineering of a fluorescent graphene-mesoporous silica material is also at the basis of the development of an optical probe for the Hg^{2+} detection in water [42]. The synthetic method requires at first the functionalization of mesoporous silica particle with a derivative of Rhodamine 6G and poly(p-phenylenevinylene) (PPV), and then the grafting of the silica particles onto the graphene oxide nanosheets. When the nanocomposite is dispersed in water, the presence of Hg^{2+} ions triggers a fluorescence resonance energy transfer (FRET) from PPV to Rhodamine 6G enabling a sensitive optical detection.

2.3 Mesoporous - graphene composite films

The previous examples have shown how much graphene and graphene oxide can be integrated in mesoporous matrices to produce materials with improved performances. One-pot preparation via self-assembly of mesoporous ordered films containing graphene is however a quite challenging task. Pristine graphene, which is hardly soluble in water without chemical modification, has in fact to be used for the synthesis to get mesoporous ordered films through self-assembly. An alternative is using graphene oxide and a post-synthesis reduction, but this is a quite complex process that increases the number of defects in the graphene structure and, at least in some cases, lowers the overall performances of the material. The approach to such type of functional nanocomposite becomes even more complex if the material is targeted for a specific application, which requires a precise design of the material properties. This is the case of photocatalytic films made of titania-graphene mesoporous nanocomposite, which should have improved performances respect to undoped layers, and, at least in some application such as self-cleaning windows, should also show a high transparency.

An example of integrated self-assembly process which employs exfoliated graphene to obtain highly ordered mesoporous anatase titania films has been reported by our research group [43]. The most popular method for producing graphene in the liquid phase is the chemical modification of graphite in acidic conditions to graphene oxide (GO) which can be later reduced to form reduced graphene oxide (RGO). An alternative method, which avoids the reduction step, is ultrasonication of graphite; exfoliated platelets formed by single- or few layer graphene sheets can be isolated in solution. Even if the exfoliated graphene (EG) cannot be directly compared to pristine graphene obtained by mechanical cleavage, it contains a much lower amount of defects in its sp^2-hybridized carbon structure and shows a higher photocatalytic activity [44].

Mixing a colloidal dispersion of graphene in 1-vinyl-2-pyrrolidone (NVP) with a titania precursor sol containing Pluronic F127 (templating agent), has allowed producing via spin or dip-coating mesoporous nanocomposite films with ordered porosity. The mesopores are highly organized achieving at the same time a good dispersion of the graphene sheets and a high optical transparency (**Figure 6**).

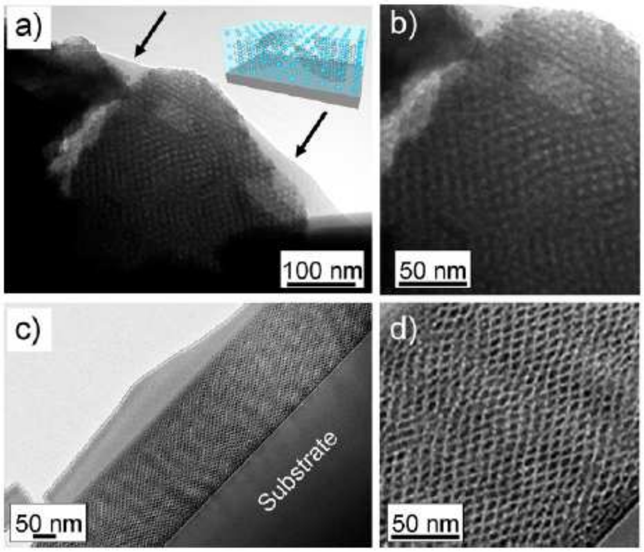


Figure 6. TEM images of representative areas taken from mesoporous graphene−titania nanocomposite films (2.5 vol % of EG dispersion). (a,b) Film fragments before calcination (thickness ≈ 280 nm); arrows indicate the graphene sheets. (c,d) Cross-section dark-field TEM images of the films after calcination. Reprinted with permission from ref. 43

The films have an enhanced photocatalytic response with respect to undoped mesoporous titania; this performance is due to different contributions, the use of exfoliated graphene with a minimized amount of defects, the formation of TiO_2 anatase nanocrystals and the highly organized mesoporosity with a cubic symmetry which enhances the diffusivity inside the matrix.

An advantage of producing graphene mesoporous films on a substrate is the possibility of patterning to fabricate different types of devices [45]. The mesoporous titania−graphene films can be processed, for instance, by deep X-ray lithography before thermal treatment for producing micrometer size functional patterns (**Figure 7**) [46,47].

Integration of the bottom-up film preparation by soft chemistry with the top-down physical patterning is one of the main advantages of sol-gel and self-assembled films to fabricate advanced functional coatings, such as those integrating the properties of graphene.

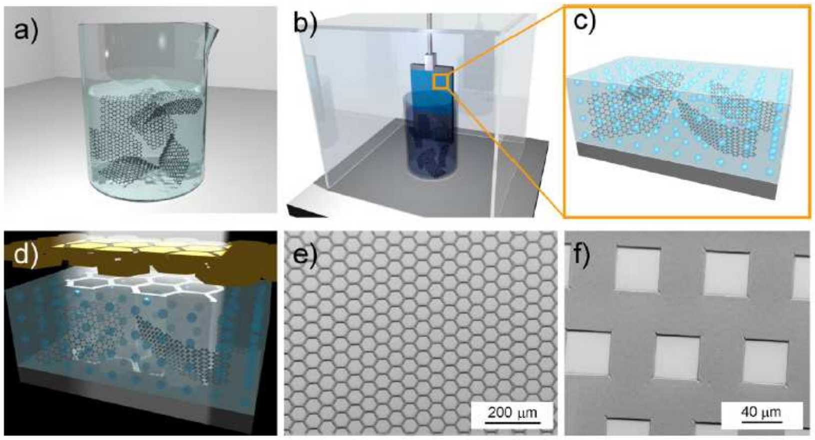


Figure 7. Scheme of the bottom-up, top-down integrated route for microfabrication of nanocomposite mesoporous titania−graphene patterns. (a) Highly acidic titania sol is loaded with graphene dispersion; (b) thin films are produced by dip- or spin-coating; (c) self-assembly process is not affected by graphene, and highly ordered mesoporous titania films are formed. (d) After deposition, thick films (thickness ≈ 800 nm) are patterned by deep X-ray lithography through a mask to obtain micrometer-sized patterns (SEM images, panels e and f). Reprinted with permission from ref. 43

Remarkably, one recent work reports on the use of a film with a multimodal and interconnected porosity, that is a hierarchical porous film [48], as a matrix for reduced graphene oxide. The hierarchical macro-mesoporous titania-graphene film, which shows 2D hexagonal (*p*6*mm*) mesostructure and well-interconnected periodic macropores, has been prepared *via* a confinement self-assembly method [49]. The regular voids of a three-dimensional (3D) periodic colloidal crystal made of polysterene particles has been used as template for the macropores, while the voids have been impregnated by an aqueous solution containing a surfactant (Pluronic P123), a titania precursor and graphene oxide to form a mesoporous scaffold. The film has been tested by adsorbing and photodegrading organic dyes, as a potential material for wastewater treatment and air purification to remove organic pollutants.

An original application of a multilayered graphene-mesoporous silica system deposited on nickel substrate has been recently used for the electrochemical deposition of an ordered array of CdSe quantum dots on the graphene sheet [50]. In this case, however, the mesoporous film merely acts as a mask for the deposition of the quantum dots with a long-range ordered fashion. After the electrochemical deposition, in fact, the oxide layer and the Ni substrate are removed, leading to a pure graphene-nanoparticle system.

As already pointed out in this review, mesoporous ordered films have the main advantage of being an interactive platform. They can absorb different species from the external environment while at the same time the oxide scaffold can interact with graphene and the host species. This property is particularly useful for developing particularly attractive sensing devices such as those based on Surface Enhanced Raman

Scattering (SERS) [51]. Graphene itself has the capability of enhancing the Raman scattering signal and this effect is indicated as graphene-mediated enhanced Raman scattering (GERS) [52] A limitation for a practical application of this property is however the small enhancement factor ($10–10^2$) because a chemical mechanism (CM) drives the charge transfer between graphene and the molecule to detect. GERS, however, could be combined with the more conventional SERS, mostly based on an electromagnetic mechanism (EM), to develop a combined effect, the graphene-mediated surface-enhanced Raman scattering (G-SERS) which is observed when graphene interacts with metal nanoparticles [53]. Respect to the other systems used for enhancing the Raman scattering, the nanocomposite G-SERS platform shows a higher stability of the Raman probe. This is mainly due to the small absorption in the UV-vis range and the high thermal conductivity of graphene, which makes the Raman probe resistant to photo-induced damage.

G-SERS effect has been reproduced in mesoporous ordered films by introducing graphene bilayer sheets and growing gold nanoparticles by thermal reduction [54]. The nanoparticles of around 6 nm preferentially nucleate on the surface of the graphene nanosheets while the presence of graphene and gold nanoparticles does not interfere with self-assembly formation of silica mesoporous films ordered as 2D hexagonal structures. The material has shown a remarkable analytical enhancement factor ranging from 80 up to 136 using rhodamine 6G as a Raman probe (**Figure 8**).

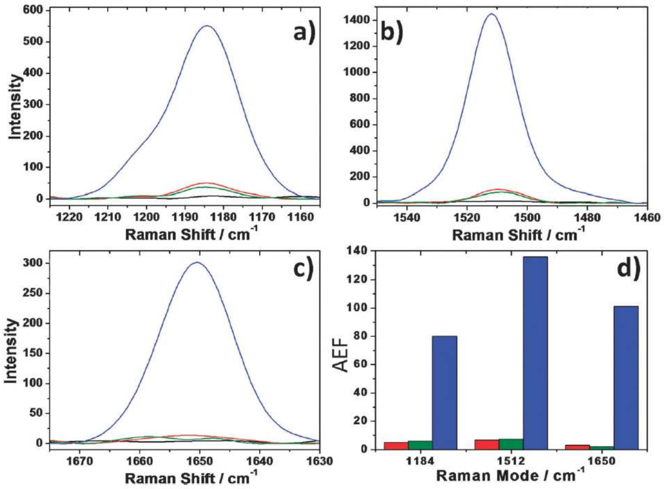


Figure 8. SERS enhancement of rhodamine 6G deposited on different mesoporous nanocomposite matrices relative to the 3 Raman modes centred at 1184 (a), 1512 (b) and 1650 cm^{-1} (c). Black line: Rh6G on mesoporous silica films; red line: Rh6G on mesoporous silica films containing exfoliated graphene; green line: Rh6G on mesoporous silica films containing gold nanoparticles; blue line: Rh6G on mesoporous silica films containing both exfoliated graphene and gold nanoparticles. (d) Analytical enhancement factors as measured from the 3 Raman modes of Rh6G deposited on different mesoporous nanocomposite matrices. Red bars: mesoporous silica films containing exfoliated graphene; green bars: mesoporous silica films containing gold nanoparticles; blue bars: mesoporous silica films containing both exfoliated graphene and gold nanoparticles. Reproduced with permission from ref. 54

3. Carbon dots in mesoporous materials

The family of carbon dots is formed by several types of carbon-based fluorescent nanomaterials whose optical properties are originated by different photoluminescence mechanisms. The group defined as carbon dots is quite general and can be divided in three main different groups, carbon nanodots, graphene quantum dots (GQDs), and polymer dots [55]. The carbon nanodots (CNDs), in turn, can be divided in two main groups, carbon nanoparticles that are amorphous and carbon quantum dots (CQDs), which have a crystalline lattice. Even if this classification is clear, there are still few uncertainties into classifying the different types of carbon nanodots, such as size and shape and the origin of their photoluminescence. In fact, depending of the type of CNDs, this property can be attributed to four different mechanisms: the quantum confinement effect, caused by conjugated π-domain; the surface state, which is determined by hybridization of the carbon backbone and the connected chemical groups; the molecule state, which only occurs if a fluorescent molecules is connected to the CND; and the crosslink enhanced emission effect, induced by the carbonization during the CND synthesis from a polymer. In general, we can define CNDs as quasi-spherical objects, that are almost isotropical in shape while the dimensions should be lower than 10 nm. The main property of CNDs is their fluorescence which is generated by different mechanisms; these are somehow similar to that of semiconductor quantum dots but the emission wavelength is in general not size-dependent and the bandwidth is much wider.

Another important property is the possibility of chemical functionalization of CNDs that make them particularly attractive for preparation of materials *via* low-temperature soft-chemistry routes, such as sol-gel. These nanomaterials are in fact soluble in water and other polar solvent and the functionalization of their surface with different organic species is quite feasible. This makes them highly compatible with sol-gel chemistry [56] and the synthesis of self-assembled mesoporous materials.

3.1 Mesoporous particles with CQDs

While mesoporous particles have a wide range of applications, especially as biocompatible materials for drug delivery and sensing, several types of luminescent mesoporous particles have also been obtained using fluorescent dyes, semiconductor nanoparticles and lanthanide ions. Even if these materials have shown remarkable properties some limitations appear clear in all the cases, the dyes show stability problems, such as photobleaching and thermal degradation, or leakage from the matrix, while most of semiconductors are toxic or exhibit a luminescence which is too low to obtain highly bright particles, such as lanthanide nanocrystals. Carbon quantum dots in mesoporous particles are an efficient alternative [57,55] because they have a high chemical and photo-stability with low toxicity and low production costs. Another advantage is the high tunability of the properties through the CQDs chemical functionalization.

Several examples of such systems, formed by combining CQDs with mesoporous silica particles, have been reported in literature. They have been applied for bioimaging [58,59,60], or more complex theranostic uses which combine fluorescent imaging with drug delivery capability. Different strategies have been also developed for fabrication of mesoporous silica particles with CQDs; they differ both by the matrix synthesis and the method for entrapping the carbon dots in the silica porous particle.

Basically two synthesis routes can be recognized, the first one is the so called "one-pot" approach, which allows forming the mesoporous silica matrix and incorporating the CQDs in a single step; the second route, instead, allows adding the CQDs to pre-fabricated silica mesoporous particles. There is also a wide choice of methods for adding the CQDs, in fact they can be capped on the particles surface, or embedded in the pores or even into the pore walls. The best strategy depends on the desired application; in theranostic, for instance, the mesoporous particles become an interactive platform with a multifunctional role, such as an environment sensitive gate. The $mSiO_2$-CQDs particles can be loaded with relatively high amounts of drugs while at the same time can perform bioimaging thanks to the strong photoluminescence of the system [61].

A quite original one-pot method to prepare mesoporous silica NPs containing CQDs is using rice husk as precursor both for silica and the carbon dots (**Figure 9)** **[**58]. Rice husk is, in fact, rich in silica and carbon and mixing a pyrolyzed powder with an ionic surfactant (cetyltrimethylammonium bromide, CTAB) gives a $mSiO_2$-CQDs nanodispersion in water with strong fluorescence.

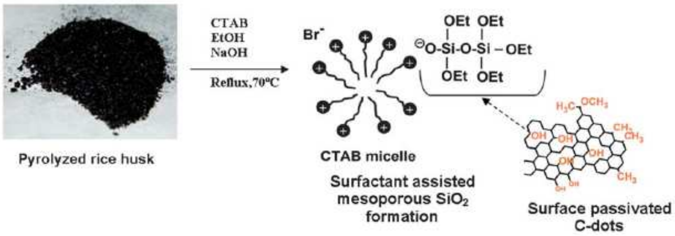


Figure 9. Schematic showing CTAB assisted synthesis of meso-SiO_2 and attachment of C-dots to form the mesoSiO_2/C-dot complex. Reprinted with permission from ref. 58.

Remarkably, $mSiO_2$–CQDs particles have shown a low or absent cytotoxicity; as proved during tests for imaging on yeast and Vero cells.

Similar systems for theranostic applications have been obtained by different routes such as forming the CQDs in the silica matrix by proper precursors. One example of such precursors are carbohydrates such as glycerol, glycol, glucose and sucrose which have been used to produce emissive CQDs [62]. A $mSiO_2$–CQDs composite is easily obtained after heating to 230°C a mixture of $mSiO_2$ NPs with glycerol; the system could be further modified if glycerol and PEG–NH_2 are simultaneously employed as precursors to get a $mSiO_2$–CQDs–PEG nanocomposite [63]. The capping of reactant derived from the polyethylene glycol (PEG) onto the $mSiO_2$–CQDs has resulted in an enhancement of luminescence, stability and bio-compatibility. These particles have been then loaded with an anti-cancer drug, doxorubicin (DOX); the release of DOX in HeLa cells has been monitored by both time-dependent and spatially resolved ratiometric fluorescence intensity for CDs versus DOX. DOX release and accumulation in nucleus is revealed by the red emission, while a separated signal (blue) is observed from the citoplasm where the $mSiO_2$–CQDs–PEG accumulates (**Figure 10**).

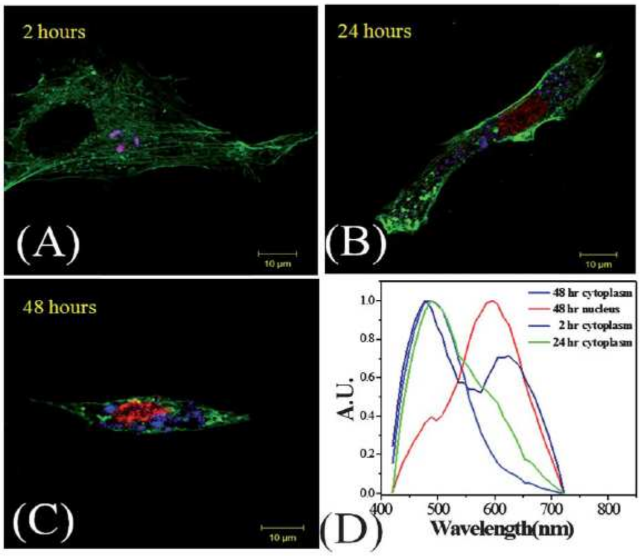


Figure 10. (A–C) The confocal images of HeLa cell treated with 100 mg ml^{-1} DOX–CQDs–mSiO$_2$–PEG for 2 h, 24 h and 48 h. (D) The time dependent ratiometric fluorescence intensity derived from the cytoplasm and nucleus after 2 h and 48 h treatment. Reprinted with permission from ref. 63.

A quite similar experiment has been reported in another work where MCM-41 silica particles have been loaded with CQDs and DOX, in this case however the carbon dots played a more sophisticated role because they also served as caps to entrap the DOX molecules within the mesopores [64]. The drug release has been hampered by CQDs at neutral pH and allowed at lower pH. The system confirmed the low citotoxicity and the combined use for imaging and efficient drug delivery while the CQDs capped particles have shown a remarkable enhancement in cancer cells suppression.

Another application of mesoporous particles combined with CQDs is in sensing. Amino-functionalized mesoporous silica particles (NH$_2$-mSiO$_2$) capped with blue luminescent CQDs have been used to develop an electroluminescence immunosensor [65]. The sensor has been based on an Ag paper work electrode with CQDs as signal label and has been able to detect the cancer antigen 125 (CA125). The Scheme of the EL immunosensor is shown in **Figure 11**.

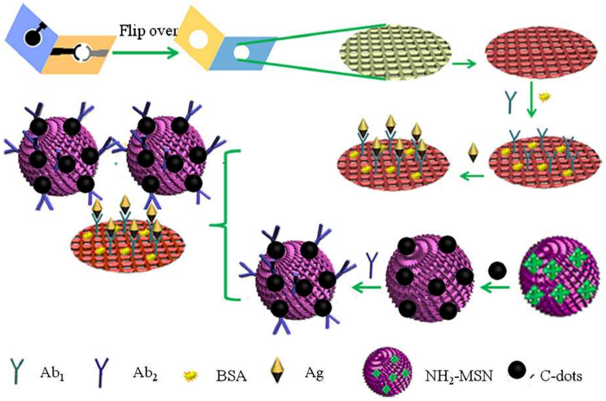


Figure 11. Schematic representation of the fabrication of the ECL immunosensor. Reprinted with permission from ref. 65.

The versatility of a mesoporous material as functional platform can be fully exploited by increasing the number of active species in the matrix. The previous examples have shown that combining the CQDs fluorescence with mesoporous silica particles allows producing relatively simple and effective devices with combined properties, such as drug release and bioimaging. These properties can be even enhanced taking advantage, as previously underlined, of the open porosity. A main issue is increasing the fluorescence of CDs-mSiO_2 particles; this can be achieved using the metal-enhanced fluorescence effect. Silica mesoporous particles containing both Ag and CQDs within the pores have been synthesised through a "one-pot" route (**Figure 12**) [66].The presence of AgNPs has produced a 3.4 fold enhancement of luminescence intensity that is very sensitive to the excitation wavelength. Beside this dependence on intensity, a general property of CQDs is that the position of the emission peak is always dependent on the excitation wavelength. This is likely due to the large variability in quantum dots size and surface properties and the presence of different emissive traps. On the other hand the excitation dependence of photoluminescence allows multicolor imaging applications

The metal-enhanced fluorescence has been attributed mainly to the localized field effect of AgNPs with some contributions from the plasmon coupling effect between the surface plasmon resonance absorption in AgNPs and the emission from the Ag-CQDs-mSiO_2 system.

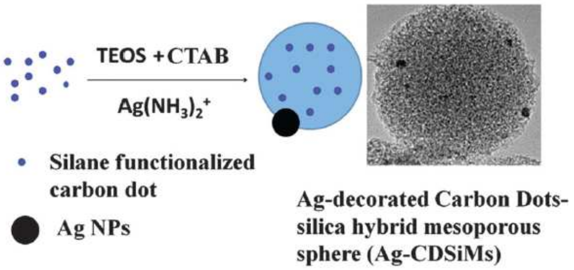


Figure 12. Preparation of Ag-CQDs-mesoSiO_2 particles. Reprinted with permission from ref. 66.

In the previous examples the CQDs have been capped on the silica mesoporous particles or embedded into the pores; there is, however, still another option which is the incorporation of CQDs within the mesopore walls. This material has been prepared by reacting methoxysilyl-modified carbon dots (Si-CQDs) [67] with tetraethylorthosilicate and CTAB as the organic template [68] (**Figure 13**).

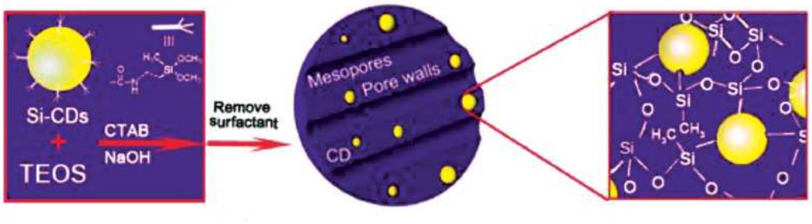


Figure 13. Synthetic procedure and structural illustration of CQDs-mesoSiO_2. Reprinted with permission from ref. 68.

The mesopores have been used as hosts for analyte-sensitive molecules while the CQDs in the silica backbone are the reference species. This allows building up a pH ratio-metric sensor; in fact, if the CQDs emission spectrum overlaps the excitation spectrum of the guest dye, fluorescent resonance energy transfer (FRET) occurs [69,70]. A ratiometric sensor for detection of Hg^{2+} ions has been realized using a rhodamine 6G derivative as the Hg^{2+} sensitive dye (**Figure 14**). On the other hand the same CQDs mesoporous platform has shown to become an efficient photocatalyst and a multichannel traceable drug delivery system.

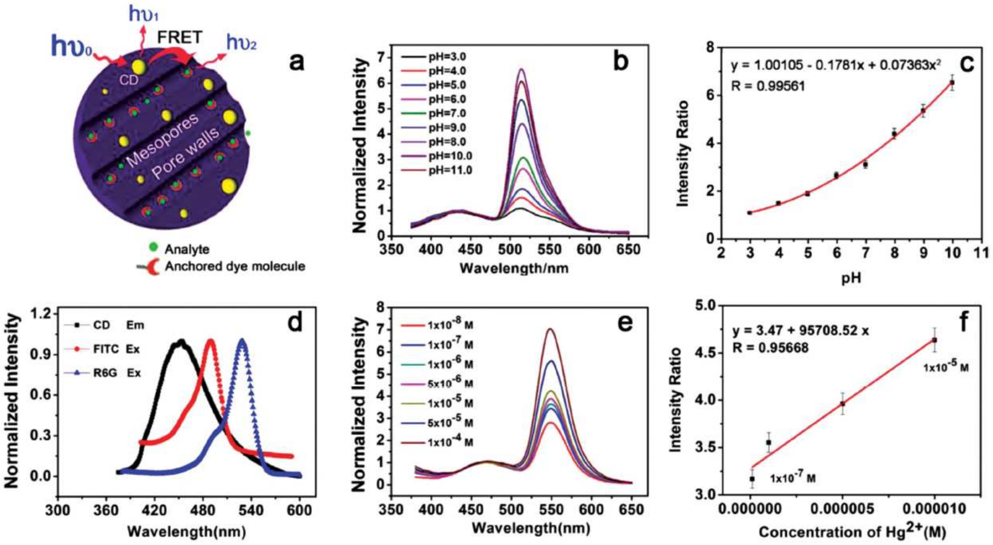


Figure 14. a) Schematic illustration of the ratiometric sensor; b) normalized fluorescence spectra of fluorescein isothiocyanate (FITC)-modified CQDs-$mSiO_2$ excited at 360 nm and at various pH values; c) ratiometric pH calibration plot detected using FITC-modified CQDs-$mSiO_2$; d) emission spectra of CQDs, and excitation spectra of FITC and RBITC; e) normalized fluorescence spectra of Rhodamine 6G derivative-modified CQDs-$mSiO_2$ excited at 360 nm and at various Hg^{2+} concentration and f) ratiometric Hg^{2+} calibration plot detected using Rhodamine 6G derivative-modified CQDs-$mSiO_2$. Reprinted with permission from ref. 68.

3.2 Carbon quantum dots in mesoporous films

As we have seen, most of mesoporous silica - CQDs composites have been developed for bioapplications and in the shape of particles, while up to now only one report has been published about CQDs in mesoporous films. Zinc oxide mesoporous films containing carbon quantum dots have been synthesised by one-pot route using a fluorosurfactant as a templating agent which can be easily removed at 200 °C leaving an accessible porosity [71]. After the thermal treatment the photoluminescence of the carbon quantum dots is retained, enabling multiple effects due to interplay between the semiconductor matrix and the luminescent nanoparticles (**Figure 15**). The 3D photoluminescence maps show a complex trend which has been attributed to energy transfer involving dipole interactions and reabsorption between ZnO and CQDs, and formation of surface defects in the inorganic oxide structure. The CQDs embedded into the ZnO matrix allow tuning the photoluminescence of the nancomposite in a wide wavelength range paving the way for applications in solar cell systems, UV shielding windows and phosphors for lighting application.

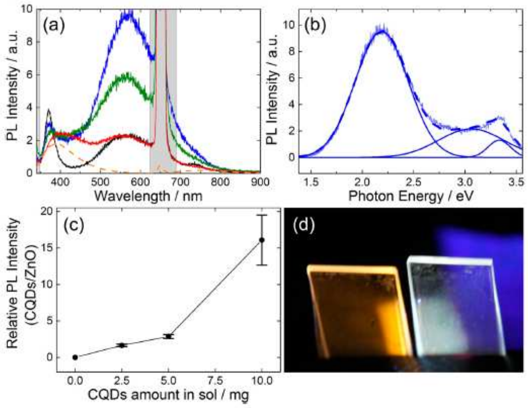


Figure 15. (a) Photoluminescence spectra of the ZnO-CQD films as a function of CQD concentrations (excitation wavelength = 325 nm): bare ZnO (black line), ZnO-CQD 2.5 mg (blue line), ZnO-CQD 5 mg (green line), and ZnO-CQD 10 mg (red line). The CQDs photoluminescence in water is also reported as a reference (dotted orange line). The ranges of the scattering incident light and its second harmonics (<348 nm and 625−690 nm) are shown as gray shadows. (b) A typical result of deconvolution of the PL spectra of ZnO-CQD 2.5 mg (excitation wavelength = 325 nm). (c) Relative PL intensity of CQDs to ZnO as a function of CQD concentrations. (d) A photo image of 2.5 mg (left) and 5 mg (right) of CQD-doped ZnO films under 376 nm light illumination. Reprinted with permission from ref. 71.

3.3 From carbon quantum dots to graphene quantum dots

Graphene quantum dots (GQDs) and carbon quantum (CQDs) dots are two specific sub-classes of the broader family of carbon nanodots [72], even if the two groups show small differences, they both have some peculiar properties which allows a clear distinction [73,74]. The GQDs have a graphene lattice which is clearly recognizable independently of the dot size. They also differ in shape, while CQDs are quasi-spherical objects smaller than 10 nm, the GQDs are anisotropic because are formed by few layers graphene (single, double or from 3 to 10) and have lateral dimensions smaller than 100 nm. In some cases, however, the carbon nanostructures do not allow a precise classification; CQDs, for instance, may contain some graphene structured parts which coexist with amorphous or crystalline carbon. Coexistence of different phases in a carbon dot can be therefore a quite common case and has to be into account to define the properties of composite materials.

Preparation of mesoporous materials containing graphene quantum dots is still behind with respect to CQDs. GQDs have been used as an efficient gate system to cap mesoporous silica particles containing DOX drug [75], in a similar way to what already reported for CQDs [64]. The luminescent GQDs are grafted on the surface of silica mesoporous particles through acetal bonds. The GQDs prevent the leakage of drug molecules at neutral pH and release them at acidic pH while providing an efficient fluorescent marker for tracking of the drug delivery in vitro.

4. A future outlook

The nanocomposites obtained by the combination of carbon-based nanostructures and mesoporous materials are revealing a tremendous potential that, at present, is having a massive impact on a large number of functional applications, such as catalysis, energy storage, nanomedicine, optics and sensing. However, despite some of the recent proof-of-concepts are seeding the development of innovative devices, there is still a lack of rationalization related to the fundamental properties of this class of materials. Indeed, deeper and systematic studies are required to reach a full understanding of the phenomena occurring at the complex interface between oxides and carbon-based structures in the mesoporous nanocomposite. This, in fact, would allow to *a priori* design of the materials, with a fine control of the properties depending on the prospected applications.

Acknowledgements

D.C. acknowledges the financial support by the Sardinian Regional Government (P.O.R. SARDEGNA F.S.E. 2007–2013 -Obiettivo competitività regionale e occupazione, Asse IV Capitale umano, Linea di Attività l.3.1.).

References

---

[1] P. Innocenzi, L. Malfatti, T. Kidchob and P. Falcaro. Order-disorder in self-assembled mesostructured silica films: a concepts review, *Chem. Mater.* 2009, **21**, 2555-2564.

[2] A. K. Geim and K. S. Novoselov. The rise of graphene, *Nat. Mater.* 2007, **6**, 183-191.

[3]P. Innocenzi, L. Malfatti, B. Lasio, A. Pinna, D. Loche, M. F.Casula, V. Alzari and A. Mariani. Sol–gel chemistry for graphene–silica nanocomposite films, *New J. Chem.* 2014, **38**, 3777-3782.

[4] W. S. Hummers and R. E. Offeman. Preparation of graphitic oxide, *J. Am. Chem. Soc.* 1958, **80**, 1339-1339.

[5] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff. Graphene-based composite materials, *Nature* 2006, **442**, 282-286.

[6] S. Yang, X. Feng, L. Wang, K. Tang, J. Maier and K. Müllen. Graphene-based nanosheets with a sandwich structure, *Angew. Chem. Int. Ed.* 2010, **49**, 4795-4799.

[7] J. Zai and X. Qian. Three dimensional metal oxides–graphene composites and their applications in lithium ion batteries, *RSC Advances*, 2015, **5**, 8814-8834.

[8] S. Yang, X. Feng and K. Müllen. Sandwich-like, graphene-based titania nanosheets with high surface area for fast lithium storage. *Adv. Mater*. 2011, **23**, 3575-3579.

[9] K. H. Kim, Y.-S. Jun, J. A. Gerbec, K. A. See, G. D. Stucky and H.-T. Jung. Sulfur infiltrated mesoporous graphene–silica composite as a polysulfide retaining cathode material for lithium–sulfur batteries, *Carbon*, 2014, **69**, 543-551.

[10] C.-W. Lee, K. C. Roh and K.-B. Kim. A highly ordered cubic mesoporous silica/graphene nanocomposite, *Nanoscale*, 2013, **5**, 9604-8608.

[11] S. W. Kim, T. H. Han, J. Kim, H. Gwon, H. S. Moon, S. W. Kang, S. O. Kim, and K. Kang. Fabrication and electrochemical characterization of TiO_2 three-dimensional nanonetwork based on peptide assembly, *ACS Nano,* 2009, **3**, 1085-1090.

---

[12] S. Yang, W. Yue, J. Zhu, Y. Ren and X. Yang. Graphene-based mesoporous SnO_2 with enhanced electrochemical performance for lithium-ion batteries, *Adv. Funct. Mater.* 2013, **23**, 3570-3576.

[13] Z.-M. Wang, W. Wang, N. Coombs, N. Soheilnia and G. A. Ozin. Graphene oxide−periodic mesoporous silica sandwich nanocomposites with vertically oriented channels, *ACS Nano*, 2010, **4**, 7437-7450.

[14] L. Shang, T. Bian, B. Zhang, D. Zhang, L.-Z. Wu, C.-H. Tung, Y. Yin and T. Zhang. Graphene-Supported Ultrafine Metal Nanoparticles Encapsulated by Mesoporous Silica: Robust Catalysts for Oxidation and Reduction Reactions, *Angew. Chem. Int. Ed.* 2014, **53**, 250-254.

[15]P. Yin, Y. Wang, Y. Li, C. Deng, X. Zhang and P. Yang. Preparation of sandwich-structured graphene/mesoporous silica composites with C8-modified pore wall for highly efficient selective enrichment of endogenous peptides for mass spectrometry analysis, *Proteomic*s, 2012, **12**, 2784-2791.

[16] P. Yin, N. Sun, C. Deng, Y. Li, X. Zhang and P. Yang. Facile preparation of magnetic graphene double-sided mesoporous composites for the selective enrichment and analysis of endogenous peptides, *Proteomic*s, 2013, **13**, 2243-2250.

[17] D. Huang, X. Wang, C. Deng, G. Song, H. Cheng and X. Zhang. Facile preparation of raisin-bread sandwich-structured magnetic graphene/mesoporous silica composites with C18-modified pore-walls for efficient enrichment of phthalates in environmental water, *J. Chromatogr. A,* 2014, **1325**, 65-71.

[18] N. Sun, C. Deng, Y. Li and X. Zhang. Size-exclusive magnetic graphene/mesoporous silica composites with Titanium(IV)-immobilized pore walls for selective enrichment of endogenous phosphorylated peptides, *ACS Appl. Mater. Interfaces* 2014, **6**, 11799-11804.

[19] S. K. Maji, S. Sreejith, A. K. Mandal, X. Ma and Y. Zhao. Immobilizing gold nanoparticles in mesoporous silica covered reduced graphene oxide: a hybrid material for cancer cell detection through hydrogen peroxide sensing, *ACS Appl. Mater. Interfaces* 2014, **6**, 13648-13656.

[20] X. Sun, S. Guo, Y. Liu and S. Sun. Dumbbell-like PtPd–Fe_3O_4 nanoparticles for enhanced electrochemical detection of H_2O_2, *Nano Lett.* 2012, **12**, 4859-4863.

[21] Y. Du, S. Guo, S. Dong and E. Wang. An integrated sensing system for detection of DNA using new parallel-motif DNA triplex system and graphene-mesoporous silica-gold nanoparticle hybrids, *Biomaterials* 2011, **32**, 8584-8592.

[22] S. Guo, Y. Du, X. Yang, S. Dong and E. Wang. Solid-state label-free integrated aptasensor based on graphene-mesoporous silica gold nanoparticle hybrids and silver microspheres, *Anal. Chem.* 2011, **83**, 8035-8040.

[23] Y. Yi Wang, K. Wang, J. Zhao, X. Liu, J. Bu, X. Yan and R. Huang. Multifunctional mesoporous silica-coated graphene nanosheet used for chemo-photothermal synergistic targeted therapy of glioma, *J. Am. Chem. Soc.* 2013, **135**, 4799-4804.

[24] L. Guardia, F. Suárez-García, J. I. Paredes, P. Solís-Fernández, R. Rozada, M. J. Fernández-Merino, A. Martínez-Alonso and J. M. D. Tascón. Synthesis and characterization of graphene–mesoporous silica nanoparticle hybrids, *Micropor. Mesopor. Mater.* 2012, **160**, 18-24.

[25] J. Liu, I. A. Aksay, R. Kou, D. Wang and D. Wang. Mesoporous metal oxide graphene nanocomposite materials. U. S. Patent US20120295027 A1, November 22, 2012.

[26] N. Li, G. Liu, C. Zhen, F. Li, L. Zhang and H.-M Cheng. Battery performance and photocatalytic activity of mesoporous anatase TiO_2 nanospheres/graphene composites by template-free self-assembly, *Adv. Funct. Mater.* 2011, **21**, 1717-1722.

[27] S. Ding, J. S. Chen, D. Luan, F. Y. C. Boey, S. Madhavi and X. W. Lou. Graphene-supported anatase TiO_2 nanosheets for fast lithium storage, *Chem. Commun*. 2011, **47**, 5780−5782.

[28] M. Zhen, M. Sun, G. Gao, L. Liu and Z. Zhou. Synthesis of mesoporous wall-structured TiO_2 on reduced graphene oxide nanosheets with high rate performance for lithium-ion batteries, *Chem. Eur. J.* 2015, **21**, 5317-5322.

[29] G. Williams, B. Seger and P. V. Kamat. TiO_2-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide, *ACS Nano*, 2008, **2**, 1487-1491.

[30] K. K. Manga, Y. Zhou, Y. L. Yan and K. P. Loh. Multilayer hybrid films consisting of alternating graphene and titania nanosheets with ultrafast electron transfer and photoconversion properties, *Adv. Funct. Mater.* 2009, **19**, 3638-3643.

[31] K. Li, Y. Huang, L. Yan, Y. Dai, K. Xue, H. Guo, Z. Huang and J. Xiong. Simulated sunlight photodegradation of aqueous atrazine and rhodamine B catalyzed by the ordered mesoporous graphene–titania/silica composite material, *Catalysis Communications* 2012, **18**, 16-20.

[32] W. Geng, H. Liu and X. Yao. Enhanced photocatalytic properties of titania–graphene nanocomposites: a density functional theory study, *Phys. Chem. Chem. Phys.,* 2013, **15**, 6025-6033.

[33] Y. B. Tang, B. Tang, C. S. Lee, J. Xu, Z. T. Liu, Z. H. Chen, Z. B. He, Y. L. Cao, G. D. Yuan, H. S. Song et al. Incorporation of graphenes in nanostructured TiO_2 films via molecular grafting for dye-sensitized solar cell application, *ACS Nano* 2010, **4**, 3482-3488.

[34] J. Qiu, C. Lai, Y. Wang, S. Li and S. Zhang. Resilient mesoporous TiO_2/graphene nanocomposite for high rate performance lithium-ion batteries, *Chem. Eng. J.* 2014, **256**, 247-254.

[35] J. Chang, J. Yang, P. Ma, D. Wu, L. Tian, Z. Gao, K. Jiang and L. Yang. Hierarchical titania mesoporous sphere/graphene composite, synthesis and application as photoanode in dye sensitized solar cells, *J. Colloid Interf. Sci.*, 2013, **394**, 231-236.

[36] S. Chowdhury, G. K. Parshetti and R. Balasubramanian. Post-combustion CO_2 capture using mesoporous TiO_2/graphene oxide nanocomposites, *Chem. Eng. J.*, 2015, **263**, 374-384.

[37] H. Huang, J. Fang, Y. Xia, X. Tao, Y. Gan, J. Dun, W. Zhu and W. Zhang. Construction of sheet–belt hybrid nanostructures from one-dimensional mesoporous TiO_2(B) nanobelts and graphene sheets for advanced lithium-ion batteries, *J. Mater. Chem. A* 2013, **1**, 2495-2500.

[38] T. Gan, J. Sun, W. Meng, L. Song and Y. Zhang. Electrochemical sensor based on graphene and mesoporous TiO_2 for the simultaneous determination of trace colourants in food, *Food Chemistry*, 2013, **141**, 3731-3737.

---

[39] Y. Wang, S. Liang, B. Chen, F. Guo, S. Yu and Y. Tang. Synergistic removal of Pb(II), Cd(II) and humic acid by Fe_3O_4@mesoporous silica-graphene oxide composites. PLoS One 2013, **8**, e65634.

[40] L. Zhao, W. Yue, and Y. Ren. Synthesis of graphene-encapsulated mesoporous In_2O_3 with different particle size for high-performance lithium storage, *Electrochim. Acta*, 2014, **116**, 31-38.

[41] S. Sreejith, X. Ma, and Y. Zhao. Graphene Oxide Wrapping on Squaraine-Loaded Mesoporous Silica Nanoparticles for Bioimaging, *J. Am. Chem. Soc.* 2012, **134**, 17346-17349.

[42] H. Zhang, C. Tong, J. Sha, B. Liu and C. Lü. Fluorescent mesoporous silica nanoparticles functionalized graphene oxide: a facile FRET-based ratiometric probe for Hg^{2+}, *Sensor Actuat .B:Chem.* 2015, **206**, 181-189.

[43] L. Malfatti, P. Falcaro, A. Pinna, B. Lasio, M. F. Casula, D. Loche, A. Falqui, B. Marmiroli, H. Amenitsch, R. Sanna et al. Exfoliated graphene into highly ordered mesoporous titania films: highly performing nanocomposites from integrated processing, *ACS Appl. Mater. Interfaces*, 2014, **6**, 795-802.

[44] Y. T. Liang, B. K. Vijayan, K. A. Gray and M. C. Hersam. Minimizing graphene defects enhances titania nanocomposite-based photocatalytic reduction of CO_2 for improved solar fuel production, *Nano Lett.* 2011, **11**, 2865-2870.

[45] P. Innocenzi, T. Kidchob, P. Falcaro and M. Takahashi. Patterning techniques for mesostructured films, *Chem. Mater.* 2008, **20**, 607-614.

[46] P. Falcaro, L. Malfatti, L. Vaccari, H. Amenitsch, B. Marmiroli, G. Grenci and P. Innocenzi. Fabrication of Advanced Functional Devices Combining Soft Chemistry with X-ray Lithography in One Step, *Adv. Mater.* 2009, **21**, 4932-4936.

[47] P. Falcaro, L. Malfatti and P. Innocenzi. Hard X-rays meet soft matter: when bottom-up and top-down get along well, *Soft Matter*, 2012, **8**, 3722-3729.

[48] P. Innocenzi, L. Malfatti and G. J. A. A. Soler-Illia. Hierarchical mesoporous films: from self-assembly to porosity with different length scales, *Chem. Mater.*, 2011, **23**, 2501-2509.

[49] J. Du, X. Lai, N. Yang, J. Zhai, D. Kisailus, F. Su, D. Wang and L. Jiang. Hierarchically ordered macro−mesoporous TiO_2−graphene composite films: improved mass transfer, reduced charge recombination, and their enhanced photocatalytic activities, *ACS Nano* 2010, 5, 590-596.

[50] Y.-T. Kim, J. H. Han, B. H. Hong and Y. -U Kwon. Electrochemical Synthesis of CdSe Quantum-Dot Arrays on a Graphene Basal Plane Using Mesoporous Silica Thin-Film Templates, *Adv. Mater.* 2010, **22**, 515-518.

[51] L. Malfatti, P. Falcaro, B. Marmiroli, H. Amenitsch, M. Piccinini, A. Falqui and P. Innocenzi. Nanocomposite mesoporous ordered films for lab-on-chip intrinsic surface enhanced Raman scattering detection, *Nanoscale* 2011, **3**, 3760-3766.

[52] X. Ling, L. Xie, Y. Fang, H. Xu, H. Zhang, J. Kong, M. S. Dresselhaus, J. Zhang and Z. Liu. Can graphene be used as a substrate for Raman enhancement? *Nano Lett.* 2010, **10**, 553-561.

[53] W. Xu, X. Ling, J. Xiao, M. S. Dresselhaus, J. Kong, H. Xu, Z. Liu and J. Zhang. Surface enhanced Raman spectroscopy on a flat graphene surface, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 9281-9286.

[54] D. Carboni, B. Lasio, V. Alzari, A. Mariani, D. Loche, M. F. Casula, L. Malfatti, and P. Innocenzi. Graphene-mediated surface enhanced Raman scattering in silica

---

mesoporous nanocomposite films, *Phys. Chem. Chem. Phys.,* 2014, **16**, 25809-25818.

[55] S. Zhu, Y. Song, X. Zhao, J. Shao, J. Zhang and B. Yang. The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective, *Nano Research*, 2015, **8**, 355-381.

[56] Z. Xie, F. Wang and C.-Y. Liu. Organic–inorganic hybrid functional carbon dot gel glasses, *Adv. Mater.* 2012, **24**, 1716-1721.

[57] S. N. Baker and G. A. Baker. Luminescent Carbon Nanodots: Emergent Nanolights, *Angew. Chem. Int. Ed.,* 2010, **49**, 6726-6744.

[58] S. Yang, L. Cao, P. Luo, F. Lu, X. Wang, H. Wang, M. J. Meziani, Y. Liu, G. Qi and Y. Sun. Carbon dots for optical imaging in vivo, *J. Am. Chem. Soc.,* 2009, 131, 11308-11309.

[59] L. Cao, X. Wang, M. J. Meziani, F. Lu, H. Wang, P. G. Luo, Y. Lin, B. A. Harruff, L. M. Veca, D. Murray et al. Carbon dots for multiphoton bioimaging, *J. Am. Chem. Soc.,* 2007, **129**, 11318-11319.

[60] S. Pandey, A. Mewada, M. Thakur, S. Pillai, R. Dharmatti, C. Phadke and M. Sharon. Synthesis of mesoporous silica oxide/C-dot complex (meso-SiO_2/C-dots) using pyrolysed rice husk and its application in bioimaging, *RSC Advances*, 2014, **4**, 1174-1179.

[61] S. C. Ray, A. Saha and N. R. Jana. Fluorescent carbon nanoparticles: synthesis, characterization, and bioimaging application, *J. Phys. Chem. C,* 2009, **113,** 18546-18551.

[62] X. Wang, K. Qu, B. Xu, J. Rena and X. Qu. Microwave assisted one-step green synthesis of cell-permeable multicolor photoluminescent carbon dots without surface passivation reagents, *J. Mater. Chem.,* 2011, **21**, 2445-2450.

[63] C.-W. Lai, Y.-H. Hsiao, Y.-K. Peng and P.-T. Chou. Facile synthesis of highly emissive carbon dots from pyrolysis of glycerol; gram scale production of carbon dots/mSiO_2 for cell imaging and drug release, *J. Mater. Chem.,* 2012, **22**, 14403-14409.

[64] L. Zhou, Z. Li, Z. Liu, J. Ren and X. Qu. Luminescent carbon dot-gated nanovehicles for pH-triggered intracellular controlled release and imaging, *Langmuir*, 2013, **29**, 6396-6403.

[65] W. Liu, C. Ma, H. Yang, Y. Zhang, M. Yan, S. Ge, J. Yu and X. Song. Electrochemiluminescence immunoassay using a paper electrode incorporating porous silver and modified with mesoporous silica nanoparticles functionalized with blue-luminescent carbon dots, *Microchim. Acta,* 2014, 181, 1415-1422.

[66] Y. Liu, C.-Y. Liu, Z.-Y. Zhang, W.-D. Yang and S.-D. Nie. Plasmon-enhanced photoluminescence of carbon dots–silica hybrid mesoporous spheres, *J. Mater. Chem. C,* 2015, 3, 2881-2885.

[67] F. Wang, Z. Xie, H. Zhang, C. Y. Liu and Y. G. Zhang. Highly luminescent organosilane-functionalized carbon dots, *Adv. Funct. Mater*. 2011, **21**, 1027-1031.

[68] J. Lei, L. Yang, D. Lu, X. Yan, C. Cheng, Y. Liu, L. Wang and J. Zhang. Carbon dot-incorporated pmo nanoparticles as versatile platforms for the design of ratiometric sensors, multichannel traceable drug delivery vehicles, and efficient photocatalysts, *Adv. Opt. Mater.,* 2015, **3**, 57-63.

---

[69] J. Tang, B. Kong, H. Wu, M. Xu, Y. C. Wang, Y. L. Wang, D. Y. Zhao and G. Zheng. Carbon nanodots featuring efficient fret for real-time monitoring of drug delivery and two-photon imaging, *Adv. Mater.* 2013, **25**, 6569-6574.

[70] H. Nie, M. J. Li, Q. S. Li, S. J. Liang, Y. Y. Tan, L. Sheng, W. Shi and S. X.-A. Zhang. Carbon dots with continuously tunable full-color emission and their application in ratiometric pH sensing, *Chem. Mater.* 2014, **26,** 3104-3112.

[71] K. Suzuki, L. Malfatti, D. Carboni, D. Loche, M. F. Casula, A. Moretto, M. Maggini, M. Takahashi and P. Innocenzi. Energy transfer induced by carbon quantum dots in porous zinc oxide nanocomposite films, *J. Phys. Chem. C*, 2015, **119**, 2837-2843.

[72] L. Li, G. Wu, G. Yang, J. Peng, J. Zhao and J.-J. Zhu. Focusing on luminescent graphene quantum dots: current status and future perspectives, *Nanoscale*, 2013, **5**, 4015-4039.

[73] S. Zhu, J. Shao, Y. Song, X. Zhao, J. Du, L. Wang, H. Wang, K. Zhang, J. Zhang and B. Yang. Investigating the surface state of graphene quantum dots, *Nanoscale*, 2015, **7**, 7927-7933.

[74] S. Zhu, S. Tang, J. Zhang and B. Yang. Control the size and surface chemistry of graphene for the rising fluorescent materials, *Chem. Commun.*, 2012, **48**, 4527-4539.

[75] T. Chen, H. Yu, N. Yang, M. D. Wang, C. Ding C. and J. Fu. Graphene quantum dot-capped mesoporous silica nanoparticles through an acid-cleavable acetal bond for intracellular drug delivery and imaging, *J. Mater. Chem. B*, 2014, **2**, 4979-4982.