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Journal Name

ARTICLE

Photoluminescence, chemiluminescence and anodic electrochemiluminescence of hydrazide-modified graphene quantum dots

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Single-layer graphene quantum dots (SGQDs) were refluxed with hydrazine (N_2H_4) to prepare hydrazide-modified SGQDs (HM-SGQDs). Compared with SGQDs, partial oxygen-containing groups have been removed from HM-SGQDs. At the same time, a lot of hydrazide groups have been introduced into HM-SGQDs. The introduced hydrazide groups provide HM-SGQDs a new kind of surface state, and give HM-SGQDs unique photoluminescent (PL) properties such as blue-shifted PL emission and relative high PL quantum yield. What is more important, the hydrazide -modification made HM-SGQDs have abundant luminol-like units. Accordingly, HM-SGQDs exhibit unique and excellent chemiluminescence (CL) and anodic electrochemiluminescence (ECL). The hydrazide groups of HM-SGQDs can be chemically oxidized by the dissolved oxygen (O_2) in alkaline solutions, producing a strong CL signal. The CL intensity is mainly dependent on the pH value and the concentration of O_2, implying the potential applications of HM-SGQDs in pH and O_2 sensors. The hydrazide groups of HM-SGQDs can also be electrochemically oxidized in alkaline solutions, producing a strong anodic ECL signal. The ECL intensity can be enhanced sensitively by hydrogen peroxide (H_2O_2). The enhanced ECL intensity is proportional to the concentration of H_2O_2 in a wide range of 3 μM to 500 μM. The detection limit of H_2O_2 was calculated to be about 0.7 μM. The results suggest the great potential applications of HM-SGQDs in the sensors of H_2O_2 and bio-molecules that are able to produce H_2O_2 in the presence of enzymes.

1 Introduction

Luminescent carbon based dots (CDs) have attracted increasing research interest since they were first isolated from single-walled carbon nanotubes in 2004.[1-12] CDs mainly include carbon nanoparticles smaller than 10 nm in size (so-called carbon quantum dots, CQDs) and graphene nanosheets of less than 100 nm in width (so-called graphene quantum dots, GQDs).[2,5] Like traditional semiconductor based quantum dots (QDs), CDs exhibit unique optical and electronic properties due to their quantum confinement and edge effects. Furthermore, compared with QDs, CDs show many advantages such as robust chemical inertness, low toxicity, easy functionalization and low cost.[13] Accordingly, CDs were proposed to be promising candidates to replace QDs.

To date, a series of easy and efficient methods have been developed to prepare various kinds of CDs. Most of the obtained CDs exhibited fascinating photoluminescence (PL) properties.[13-15] Furthermore, many CDs have been applied in many fields based on their PL properties, such as bio-imaging,[13] cell-imaging and sensors.[2,8,17,18] Apparently, PL is one of the most important properties of CDs. Much attention has been focused on the PL CDs, in order to prepare CDs with better PL properties and study the PL mechanism of CDs. Accordingly, many avenues have been proved to be able to enhance the PL of CDs, mainly including surface-passivation with polymers,[2,13] doping with heteroatoms or ZnS,[4,23] and reducing with NaBH$_4$.[21] Furthermore, although the exact PL mechanism of CDs is still argumentative, more and more evidences implied that the PL properties of CDs are related to the surface states of CDs.[4,21-23]

Besides the excellent PL properties, some CDs were found to have chemiluminescence (CL) activities.[24,25] For example, the CQDs prepared by microwave heating glycerine and polyethylene glycol can produce CL in the presence of peroxynitrous acid, based on which a CL sensor was developed for the nitride detection.[24] Actually, CL is a powerful analytical technique, which has high sensitivity, low background interference, and simple instrumentation.[26,27] The CL properties of CDs would promote greatly the application of CDs in analytical detections. However, little attention has been paid to the CL of CDs.

Electrochemiluminescence (ECL) is another important property of CDs. As a powerful analytical technique, ECL combines advantages of CL analysis and electrochemical analysis, and accordingly shows many advantages over FL technique, such as low cost, wide response range, and high sensitivity.[28,29] Since the ECL behavior of Si nanoparticles was first reported in 2002,[30] many studies have been focused on the ECL of various quantum dots,[31,32] including CDs (both CQDs and GQDs).[23,33-36] CDs were found to have excellent ECL activities, and would be promising candidates to replace traditional ECL luminophores, such as ruthenium complexes, luminol and even QDs.[37] However, most researchers focused their attention mainly on the cathodic ECL behaviours.[23,33-36] In contrast, attention has been seldom paid to the anodic ECL properties of CDs, which is unfavourable for further applications of CDs in sensing.

In this work, single-layer GQDs (SGQDs) were refluxed with hydrazine (N_2H_4) to prepare hydrazide-modified single-layer GQDs (HM-SGQDs). Due to the abundant introduced hydrazide groups, the obtained HM-SGQDs show many unique optical properties. First of all, the PL spectra of HM-SGQDs blue-shift obviously compared with those of SGQDs. At the same time, the PL quantum yield of HM-SGQDs excited at 400 nm is much higher than that of SGQDs. Secondly, HM-SGQDs show excellent CL activity in alkaline solutions in the presence dissolved oxygen (O_2). The CL intensity of HM-SGQDs is sensitive to the pH value of solution and the concentration of O_2, Thirdly, HM-SGQDs produce strong anodic ECL signal in alkaline solutions. And the anodic ECL signal can be enhanced greatly by hydrogen peroxide (H_2O_2) due to the co-reaction. To the best of our knowledge, this was the first report on CL of CDs in the absence of strong oxidant. Also, this was the first report on the anodic ECL behavior of CDs. Therefore, it would be great significant for promoting the applications of CDs.

2 Experimental

2.1 Materials

Vulcan XC-72 carbon black was purchased from Cabot Corporation (USA). $K_2S_2O_8$, $NaBH_4$ were purchased from Sigma-Aldrich. N_2H_4 and H_2O_2 were obtained from Fuchen Chemical Reagent Co. (Tianjin, China). All other reagents were of analytical reagent grade and used without further purification. 0.1 M phosphate buffer solutions (PBS) of different pH value were used as the electrolyte. Doubly distilled water was used throughout the work.

2.2 Synthesis of SGQDs

SGQDs were prepared according the method reported in a previous work.[38] In brief, 1g XC-72 carbon black was refluxed with 250 mL 8 M HNO_3 for 24 h. Then the suspension was cooled to room-temperature and centrifuged at 2770 g for 10 min. The supernatant was collected and dried at 150 °C on a hotplate. Finally, about 300 mg orange powder (SGQDs) was obtained.

2.3 Synthesis of HM-SGQDs

SGQDs obtained above were refluxed with N_2H_4 to prepare HM-SGQDs. In a typical experiment, 100 mL 2.5 mg/mL SGQD solution was heated with an oil bath to 65 °C. Subsequently, 2 mL N_2H_4 was added into the solution. The mixture was refluxed at 65 °C for 24 h. Then stopped heating and cooled the solution naturally to room temperature. Subsequently, the solution was dried in vacuum to remove water and the redundant N_2H_4. Finally, the black solid was collected for the following study.

2.4 Synthesis of R-SGQDs

SGQDs were reduced by $NaBH_4$.[21] In a typical experiment, 20 mL 2.5 mg/mL single-layer GQD solution was heated to 80 °C. And then 10 mg $NaBH_4$ was added into the solution. The mixture was refluxed for 12 h. Stopped heating and cooled the solution to room temperature. Thus then, reduced GQDs (R-SGQDs) were obtained.

2.5 Instrumentation

Atomic force microscopy (AFM) images were obtained by tapping-mode on a Nanoscope IIIa Digital Instruments with NSC15 tips (silicon cantilever, MikroMasch). Electrochemical (EC) and ECL measurements were carried out on an EC and ECL detection system (MPI-E, Remex Electronic Instrument Lt. Co., Xi'an, China) equipped with a three-electrode system, i.e. a GC disc working electrode (0.0707 cm²) for the anodic ECL measurement and a Pt wire (with an area of 0.31 cm²) working electrode for the cathodic ECL measurement, a Pt wire counter electrode, and a Ag/AgCl (3 M KCl) reference electrode. ECL spectrum measurements were carried on a Fluorescence Steady State and TCSPC Fluorescence Lifetime Spectro-Fluorimeter (FLS920, Edinburgh Instruments, UK) combined with an electrochemical workstation (CHI660C, CH Instruments, USA). The infrared (IR) spectrum of dried CQDs was obtained on a FT-IR spectrophotometer (Thermo Nicolet 360). UV–Vis absorption was characterized by a UV/Vis/NIR spectrophotometer (Lambda 750, Perkin Elmer Inc., Waltham, MA, USA). All FL spectra and the CL spectrum of HM-SGQDs were measured by a FL spectrophotometer (F 4600, Hitachi, Japan). X-ray photoelectron spectroscopy spectra of carbon QDs was measured by a ESCAlab 250 XPS system having an Al K source for determining the composition and chemical bonding configurations.

3 Results and discussion

3.1 Characterization of HM-SGQDs

AFM images (Fig. S1) indicate the thickness of the SGQDs used for the preparation of HM-SGQDs ranges from 0.3 to 0.9 nm with an average value of ~0.5 nm. The obtained HM-SGQDs have a similar thickness distribution to that of SGQDs, suggesting that the refluxing treatment with N_2H_4 has no obvious effect on the morphology of SGQDs. However, the surface functional groups are changed greatly, which is confirmed by the experimental results of both FTIR and XPS. Upon treatment with N_2H_4, the relative IR absorption intensities of C–O and C=O groups to that of C=C group are decreased obviously (Fig. S2). Furthermore, two new absorption bands attributed to N–H and C–N groups can be observed at 3310 and 1120 cm⁻¹, respectively. Meanwhile, a distinct decrease of oxygen content and an obvious increase of nitrogen content can be observed in the XPS determination (Fig. 1a). The high resolution spectra of C_{1s} (Fig. 1b, c) indicate that the binding energy peak of C=O decreases obviously. Furthermore, a new binding energy peak of C-N appears. Based on the experimental results discussed above, it can be inferred that refluxing with N_2H_4 can not only remove partial oxygen-containing groups from SGQDs (so-called "reduction") but also introduce some N-containing groups into SGQDs. The introduced N-containing groups are most like hydrazide groups produced by the reaction between N_2H_4 and the carboxyl groups of SGQDs.[39] In other words, HM-SGQDs should be reduced and hydrazide-modified SGQDs. It should be mentioned that hydrazine can reduce greatly the oxygen-containing functional groups on graphene materials, and reducing their aqueous dispersion. However, the characterization results mentioned above indicate that hydrazine is not able to remove all oxygen-containing functional groups from SGQDs. Therefore, the small-size HM-SGQDs can be well dispersed in the aqueous solution due to the residual oxygen-containing functional groups, such as –COOH and -OH.
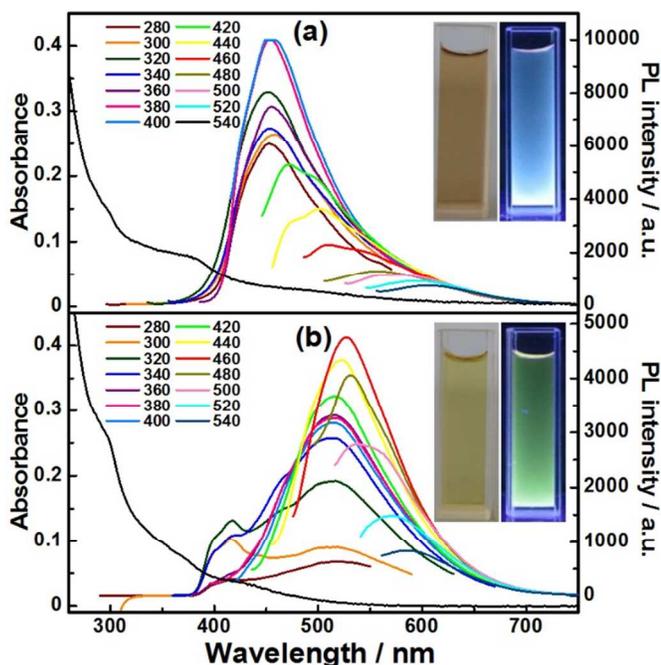
3.2 PL of HM-SGQDs

HM-SGQDs show markedly different PL property from SGQDs (Fig. 2). The brown HM-SGQD solution shows bright blue luminescence under irradiation of 365 nm UV light. When the excitation wavelength is increased gradually from 280 to 400 nm with an interval of 20 nm, the emission wavelength of HM-SGQDs is nearly excitation-independent. However, when the excitation wavelength is further increased from 400 to 540
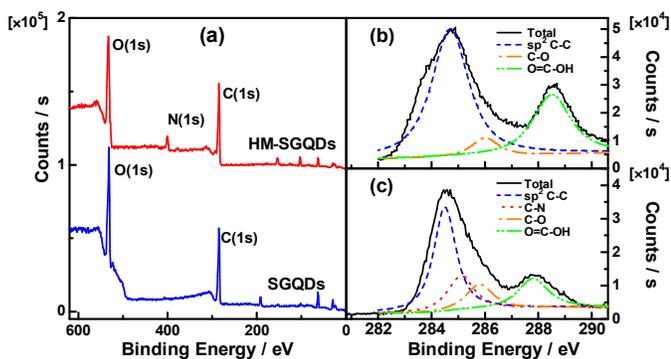
Fig. 1 XPS spectra of SGQDs and HM-SGQDs (a), high-resolution C1s spectra of SGQDs (b) and HM-SGQDs (c).

nm, obvious red-shift of emission wavelength can be observed accompanied with great decrease in peak intensity. The main emission band of HM-SGQDs is centered at around 455 nm, with a maximum excitation wavelength of about 380~400 nm. In contrast, the yellow SGQD solution shows green-yellow luminescence under irradiation of 365 nm UV light. The main emission band of SGQDs is centered at around 525 nm, with a maximum excitation wavelength of about 460 nm. Apparently, the main emission band of HM-SGQDs is markedly blue-shift when compared with that of SGQDs. Furthermore, the PL quantum yield (PLQY) of HM-SGQDs under excitation of 400 nm was calculated to be about 5.8%, which is much higher than that of SGQDs (about 1.3%). The comparison of UV-vis absorption spectra of HM-SGQDs and SGQDs informs that HM-SGQDs have a new and obvious absorption band centered at around 385 nm, which

Fig. 2 UV-vis absorption and PL emission spectra (recorded for progressively increasing excitation wavelengths in 20 nm increments) of HM-SGQDs (a) and SGQDs (b). Insets are the optical photographs of GQD solutions under visible light (left) and a UV light of 365 nm (right).
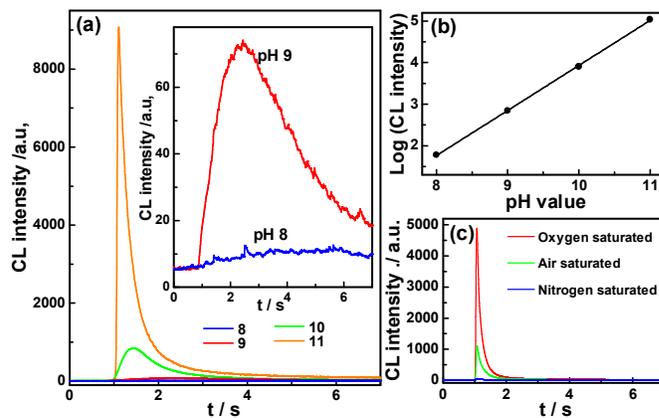
Fig. 3 CL curves of HM-SGQDs in various air-saturated PBS of pH 8-11 (a), semilogarithmic plot of CL intensity of HM-SGQDs vs pH value of solutions (b), CL curves of HM-SGQDs in pH 11 PBS saturated by oxygen, air and nitrogen, respectively (c). Inset in (a) are amplified CL curves of HM-SGQDs in air-saturated PBS of pH 8 and 9. The concentrations of HM-SGQD solutions are all 20 μg/mL.

is well consistent with the maximum excitation wavelength of HM-SGQDs. These results indicate that the unique PL property of HM-SGQDs should be related to the new absorption band.

As has been discussed above, HM-SGQDs are "reduced" and hydrazide group-modified SGQDs. To investigate whether the unique PL property of HM-SGQDs are resulted from the "reduction" or the " hydrazide group modification", a control experiment was carried out using NaBH$_4$ reduced SGQDs (R-SGQDs). Experimental results indicate that the PL spectra of R-SGQDs are also blue-shifted when compared with those SGQDs (Fig. S3). However, the main emission band of R-SGQDs is centered at around 443 nm, which is even shorter than that of HM-SGQDs (455 nm). And the maximum excitation wavelength is about 360 nm rather than the 400 nm of HM-SGQDs. Furthermore, UV-vis absorption spectrum of R-SGQDs shows no obvious absorption band at around 385 nm.

Summarily, based on above experimental results and discussion, it can be inferred that the absorption band at around 385 nm and the unique PL property of HM-SGQDs should be mainly caused by the hydrazide group modification.

3.3 CL of HM-SGQDs

CL properties of HM-SGQDs were also investigated. Different from other CL-active CDs,[24,25] HM-SGQDs can produce strong CL signal in the absence of any strong oxidant. As shown in Fig. 3a, strong CL signal can be detected as soon as HM-SGQDs are injected into air-saturated alkaline PBS. In contrast, neither SGQDs nor R-SGQDs produced any detectable CL signal, even in the presence of strong oxidant. Therefore, it can be known that the CL property of HM-SGQDs should be related to the modified hydrazide groups.

The CL behaviors of HM-SGQDs are dependent on the pH value of solution. As shown in Fig. 3a, HM-SGQDs produce nearly no CL activity in acidic and neutral solutions, but exhibit strong CL activity in alkaline solutions. In the pH range from 8 to 11, the CL intensity increases dramatically with the pH value. There is a good semilogarithmic correlation between the CL intensity and the pH value (Fig. 3b), suggesting that the CL intensity of HM-SGQDs is proportional to the concentration of hydroxyl ion (OH$^-$). The pH-dependent CL behaviors of HM-
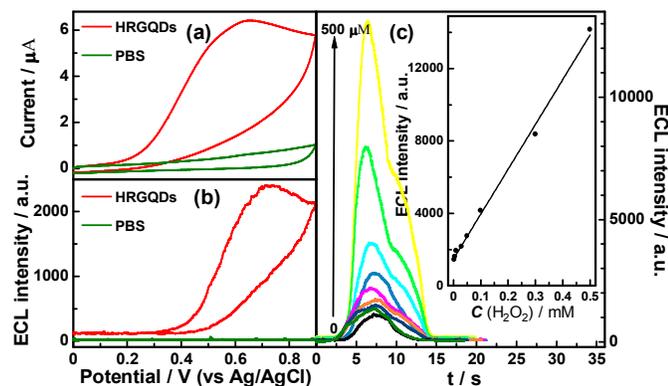
Fig. 4 Cyclic voltammograms (a) and ECL emission curves (b) of blank and 40 μg/mL HM-SGQDs in pH 9 PBS, and ECL responses of 40 μg/mL HM-SGQDs upon addition of various concentrations of H_2O_2 (from bottom: 0, 3, 5, 10, 30, 50, 100, 300 and 500 μM) (c). Inset in (c) is the linear calibration plot of ECL responses *vs* the concentration of H_2O_2 in the range from 3 μM to 500 μM.

SGQDs imply the potential applications of HM-SGQDs in pH sensors for alkaline solutions. The CL intensity of HM-SGQDs is also affected by the concentration of O_2. As shown in Fig. 3c, the CL intensity is decreased obviously upon bubbling nitrogen gas into the solution, whereas it is increased dramatically upon bubbling oxygen gas. Apparently, this result suggests that HM-SGQDs can also be applied in O_2 sensing.

3.4 ECL behaviors of HM-SGQDs

Many CDs have been reported to be ECL active. In particular, in the presence of peroxydisulfate ($S_2O_8^{2-}$), most CDs produced strong cathodic ECL signal. Accordingly, the ECL property of HM-SGQDs was also investigated. Unexpectedly, HM-SGQDs exhibit poor cathodic ECL activity. When the potential is scanned from 0 to -1.5 V, HM-SGQDs produce only a very weak cathodic ECL signal, even in the presence of 1 mM $S_2O_8^{2-}$ (Fig. S4). In contrast, both SGQDs and R-SGQDs show excellent cathodic ECL activities. They emit strong cathodic ECL signals in the presence of 1 mM $S_2O_8^{2-}$. The ECL spectra of R-SGQDs/$S_2O_8^{2-}$ system is similar with that of SGQDs/$S_2O_8^{2-}$ system (inset of Fig. S4). All the experimental results imply that SGQDs have strong cathodic ECL activity, and the reduction does not affect obviously the cathodic ECL property of SGQDs. In other words, the poor cathodic ECL activity of HM-SGQDs should be a result of the introduction of hydrazide groups.

Although HM-SGQDs show poor cathodic ECL activity, but they exhibit strong anodic ECL activities. Cyclic voltammogram (CV) and ECL-voltage curve of HM-SGQDs in pH9 PBS are shown in Fig. 4. When the potential is scanned positively from 0 to +0.90 V, HM-SGQDs produce an obvious electro-oxidation peak at around +0.64 V (Fig. 4a), with an onset potential of about +0.12 V. Correspondingly, an intensive anodic ECL emission is detected, with an onset potential of about +0.32 V and a peak potential of around +0.72 V (Fig. 4b). CV and ECL-voltage curves of SGQDs and R-SGQDs were also investigated in pH 9 PBS as contrast experiments. Neither SGQDs nor R-SGQDs produce any electrochemical or ECL signal in the potential range of 0 to 0.90 V. Therefore, the unique anodic ECL properties of HM-SGQDs are also attributed to the introduced hydrazide groups.
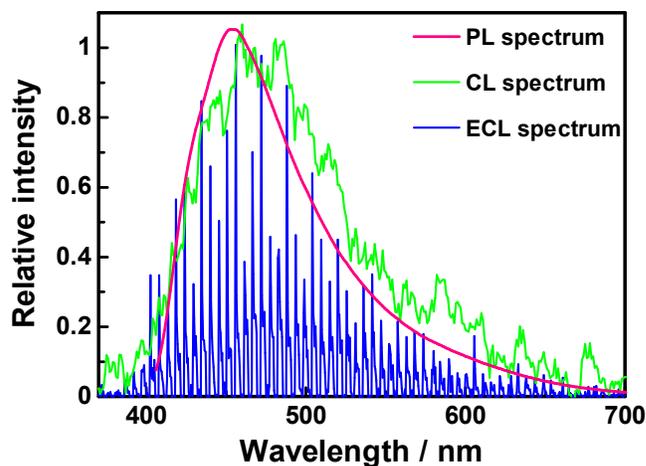
Fig. 5 PL (excited at 380 nm) and CL spectra of HM-SGQDs, and ECL spectrum of the HM-SGQDs/H_2O_2 system.

The ECL behaviors of HM-SGQDs are substantially pH-dependent (Fig. S5). HM-SGQDs produce nearly no detectable ECL signal in solutions of pH < 6. When the pH value is increased gradually from 6 to 9, the ECL intensity of HM-SGQDs is first increased with the pH value. When the pH value is further increased to 11, the ECL intensity decreases while the baseline increases. The strong baseline in alkaline solutions should result from the CL reaction between HM-SGQDs and O_2 as has been mentioned above. Therefore, to get a sensitive ECL signal and avoid the interference from CL, pH 9 PBS was used in the following research. The anodic ECL signal of HM-SGQDs can be enhanced dramatically by hydrogen peroxide (H_2O_2). As shown in Fig. 4c, the enhanced ECL intensity increases linearly with the concentration of H_2O_2 in a wide range of 3 μM to 500 μM. The detection limit of H_2O_2 based on
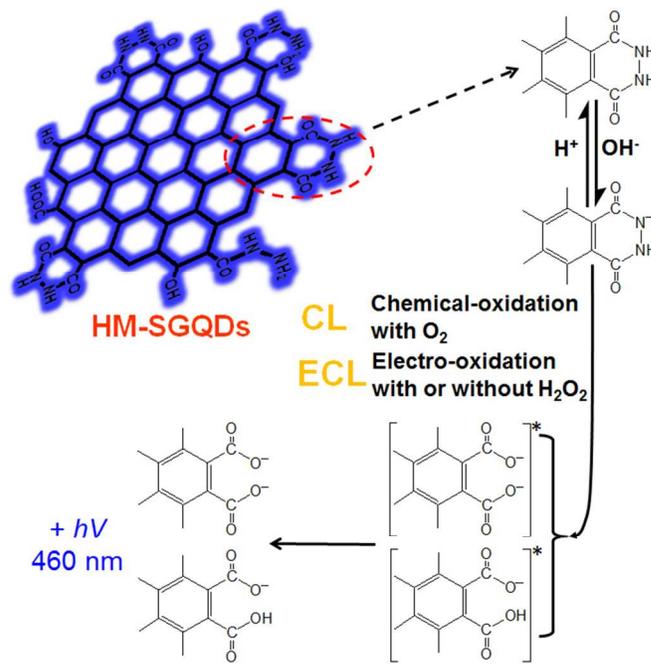
Fig. 6 CL and ECL mechanisms of HM-SGQDs.

the enhanced ECL signal of HM-SGQDs was calculated to be about 0.7 μM. H_2O_2 is an important signal molecule for a number of biological processes. The sensitive response of the anodic ECL of HM-SGQDs to H_2O_2 implies that HM-SGQDs would have great potential application in bio-analysis.

3.5 Luminescent mechanisms of HM-SGQDs

As discussed above, the unique PL, CL and ECL properties of HM-SGQDs are related to the introduced hydrazide groups. However, the luminescent mechanisms are still unclear. Herein, the PL, CL and ECL mechanisms are further discussed.

The CL spectrum and ECL spectrum of HM-SGQDs were measured and compared with the main PL spectrum of HM-SGQDs (excited at 380 nm). As shown in Fig. 5, the three spectra are essentially the same, implying they are given by similar excited states. It has been reported that refluxing GQDs with N_2H_4 would result in the formation of abundant luminol-like units at the edges of GQDs.[39] Luminol is a well-known luminophore exhibiting excellent PL, CL and ECL properties. Indeed, the main PL spectrum of HM-SGQDs is quite similar to the PL spectrum of luminol, suggesting that the bright blue PL of HM-SGQDs may be mainly originated from their luminol-like units. Furthermore, the CL and ECL properties of HM-SGQDs are also quite similar to those of luminol. Therefore, it follows that HM-SGQDs should share similar CL and ECL mechanisms with luminol. As shown in Fig. 6, the hydrazide group of HM-SGQDs is deprotonated in basic solution to form an anion. Subsequently, the anion is either chemically oxidized by O_2 or electrochemically oxidized in the presence (or absence) of H_2O_2.[37] Two kinds of excited states might be produced after the oxidation, which finally results in strong light emission.

4 Conclusions

HM-SGQDs with unique PL, CL and anodic ECL properties have been synthesized by refluxing SGQDs with N_2H_4. The unique optical properties are contributed to the introduction of hydrazine groups and the formation of abundant luminol-like units. First of all, the PL of HM-SGQDs is obviously blue-shifted from that of SGQDs. The main emission band of HM-SGQDs is centerd at around 445 nm, with a maximum excitation wavelength of around 390 nm. Furthermore, the PLQY is much higher than that of SGQDs. Secondly, HM-SGQDs show strong CL in alkaline solutions. The CL intensity of HM-SGQDs is mainly dependent on the pH value of solution and the concentration of O_2 in the solution. Thirdly, HM-SGQDs show poor cathodic ECL activity, but have strong anodic ECL activity in alkaline solution. Furthermore, the anodic ECL intensity of HM-SGQDs can be enhanced greatly by H_2O_2. The unique PL, CL and ECL properties would make HM-SGQDs have great potential applications in many fields such as bio-imaging, sensor and bio-sensor. This study might be a major breakthrough in promoting the application of CDs.

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Notes and references

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Table of Contents Graphic
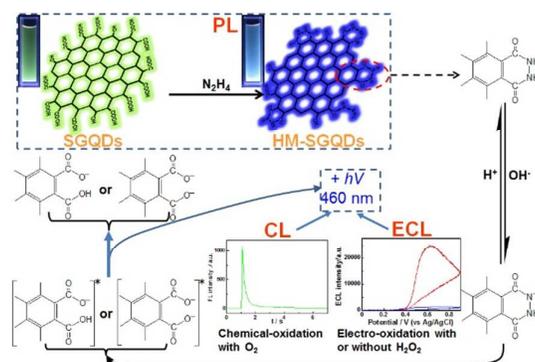
Hydrazide groups modified single-layer graphene quantum dots exhibit unique photoluminescence, chemiluminescence and anodic electrochemiluminescence properties.

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