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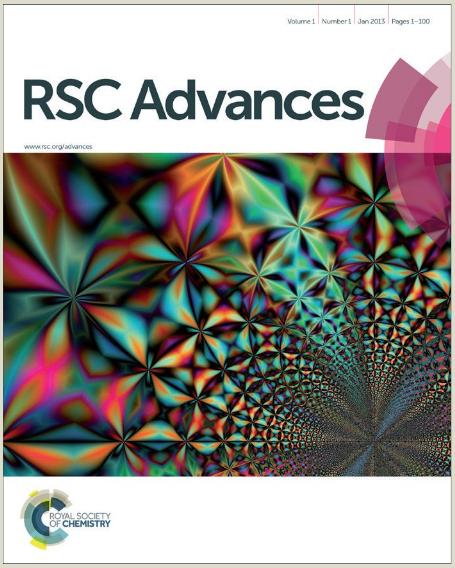

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ARTICLE

The Sonochemical Synthesis of Ga@C-dots Particles

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Abstract

This research article is focused on a one-step sonochemical fabrication of carbon dots (C-dots) doped with Ga atom (Ga@C-dots). The synthesis is carried out by sonicating in molten Ga, polyethylene glycol (PEG-400) as the reaction medium for 30-120 mins. The produced Ga@C-dots is present in the PEG supernatant and has an average diameter of 5±2 nm. Herein, fluorescence is used to probe the emission of Ga@C-dots and to examine if it differs from that of pristine C-dots. The new product was also characterized by fluorimetric, surface charge potential, and XPS (X-ray photoelectron spectroscopy) measurements. It was revealed that the physical properties of the Ga@C-dots are different from pristine C dots. We attribute the fluorescence spectrum to energy transfer from the C-dots to the Ga particles. Ga@C-dots showing the high photosensitization with respect to that of pristine C-dots.

KEYWORDS: Polyethylene glycol, Ga@C-dots, Liquid Gallium, Fluorescence, Sonochemistry

Introduction

Last three decades, carbon nanomaterials like as fullerenes, carbon nanotubes, and graphene have attracted significant attention of the scientific community due to their unique electronic, optical, mechanical, chemical, and thermal properties. Among these carbon-based nanomaterials, C-dots, which are the last to be discovered, are one of the most promising types of fluorescent quantum dots. Due to their superior optical properties, excellent biocompatibility, small size, and low cost.[1-3] The fascinating physical properties of C-dots are responsible for a wide range of potential applications [2, 3], in bioimaging [4, 5], solar cells [6, 7], photocatalysts [8] nanoelectronic devices [9], photo-physical properties [10] and gene delivery [11]. Carbon dots are a new class of functional materials having their unique florescence properties and tuneable wavelength properties.[12-14].

Recently, continuous efforts have been made to fabricate doped carbon nanomaterials, which exhibit good electrochemical performance for fuel cells and Lithium ion batteries, as well as enhancing the conductivity in field effect transistors (FETs)[15]. The C-dots have been prepared by a variety of synthetic methods, using different precursors. The first time C-dots were synthesized was in 2004 by Scrivens et al. [16]. They employed the Arc-synthesis method from single-walled carbon nanotubes. Other reported method are laser ablation [17, 18], pyrolysis [19], combustion [20], a hydrothermal process [21, 22] precipitation method [23], and ultrasonication.[24-25] Nitrogen, phosphorous and boron containing carbon dots have been synthesizes by Barman et al. using the hydrothermal treatment.[10] Xu et al. have prepared the Sulphur doped C-dots via a hydrothermal method, by using sodium citrate and sodium thiosulfate as precursors.[26] Gong et al. have synthesized polyol mediated Gd-doped green fluorescence C-dots by microwave irradiation for a novel bimodal MRI/optical nanoprobe.[27]

The most significant property of the carbon dots is their intense fluorescence which has found applications in bioimaging.[4, 5, 28] Fan et al. synthesized the photoluminescent C dots using polyol. They have found low cytotoxicity, good photostability and demonstrated the presence of carbon-dots in the cancer cells. This made the C-dots appropriate candidates for two photon cellular imaging and labelling.[28] There are few papers describing the sonocochemical synthesis of carbon dots.[24, 25] Li et al. prepared monodispersed water-soluble fluorescent carbon nanoparticles from glucose by acid assisted ultrasonic treatment.[24]

In the current manuscript, we have introduced for the first time a simple sonochemical synthesis of C-dots by a polyol (PEG-400) mediated reaction following Li et al.[24], and extended it to dope the C-dots by Gallium (Ga) or Indium (In) metals. This was accomplished by conducting the sonication of the polyol, PEG-400, over liquid Ga (or In). This enabled us to insert Ga atoms into the C-dots. The chemical/physical properties of this novel Ga@C-dots were studied using a series of characterization techniques including transmission electron microscopy (TEM), Atomic force microscopy, fluorescence spectroscopy, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, inductively coupled plasma (ICP), and Zeta potential measurements. Different fluorescence properties from those of C-dots, were detected for the Ga@C-dots. We propose a mechanism outlining the process that the polyethylene glycol and metallic Ga undergo to form the Ga@C-dots. Furthermore, the synthesized materials Ga@C-dots were applied for photosensitization studies.

Experimental Section

Chemicals: Polyethylene glycol-400 (99.998%), Gallium (Ga, 69.7 g/mole, 99.999%), Nitric acid (HNO_3, 99.8%), and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, 99.99%) were purchased from Sigma-Aldrich and used without any further purification.

Experimental setup and procedure: A granule of gallium (~0.42 g) was inserted into a spherical glass test tube containing 12 mL of polyethylene glycol (PEG-400). The test tube was dipped in a water bath at 50 ^{o}C and the tip of an ultrasonic transducer was dipped to the solution, ca. 1 inch above the molten gallium, as described prevoiusly.[29-31] The ultrasonic transducer (model VCX 750, frequency 20 kHz, volt 230V AC) was obtained from Sonics and Materials Inc., USA. When the gallium was molten, ultrasonic irradiation was applied for 4 different time periods 30 min., 60 min., 120 and 180 min. causing dispersion of the gallium and the formation of a grey suspension of particles. The sonication time and amplitude played an important role in the formation of fluorescing C-dots. It was found that a certain sonication irradiation time (120 min) and amplitude (50%) were required to produce fluorescing C-dots and Ga@C-dots. Longer sonication (180 min) led to particles with smaller fluorescence intensity. This is probably due to the formation of large C-dot particles (>10nm). Shorter sonication time (3 min. and 30 min.) did not show any fluorescence. Moreover, we did not observe formation of C-dots in 3 min. and 30 min sonication time. In all the experiments, at the end of the sonication the solid particles were separated by centrifugation at 9000 rpm for 10 min. The C-dots did not precipitate even after 10 minutes centrifugation at 12000 rpm. The supernatant was collected and the C-dots were found in the supernatant. The color of C-dots produced from PEG and Ga was light pale yellow. For the determination of particles size by HRTEM, we measured more than 200 particles. The samples were prepared for AFM by applying a suspension of Ga@C-dots PEG on Silicon wafer by spin coating at 6000 rpm for 1 min. The Si-wafer containing the Ga@C-dots was dried in vacuum chamber at room temperature. Photosensitization properties of Ga@C-dots have been studied using the Electron Paramagnetic Resonance (EPR)-spin trapping technique coupled with the spin traps 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, 0.02 M) (Sigma, St. Louis, MO.). The C-dot and Ga@C-dots/DMPO solution was placed in tube, then placed in the EPR cavity and the spectra were recorded, on a Bruker EPR 100d X-band spectrometer. Illumination was done with UV lamp (360nm).

Analytic equipment: The fluorescence of the Ga@C-dots was measured by (Varian Cary Eclipse Fluorescence spectrophotometer). The High resolution transmission electron microscopy (HRTEM) of Ga@C-dots was carried out on a JEOL 2100, with an accelerating voltage of 200 kV and elemental analysis was done by Energy Dispersive X-ray Spectroscopy (EDS). The analysed samples were prepared by evaporating a drop of PEG product on a carbon coated copper TEM grid. The AFM measurement was performed by Bio FastScan Scanning Probe Microscope (Bruker corp., USA). The microscope was covered with an acoustic hood to minimize vibrational noise. The FastScan-C cantilevers (Bruker) with spring constants 18 N/m were used. Topographic height images were recorded at 512 x 512 pixels at 1.400 kHz. X-ray diffraction (XRD) measurements of Ga@C-dots were performed with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation operating at 40 kV/30 mA with a 0.0019 step size/ 1 s step. Raman spectra of Ga@C-dots were recorded on Renishaw inVia Raman microscope equipped with RL785 and RL830 Class 3B wavelength-stabilized diode lasers and Leica DM2500 M (Leica Microsystems) materials analysis microscope. A sample was prepared by locating a PEG suspension containing C-dots on a glass slide and dried on a hot plate (150 ^{0}C). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis was done with the Horiba instrument model Ultima 2. A spectrum could be obtained by focusing the instrument lens on the sample and irradiating it with 514 nm laser. X-ray photoelectron spectroscopy (XPS) analyses of samples were recorded using an ESCALAB 250 spectrometer with a monochromatic X-ray source with Al Ka excitation (1486.6 eV). Binding energy calibration was based on C1s at 285 eV. Zeta potential measurements of the particles was performed on ZetaSizer Nano-ZS (Malvern Instruments Ltd., Worcestershire, UK). The EPR measurement conditions were as follow; Frequency, 9.74 GHz; microwave power, 20 mW; scan width, 65 G; resolution, 1024; receiver gain, 2 × 105; conversion time, 82 ms; time constant, 655 ms; sweep time, 84 s; scans, 2; modulation frequency, 100 kHz. After acquisition, the spectrum was processed using the Bruker WIN-EPR software version 2.11 for baseline correction.

The synthesis of In@C-dots was similar except that the temperature was 190 ^{0} C instead of 50 ^{0} C as for the Ga@C-dots. Since similar results were obtained for In@C-dots they will not be reported herein. In a few cases results related to undoped C-dots will be presented in the Results and Discussion section. C-dots are not the focus of this manuscript; they are showed only for comparison.

Results and Discussions

High resolution transmission electron microscopy (HRTEM) images reveal that the Ga@C-dots taken from the supernatant solution are mono-dispersed and spherical in shape. HRTEM images of two PEG samples sonicated without Gallium and with Gallium are presented in **Fig. 1a** and **Fig. 1b**, respectively, together with diagrams of the size distribution. It is apparent that the C dots which were prepared with Ga are in the size range of 3 to 8 nm with an average size of ~5 nm, while the average size of C-dots without Ga is ~6 nm, i.e. they have a similar size. A TEM image of the Ga@C-dots is shown in **Fig. 1c** with selected area electron diffraction (SAED) pattern.

SAED results of C-dots doped with Ga revealed a ring pattern and the rings correspond to the {01.3} {10.6} {11.0} planes of a hexagonal carbon structure (PDF 26-1083). The high resolution image of individual carbon particle is presented in F**igure 1d.** According to the Fourier micrograph, the diffractions are corresponded to d spacing of 0.2 and 0.18 nm, of a hexagonal carbon (PDF 26-1023) with a cell parameter of: a=2.522 and c=20.59. This spacing is consistent with earlier reports. [32, 33]. It is worth emphasizing that a very careful EDS check over the whole grid of a drop taken from the supernatant didn't reveal any particle that is solely composed of Ga. In the solid phase on the other hand, large Ga particles were detected. It leads to the conclusion that the Ga is doped in the C-dot. Here we wish to emphasize that the presence of Ga induces the crystallinity of the C dots as well as formation of more C dots with uniform size.

XRD has been recorded for the supernatant sample of Ga@C-dots. The supernatant was evaporated at 150 ºC for 3 days on a hot plate. After the drying the weight of the precipitate was measured and it has given a dried yield of 1.4 weight % of the Ga@C-dots of PEG-400. This should be considered as an upper limit for the amount of C-dots in the supernatant, because it might be that the PEG was not completely removed. The same dried powder was used for the XRD analysis. A single broad peak ($2\theta=24.3$) is measured which is the signature of Ga@C-dots as shown in **Fig. 2.**

There are several reports on XRD of C dots [34-36], the current pattern is very similar to the previously reported patterns. The diffraction peak is assigned to the reflection centered at $d_{(002)} = 0.34$ nm, which is very close to the graphite 002 lattice spacing (F**ig. 2**). The second peak detected at $2\theta = 56^{0}$ may be due to the solid product Ga@C-dots. This is because this diffraction peak does not appear in any of the previous C-dots XRD measurments, or in our XRD of the pristine C-dots.

ICP analysis: To determine the presence of Ga ion/atom in Ga@C-dots, ICP analysis was performed. Two samples have been prepared for the ICP analysis. The first was obtained by dissolving the Ga@C-dots in 1.0M HNO_3 in a small beaker (100 mL), which was heated on a hot plate (60 ^oC) for 2 hours. The HNO_3 was evaporated and DD water was added to the beaker. This process was repeated three times to reduce the HNO_3 acid concentration. The final solution was analysed by ICP and Ga ion concentration was found to be 9.52 ppm. The same Ga@C-dot was also analysed by ICP without any acid treatment and the concentration of Ga was found to be 8.65 ppm. The low level of Ga is the reason that it was not detected in the EDS measurements. Finally the morphology of Ga@C-dots was confirmed by AFM. AFM is a very high resolution type of scanning probe microscope that has resolution of fractions of a nanometer. **Fig. 3** illustrates a topography scan of an area of 500 × 500 nm of the Ga-@C-dots on Si-wafer. As we can see, the Ga@C-dots are spherical in nature and the measured particles sizes were ~5-8 nm.

Fluorescence analysis of Ga@C-dots and C-dots: The sonochemically prepared C dots have shown the well-known [37] broad absorption (300–390 nm) as well as a broad emission in the violet blue spectral range (370–520 nm, Fig. 3a) when excited at 345 nm. The Ga@C-dots suspension exhibited a pale yellow transparent colour in day light and remained stable for several months. When the suspension was excited by 345 nm photons, it emitted a violet blue signal, which is shown in **Fig. 4a**, peaking at 440-460 nm, as expected for C-Dots. Furthermore, the fluorescence spectra and the intensity at different excitation wavelengths is shown in **Fig. 4b**. For the Ga@C-dots emission a different pattern was discovered. While in the excitation range of 330-380 nm the emission spectrum was similar to that of the pristine C-dots, very sharp fluorescence emission at 416 nm was detected upon excitation at 390 nm. The FWHM of this peak is 8.9 nm. We attribute the 416 nm emission to the transition from the first excited state of Ga to its ground state. The first excited state of Ga is populated by energy transfer in the 5 nm Ga@C-dots particle, and not between C-dots and Ga particles in the supernatant, since the concentration of the nanoparticles is small indicating large distances between particles. The energy is transferred from the C-dots to the Ga atoms inside the same particle. When the pristine C-Dots were excited by various wavelengths from 330 to 490 nm, the intensity of florescence increased upto the 390 nm and then decreased (**Fig. 4c**). The full width at half maximum (FWHM) of the fluorescence band varied between 96 and 119 nm. In addition, we have also measured the fluorescence activity of 1 hour sonicated PEG, which are also giving a nice florescence peak (**Fig. 4c**), but when excited at 390 nm, we did not observe any sharp band for Ga@C-dots prepared in PEG. The pristine C dots suspension was exhibited a pale yellow transparent colour in day light and remained stable for several weeks. When the suspension was excited by 390 nm photons, it emits a violet blue signal, peaking at 440 nm, as expected for C-Dots. No fluorescence was observed for PEG solution without sonication.

Raman analysis: In **Fig. 5** shows a Raman spectrum of Ga@C-dots and C-dots. For C dots, two prominent peaks appear at 1380, 1549 cm^{-1}, corresponding to the D, G peaks respectively. Similar peaks have been reported in earlier C-dots reports [34, 35]. One additional peak is appearing at 1196 cm^{-1} is due to PEG molecules present on the surface of Ga@C dot. The Ga@C-dots was freely dispersed in PEG-400 transparent and a brown yellow solution is formed. The Ga@C-dots can also freely disperse in water, and the formed aqueous solution is transparent.

The chemical composition of Ga@C-dots was further analysed by XPS. The characteristic peaks corresponding to C 1s (284.929 eV), O 1s (532.345 eV), Ga 2p (1118.621 eV), Ga 3p (106.394 and 109.473 eV), and Ga 3d (20.290 eV) were observed in the XPS scan spectrum (**Fig. 6a**), confirming that Ga@C-dots are composed of C, O, and Ga. The high-resolution XPS C 1s spectrum (**Fig. 6b**) could be deonvoluted to three Gaussian peaks. Specifically, the peak at 284.929 eV is attributed to C atoms in the carbon dots or graphitic structure, implying that the as-prepared Ga@C-dots possess predominantly sp^2 carbon. The other two peaks were assigned to the carbon atoms in C–O (286.262 eV), and COO (289.336 eV), verifying the presence of hydroxyl, carbonyl, and carboxylic acid groups on the surface of Ga@C-dots.[38-39] The O 1s peak at 532.345 eV shown in **Fig. 6c** is assigned with oxygen either in the of Ga_2O_3, or C-O and C–OH/C–O–C. Meanwhile, the XPS Ga 2p spectrum (**Fig. 6d**) exhibited Ga 2p3/2 line at 1118.621 eV which is attributed to Ga_2O_3. The Ga 3p peaks at 106.394 and 109.473 eV shown in **Fig. 6e** are assigned to Ga. The Ga 3d peak at 20.290 eV shown in **Fig. 6f** is also an evidence for the oxidation of Ga **to** $\mathbf{Ga^{+3}}$.[40] This verifies that the synthesized C-dots are Ga doped or surrounded by Ga ion. The oxidation of surface Ga atoms is unavoidable in a 5 nm size particle.

Surface charge analysis: A more extensive measurement of the surface charge of C dots was analysed by Zeta potential measurement of C-dots and Ga@C-dots suspended in PEG. 1 ml of water was added to 1 ml of these two suspensions to enable the Zeta potential measurements. **Fig. 7a** and **7b** presents the Zeta potential plot of C-dots and Ga@C-dots, respectively. The graph displays three consecutive measurements with excellent repeatability. The average values of the zeta potential of C-dots were -19.4 mV and these results are in agreement with a previous experiment reporting a value of -20 mV [41]. On the other hand, the Zeta potential of Ga@C-dots is +21 mV. The positive Zeta potential is also an indication that metallic Ga or Ga^{+3} ions are doped in or are on the surface of C dots.

The quantum yield of the Ga@C-dots and C-dots were estimated by comparing the integrated fluorescence intensities (excited at 360 nm) and the absorbance values (at 360 nm) of the C-dots with that of the quinine sulphate in 0.2 M H_2SO_4 (quantum yield = 54%). Specifically, the absorbance values of C-dots and quinine sulphate were measured at 360 nm. The quantum yield was measured for the Ga@C-dots was ~1% and C-dots were ~2%.

Mechanism of formation of Ga@C-dots: The sonochemical degradation and carbonization of PEG is a complex chemical process and it is difficult to determine the exact chemical reaction. Previous research has been illustrated by Dong et al. [34] showed that heating pure ethylene glycol, diethylene glycol, polyethylene glycol (PEG400) at 180 to 230 °C (T/PEG), instantaneously resulted in colloidal stable C-dots suspensions. [34] The carbonization may arise from cross-linking induced by intermolecular dehydration of PEG-400 due the extreme condition of pressure (ca. 500 atm.) and temperatures (ca. 5000 K) which develop for extremely short times during the cavitation process.[42] Even if the vapor pressure of PEG is low and only a small amount of PEG vapors are found inside the collapsing bubble, the temperature in the 200 nm ring around the collapsing bubble is still very high, estimated at around 2000K, and may still carbonize the PEG molecules. The insertion of the Ga into the C-dots is due to the dispersion of the molten Ga by the ultrasonic waves moving it to the surrounding of the collapsing bubble.

To prove the Ga doping in the carbon dots in Ga@C-dots, we have analysed the EDS, XRD, XPS, ICP and Zeta potential measurement. The EDS is not showing the presence of Ga due to low concentration (~ 12 ppm) of Ga doping in Ga@C-dots. The XRD plot of Ga@C-dots is not showing any Ga, Ga_2O_3 and GaO(OH) peaks due to the low concentration of Ga. But high resolution XPS and ICP analysis have proved the presence of Ga, which has been already discussed in consecutive section. Earlier there are several reports on doping of carbon dots and they have proved the doping by XPS analysis.[10, 25-27] Moreover Zeta potential of Ga@C-dots are positive, while that of the C-dots are negative which is also supporting the assumption of the Ga doping the C-dots. To further prove the Ga doping in C-dots more measurements are needed.

Photosensitization study of Ga@C-dots:

We have probed the production of Reactive oxygen species (ROS) by the photoexcitation of C-dots and Ga@C-dots. The presence of the defects and free radicals at the surface of C-dots and Ga@C-dots indicates their potential for singlet oxygen generation. Christensen et al., has reported on the formation of singlet oxygen of carbon dots. They have initiated the formation of singlet oxygen either chemically or by radiation with a blue light source emitting between 390-470 nm. Two reagents, dihydrorhodamine 123 (Dhr123) and singlet oxygen sensor green (SOSG), were used as radical probes. [43] Here, we employed a spin trap-based EPR spectroscopy as a sensitive and selective method for photosensitization. The intensity of the EPR signal produced by UV-light (360 nm)-irradiated C-dots and Ga@C-dots with spin traps 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, 0.02 M) was larger than that of the control samples of the non-irradiated samples (Fig.8A, Fig.8B). The increase in the signal intensity of the Ga@C-dot nanoparticles as compared to the control signal (≈ 6 fold), was significantly larger compared to that of the C-dot (≈ 3 fold). This result indicates that Ga@C-dots can generate more ROS in the form of singlet oxygen as compared to C-dots. Since singlet oxygen is an important agent in photodynamic therapy [44], the possible application of Ga@C-dots in this field is straight forward. Fig.8A, Fig.8B showed EPR signal at g=2.0033, which may demonstrates a singly occupied orbital in ground state C-dots. The Ga@C-dots and C-dots have six hyperfine resonances arising from singlet oxygen species. The result indicated that Ga@C-dots can produce more singlet oxygen with respect to C-dots. Sonochemically synthesized Ga@C-dots could produce a large amount of ROS, when photostimulated.

Conclusions

We have developed a novel, one-step method for the preparation of fluorescing Ga@C-dots using a sonochemical process. The fluorescence of the Ga@C-dots was found to be different from C-dots stabilized in PEG prepared under similar sonochemical conditions. Similar fluorescing results were obtained for In@C-dots indicating that the doping of C-dots is a general phenomenon. The photosensitization result indicated that Ga@C-dots can produce more singlet oxygen with respect to C-dots. Sonochemically synthesized Ga@C-dots could be used for biomedical applications.

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Figures

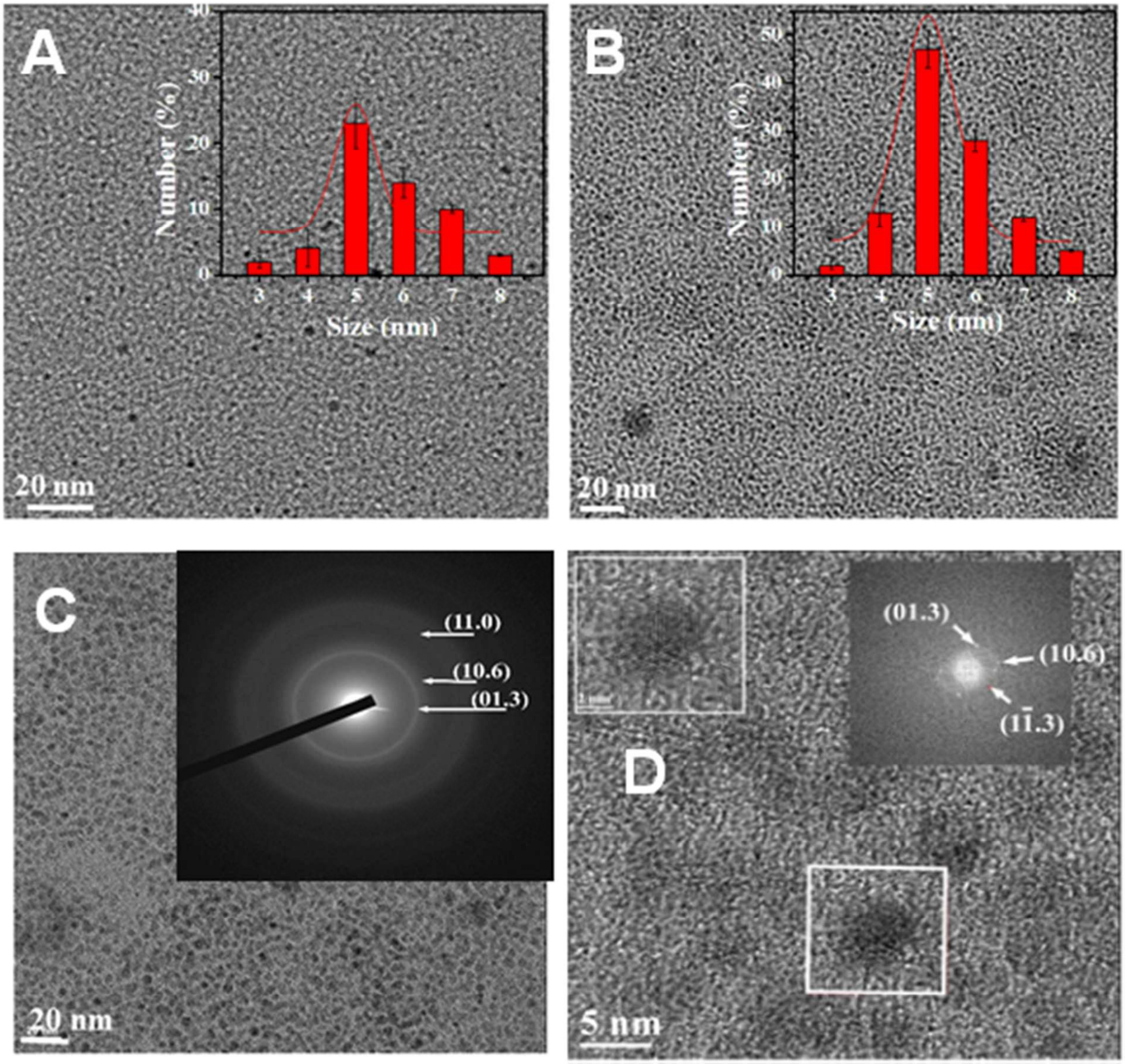

Fig. 1. TEM images of C dots (a) PEG sonicated without Gallium and (b) with Gallium are presented with size distribution plot. (c) HRTEM image of Ga@C-dots synthesized by PEG in presence of molten Ga (inset SAED marked by plane), (d) HRTEM images of Ga@C-dots (inset lattice fringes of Ga@C dots).

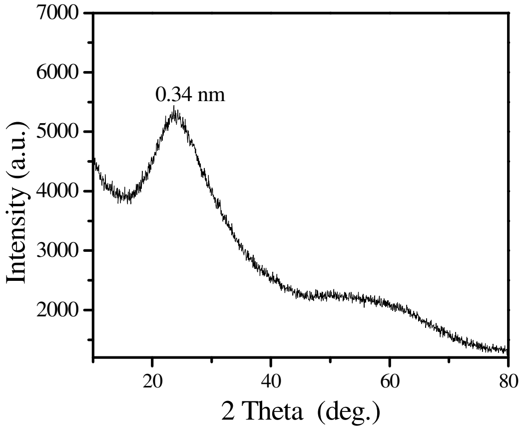

Fig. 2. XRD of Ga@C-dots which have been obtained after drying the liquid sample.

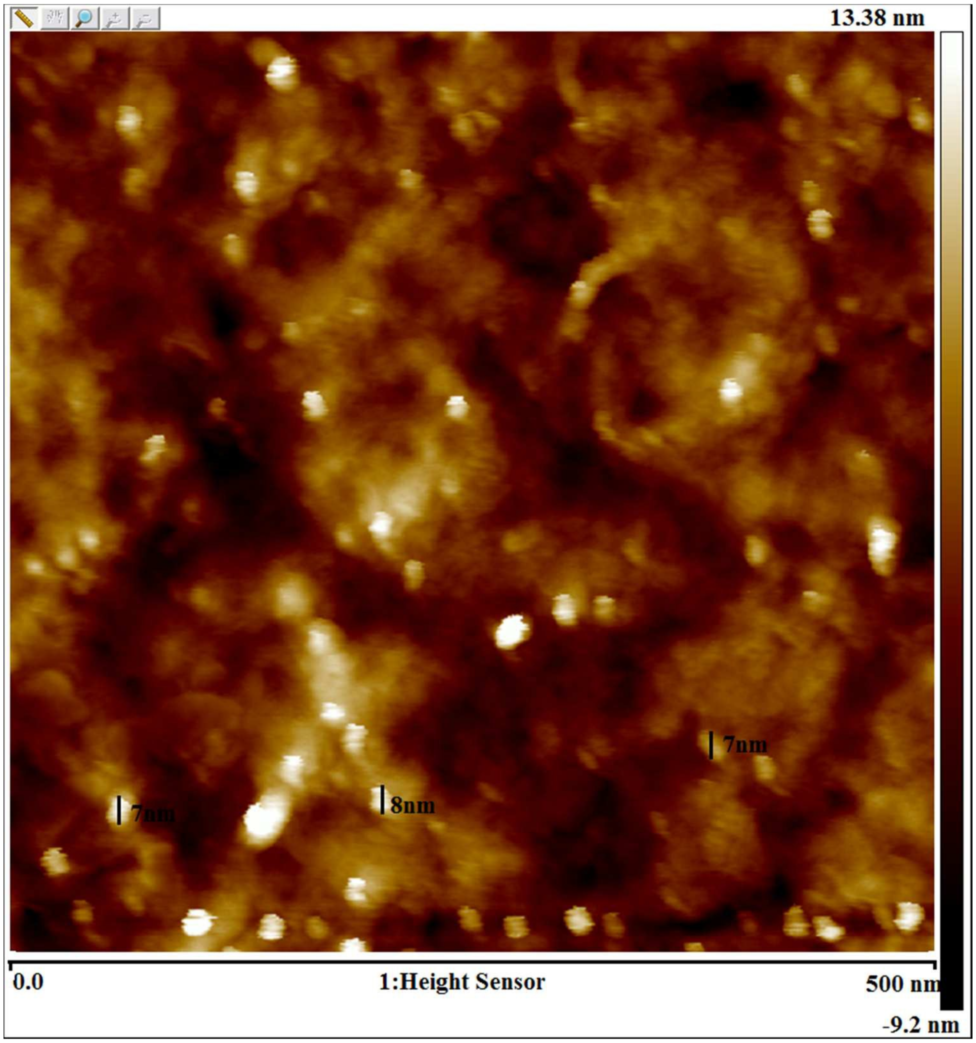

Fig. 3. The AFM images of Ga@C-dots.

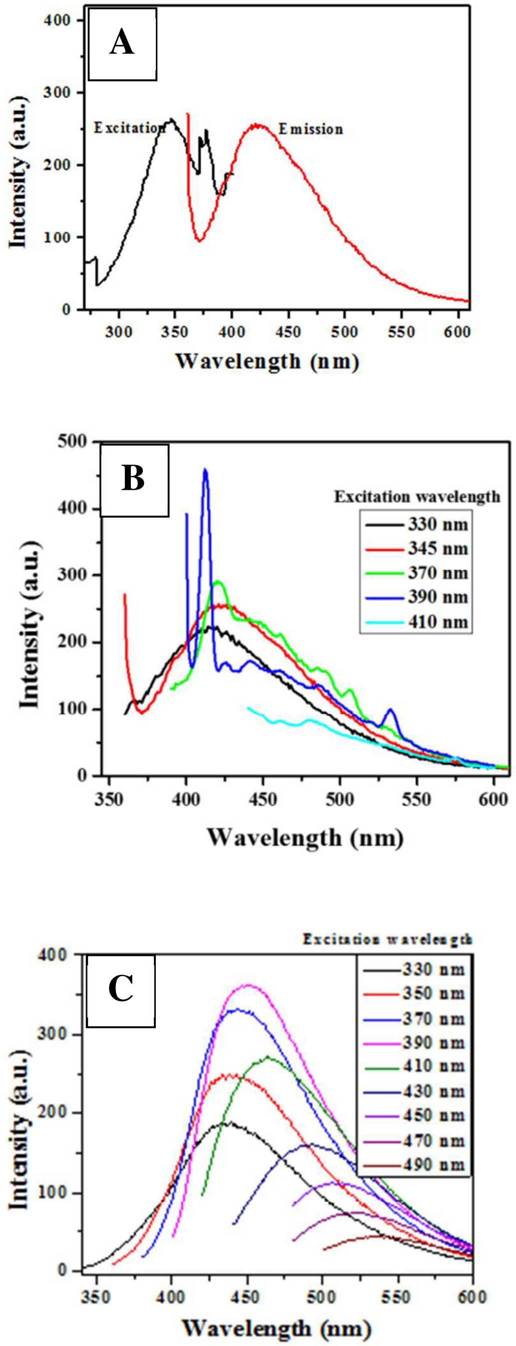

Fig. 4. Fluorescence at different excitation wavelength (a) excitation emission fluorescence spectra of Ga@C-dots (b) emission of Ga@C-dots synthesized by sonication from PEG in presence of molten Ga, (c) emission of Pristine C dots (sonicated PEG for one hour).

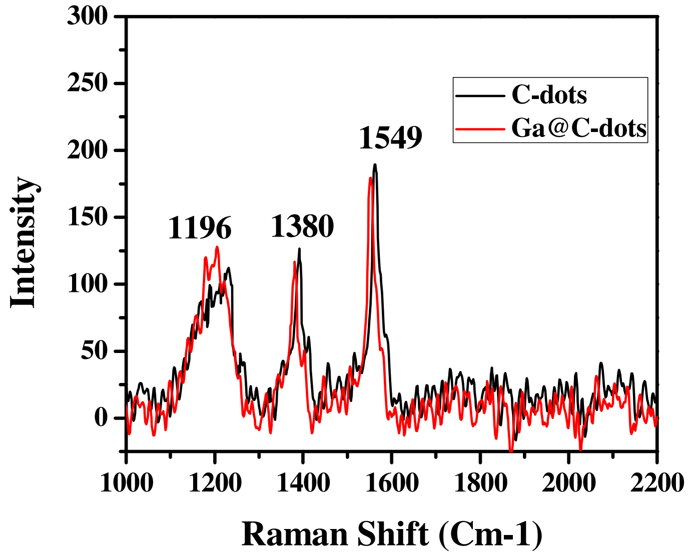

Fig. 5. Raman spectra of C-dots and Ga@C dots which have been synthesized in PEG-400.

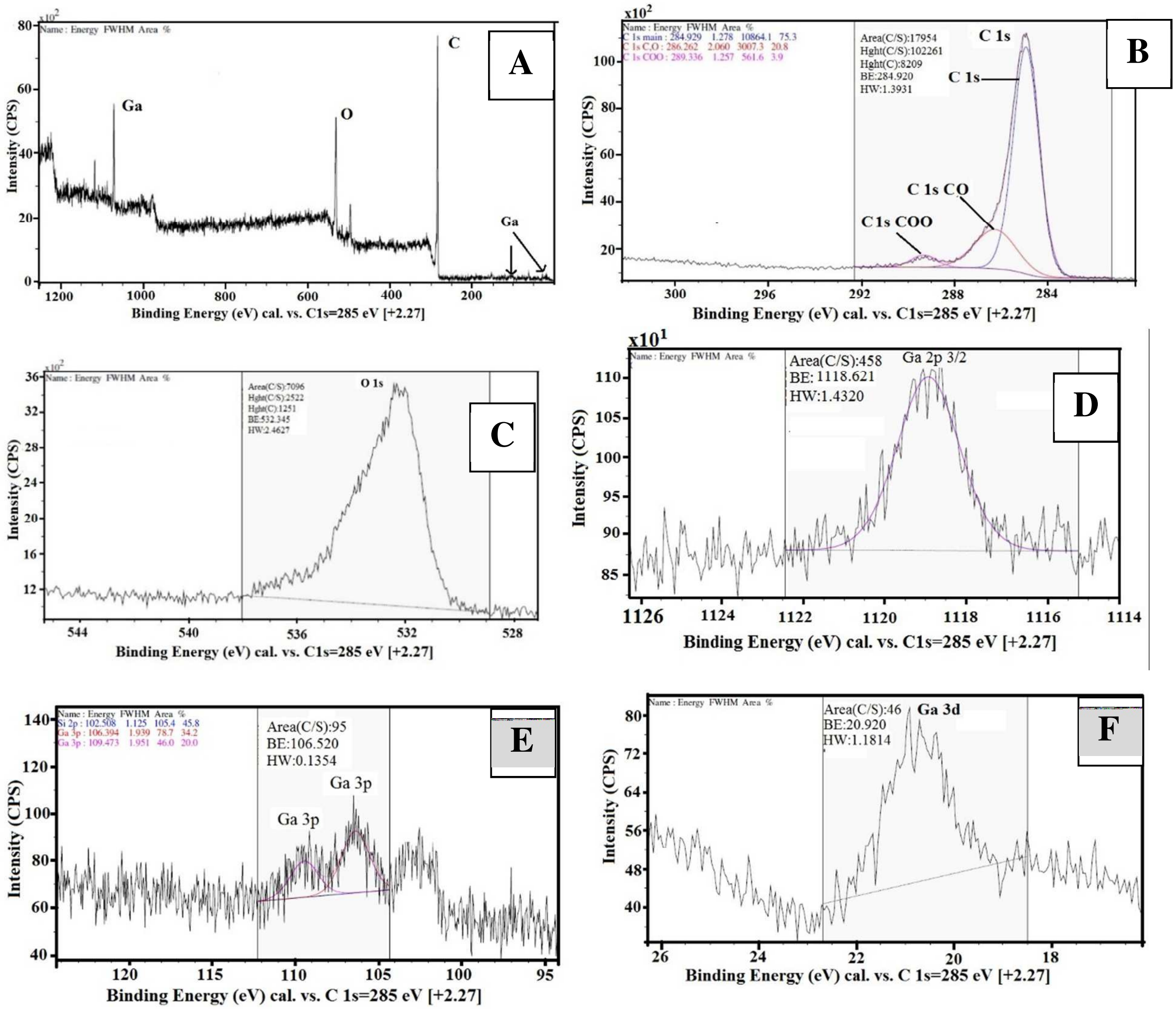

Fig. 6. (A) Full XPS spectrum, (B) XPS spectrum of C 1s, (C) XPS spectrum of O 1s, (D) XPS spectrum of Ga 2p (E) XPS spectrum of Ga 3p and (F) XPS spectrum of Ga 3d of Ga@C-dots.

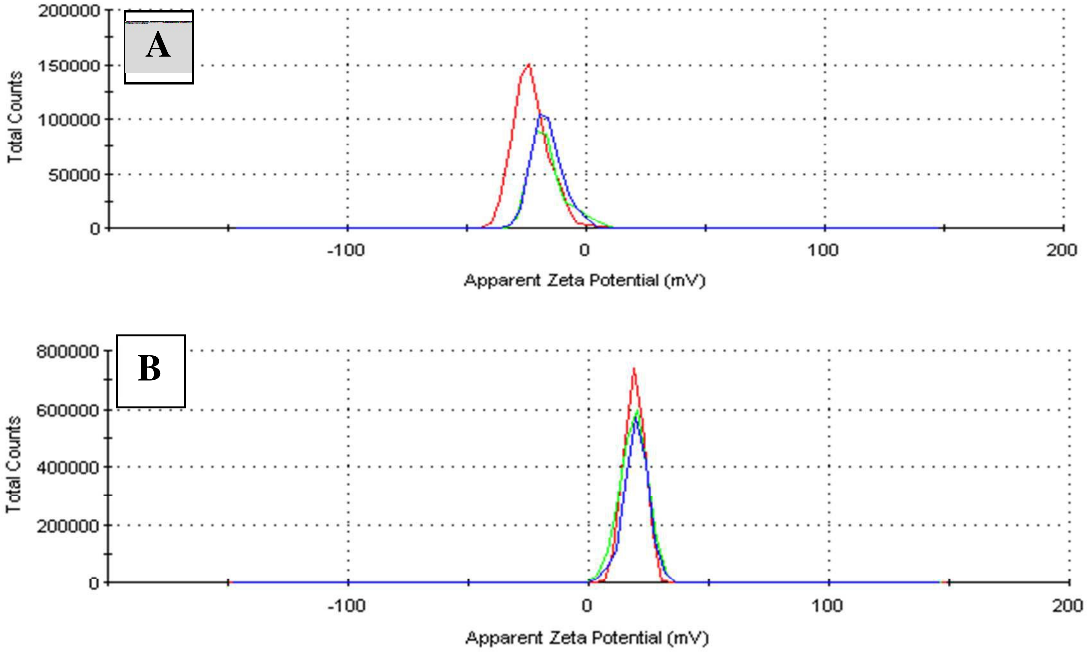

Fig. 7. Zeta potential plot obtained in water suspensions of the (a) C-dots suspended in PEG, (b) Ga@C-dots suspended in PEG. Triplicate measurements were carried out.

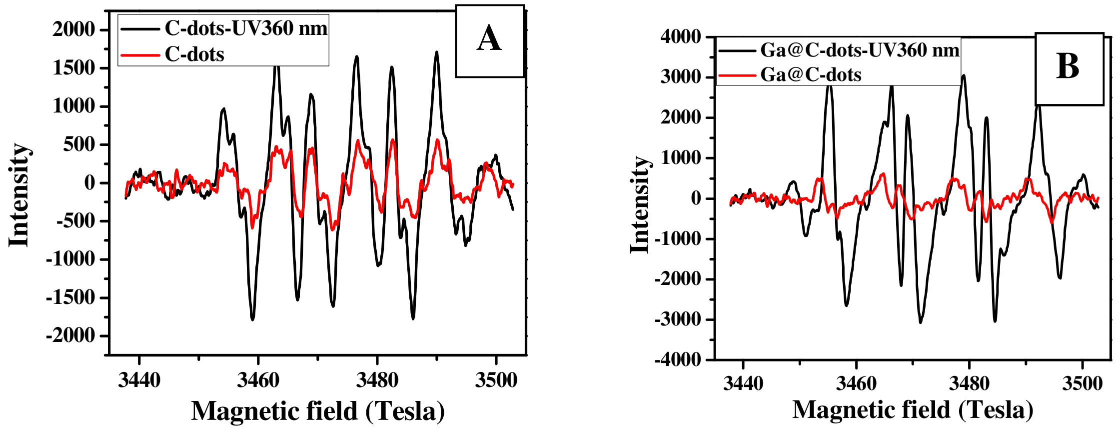

Fig. 8. (a) EPR of C-dots, and (b) EPR of Ga@C-dots analysis of phtosensetization properties in UV-light-irradiated (360 nm, 1W, 30 min).

Table of Contents Graphic

The Sonochemical Synthesis of Ga@C-dots Particles.

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