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Facile Ionic-Liquid-Assisted Electrochemical Synthesis of Size-Controlled Carbon Quantum Dots by Tuning Applied Voltages

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Abstract: Carbon quantum dots (CQDs) were prepared by electrochemical ablation of graphite rods in the mixture of water and ionic liquid as electrolyte. Size-controlled CQDs were achieved by changing the voltages applied to the electrodes and the forming mechanism would be also discussed in this paper. The monodisperse and spherical CQDs with the size of 2.9, 4.4 and 6.6 nm were obtained at voltages of 9, 15 and 30 V, respectively. The obtained aqueous solution of CQDs exhibited both dependence of excitation-wavelength and size in photoluminescence spectra, and these phenomenona might be caused by the surface energy traps from passivation of ionic liquid. The UV-vis absorption spectra of CQDs with similar shape and different intensities may be caused by the change of size.

Key Words: carbon quantum dots, electrochemical method, size-control

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1 Introduction:

Recent years, Carbon quantum dots (CQDs), which are carbon nanocrystals with diameters less than 10 nm, have attracted more and more research interests due to their fascinating optical properties, excellent biocompatibility and water solubility [1]. Owing to these unique and novel properties, they have been successfully used for fluorescent probes [2], photovoltaic devices [3], photocatalysis [4, 5], and bioimaging [6-9]. Up to now, various approaches have been used to synthesize CQDs, such as microwave synthesis [10], ultrasonic treatment [11], carbon soot [12], reverse micelles [13], hydrothermal treatment [14] and electrochemical method [16-18]. Therein, electrochemical fabrication has become popular due to facile control conditions and synthesis at room temperature. In this paper, we reported a facile and self-passivated electrochemical route to prepare size-controlled CQDs, followed by a simple purification.

For electrochemical route, it is known that there are two key factors to influence the properties of CQDs: one is applied voltage as main driving force in electrochemical reaction, the other is the properties of electrolyte [16-18]. Several reports about the electrochemical synthesis of CQDs and other carbon materials in the electrolyte of ionic liquid and water have been published [19-21]. Ionic liquids in the electrolyte have been proposed as "green" alternatives to conventional solvent due to their unique performances, such as negligible vapor pressure, thermal stabilities, wide electrochemical potential window, low viscosity, good ion conductivity and recyclability [22]. These properties render ionic liquid as a perfect candidate for electrochemical electrolyte. Moreover, ionic liquid also play another role of passivating the surface of CQDs, which avoid redundant step of passivation. The addition of distilled water mixed with ionic liquid not only disrupts the internal organization and modifies the liquid structure by forming a new hydrogen-bonded network, but also it is dissociated to oxygen and hydroxyl radicals, and the hydroxyl radicals was essential to prepare CQDs in previous reports [23, 24].

Besides, the size of CQDs is a key factor to influence their properties and performance. The CQDs with different sizes have been fabricated using various methods such as: changing the laser pulse widths in laser synthesis, by employing reverse micelles as nanoreactors in carbonization of sugar or by heating various carbon sources in different concentrations. The behavior of size-dependent photoluminescence (PL) had also been observed [25-27]. However, as far as we know, there was no literature investigating and realizing the size control of CQDs using electrolyte consisting of ionic liquid and distilled water. Thus, in this paper, the size-controlled CQDs have been prepared by adjusting the voltages applied to the electrodes, in which the mixture of ionic liquid and distilled water was used as electrolyte. Meanwhile, the dependence of both excitation-wavelength and size in PL spectra were observed, and the related mechanisms on these behaviors are to be presented in this paper.

2 Experimental

2.1 Preparation of CQDs

The CQDs were synthesized through a method of electrochemical ablation of graphite rods in a two-electrode configuration, in which the rods were adopted as electrodes and the carbon source. Successively rinsed by ethanol and deionized water, two same graphite rods (10 cm in length and 0.6 cm in diameter) were vertically inserted in the electrolyte with a distance of 2 cm, and the electrolyte was a mixture of 5ml distilled water, 4 ml 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]) and 4 ml 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]). Three different values of static potentials (9, 15 and 30 V), provided by a direct current power supply, were applied to two graphite rods. The electrolyte was continuously stirred by magnetic stirrer during the reaction. With increasing reaction time, distilled water was dissociated into hydrogen and oxygen releasing in the form of bubbles and the solution changed from colorless to yellow and finally to dark brown. It was worth pointing out that both the intensity and consuming time of electrochemical reaction were distinct from each other, owing to different voltages applied to the electrodes. The reaction time were 59, 25 and 10 minutes, respectively, corresponding to 9, 15 and 30 V. The statistic voltage of 30 V applied to the electrodes stimulated the most violent reaction in the electrochemical cell. Meanwhile, the sample also spent the shortest time in finishing the electrochemical reaction until there were no appearing bubbles from electrolyte. After exfoliation, 1 ml the obtained electrolyte was mixed with 9 ml distilled water, and the obtained mixture was processed using ultrasonic wave for 30 min and subsequently centrifuged at 10000 rpm for 5 min to remove precipitates and bulky graphite fragments. Finally, the supernate solution contained soluble CQDs.

2.2 Characterization

Transmission electron microscopy (TEM) images were obtained using a JEM-2100 transmission electron microscope at an acceleration voltage of 200 kV. The normal TEM samples were prepared by dropping the solution onto a copper grid and dried under drying lamp. The statistics of size distribution were performed by the software of Nano Measurer 1.2 in size distribution. Fourier transform infrared spectroscopy (FTIR) patterns were measured in the range of 400-4000cm^{-1} on a Nicolet 5700 FTIR spectrophotometer. The PL study was carried out on a Fluoromax-4 fluorescence spectrophotometer. Light absorption properties were obtained using ultraviolet-visible (UV-vis) spectrophotometer (UV-3600).

3 Results and discussion

The TEM images of CQDs synthesized at 9, 15 and 30 V were shown in Fig.1 (a), (b) and (c), and high-resolution TEM (HRTEM) of the sample prepared at 15 V was also shown in Fig.1 (d). The insets showed the corresponding size distribution of CQDs in TEM images, respectively. It can be clearly identified that the as-synthesized CQDs were monodisperse and spherical in shape, which were well agreed with previous reports [5, 28]. The center values in the fitted Gaussian curves for the sizes of CQDs grown at 9, 15 and 30 V were 2.9, 4.4 and 6.6 nm, respectively, suggesting that the sizes increased with the rise of voltages applied to the electrodes. Besides, it was also clearly identified that the full width at half maximum (FWHM) of the fitted Gaussian curves in insets were 1.8, 1.4 and 4 nm, corresponding to the voltages of 9, 15 and 30 V, respectively, which indicated that the sample at 30 V possessed the broadest size distribution in all specimens. Both the biggest size and the broadest size distribution observed in specimen synthesized at voltage of 30 V may be explained by the following forming mechanism. The HRTEM image (Fig.1 (d))showed that the lattice spacing in the zones labeled A and B were 0.21 nm revealing that CQDs were single crystalline grain and possessed graphite crystalline structure due to the values agreeing well with the (100) facet of graphite [28-30], which originated from the graphite rods used for the ablation. The interface of C zone was attributed to the overlap of two CQDs.

In this approach, the formation of the CQDs by electrochemical ablation was mainly influenced by two electrochemical conditions: electrolyte and applied voltages. The electrolyte used was the mixture of ionic liquid consisting of two kinds of imidazoliun ions ([BF_4] and [PF_6]) and distilled water, and the exfoliation of CQDs was influenced by ionic liquid and distilled water. Obtaining the free electron from direct current power supply, the imidazoliun ion of ionic liquid in the electrolyte was reduced into the imidazolium free radicals [31] at the cathode, which can be inserted into the π bonds of graphite plane to ablate carbon fragments and nanoparticles from graphite rods. In addition, due to the voltages applied to electrodes beyond narrow electrochemical potential window of water, the water would be dissociated into hydroxyl and oxygen radicals, and the hydroxyl radical was an essential factor to the generation of CQDs [23, 24]. During the electrochemical reaction, the produced hydroxyl radicals attacked and sacrificially corroded the graphite rods from edge sites, grain boundaries or defect of surface by disrupting the bond of graphite, and imidazolium radicals could intercalate the opening up sheet of graphite rods destroyed by hydroxyl radicals, which leaded to the expansion of nanomaterials from graphite electrodes [32]. The ablated products might contain nanoparticles. With the increase of reaction time, these ablated materials from graphite rods would be continuously attacked by various radicals in the electrolyte and broken into smaller fragments, leading to the formation of CQDs. The more reaction time was consumed, the more attacks were carried out and the more nanoparticals with smaller size appeared in the electrolyte.

During these experiments, the synthesis of CQDs consumed 59, 25 and 10 minutes at voltages of 9, 15 and 30 V, respectively. The sizes of obtained CQDs were

2.9, 4.4 and 6.7 nm corresponding to 9, 15 and 30 V, suggesting that the size increased with the rise of applied voltages. The CQDs fabricated at 30 V consumed the least time about 10 minutes, possessing the largest size of 6.7 nm in all samples. The higher voltage was applied, the less reaction time was cost. The less attacking by various radicals occurred, and the bigger CQDs were obtained. Besides, due to consuming the least time, appearing less attacks and leaving larger nanoparticles in the electrolyte, the size distribution of 30 V was also wider than other two samples, which had been identified by the latter results of FWHM in PL spectrum.

The FTIR spectra of CQDs synthesized at different voltages were shown in Fig.2. All spectra of FTIR displayed the similar shape as well as peak positions, indicating all samples with similar composition. The typical peaks around 3458 and 1465 cm^{-1} are associated with the stretching vibration and in-plane bending vibration of -OH, respectively [33]. The peaks of 2957 and 2875 cm^{-1} are ascribed to the stretching vibration of C-H in the group of -CH_3 or -CH_2 [33], suggesting that the surface of CQDs be passivated by ionic liquid and more surface energy traps be formed. It is worth pointing out that the surface passivation of CQDs is generally considered as a facilitating way to enhance PL. The band of 1654 cm^{-1} manifests the presence of carbonyl (C=O) [33]. The band of 1637 cm^{-1} is present evidence of aromatic C=C and the 1384 cm^{-1} peak is assigned to the absorption on graphite C-O [15]. The peaks in the spectrum corresponded to the oxygen-containing groups and other new functional groups indicating successful oxidation of graphite and the formation of hydrophilic groups. On the basis of the above results, it can be concluded that the oxygen function groups were formed through electrochemical oxidation. Due to the abundant oxygen-containing groups at their surface, CQDs exhibited very good solubility in water.

Fig.3 (a, b) shows the normalized PL spectra and the PL spectra of CQDs synthesized at voltage of 15 V, which was excited by using different wavelengths. It is obvious that PL phenomenon was found in solution of CQDs. The PL from CQDs may be attributed to the presence of surface energy traps that become emissive upon stabilization as a result of the surface passivation by ionic liquid [33]. The requirement for surface passivation to PL is apparently shared by the CQDs and the silicon nanocrystals, for which a widely accepted mechanism for luminescence emission is the radiative recombination of excitons [34]. To explore the PL properties of as-synthesized CQDs, a detailed PL study was investigated. When the wavelengths changed from 320 to 500 nm, the PL emission peaks relevantly red shifted from 448 to 568 nm, obviously identified by the normalized PL spectra shown in Fig.3 (a). For the other samples synthesized at 9 and 30 V, the normalized PL spectra had a similar red-shift behavior (not shown). It is easily found that the as-synthesized CQDs at different voltages exhibited excitation-wavelength-dependent PL performance, in which the PL peak centers shifted to longer wavelengths as increasing the excitation wavelength and was consistent with previous reports [25, 35, 36]. The strongest emission peaks were also determined by the wavelength of excitation. The strongest fluorescence emission band, located at 438 nm, was observed under 300 nm excitation for the sample synthesized at 9 V. The strongest emission peak located at 465 nm with the excitation wavelength of 360 nm in the sample synthesized at 15 V, and the most intensity of emission band for the specimen at 30 V, located at 490 nm, excited by 400 nm (not shown in this paper). These results revealed that an interesting dependence of the emission wavelength on the excitation wavelength for CQDs.

A further investigation on the PL properties was carried out by exciting all samples using the same wavelength of 340 nm, and the correspondingly normalized PL spectra were shown in Fig.4. Interestingly, the emission peaks of PL red shifted from 445 to 487 nm as the size of CQDs increase from 2.9 to 6.6 nm, which might be caused by the increasing size of CQDs. For the passivated CQDs reported here, there must be a quantum confinement of energy traps on the surface. With the increase of size, the quantum confinement decreased and red shift occurred.

Fig.5 showed the UV-vis absorption spectra of CQDs with different sizes. The three curves of absorption showed a similar shape in the range of 250-800 nm, which featured a peak at 270 nm and a broad shoulder peak at around 320 nm. The former peak was ascribed to π-π^* the transition of C=C [37], while the latter one indicated the formation of the n-π^* transition from C=O [37, 38]. As the size increased, the shoulders of absorbance spectra in the UV region and absorption in the visible light region became prominent. For example, the sample fabricated at 30 V showed the highest intensity in absorption spectra, and these may be ascribed to the increasing size of CQDs.

3 Conclusions

In summary, we reported a facile electrochemical synthesis of size-controlled CQDs by changing the applied voltages on the electrodes in the mixed electrolyte of ionic liquid and water. With the increased voltages of 9, 15 and 30 V, the sizes of as-synthesized CQDs were 2.9, 4.4 and 6.6 nm, respectively, indicating that the adjusting size of CQDs was realized by changing applied voltage. The mechanism of changing size was the results of reduced reaction time caused by the enhancing of voltage. Owing to the energy trap and its quantum confinement on the surface of CQDs, the excitation-length-dependent and size-dependent red-shift of PL were observed in the solution of CQDs.

Acknowledgement

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Fig.1TEM images of CQDs fabricated by electrochemical exfoliation at different voltage of 9, 15 and 30 V corresponding to (a) (b) and (c), respectively. The insets showed corresponding size distribution and fitted Gaussian curves. HRTEM image of CQDs synthesized at 15 V was shown in (d).

Fig.2 FTIR spectra of CQDs synthesized at different voltage

Fig.3 Normalized PL and PL spectra of the as-synthesized CQDs at voltage of 15v, corresponding to (a) and (b), respectively

Fig.4 Normalized PL spectra of CQDs with different sizes excited by the same wavelength of 340 nm

Fig.5 UV-vis absorption spectra of CQDs synthesized with different sizes

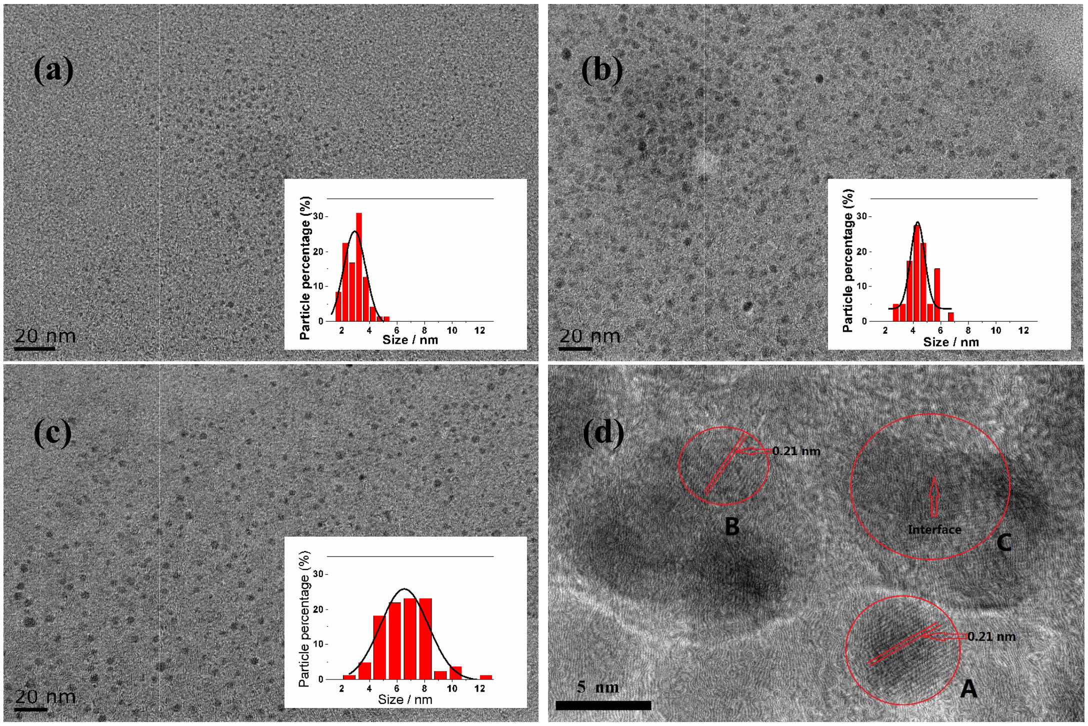
(a)
20 nm
Particle percentage (%)
0
10
20
30
2
4
6
8
10
12
Size / nm
(b)
20 nm
Particle percentage (%)
0
10
20
30
2
4
6
8
10
12
Size / nm
(c)
20 nm
Particle percentage (%)
0
10
20
30
2
4
6
8
10
12
Size / nm
(d)
0.21 nm
B
Interface
C
0.21 nm
A
5 nm

Fig.1

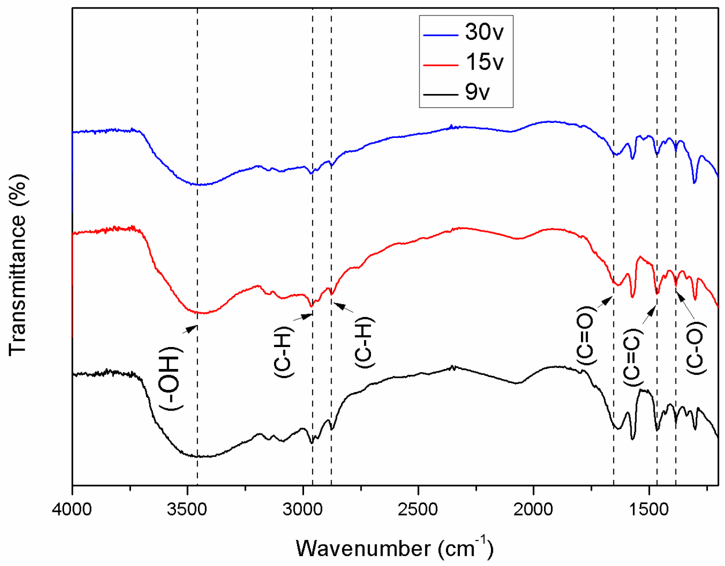
30v
15v
9v
Transmittance (%)
(-OH)
(C-H)
(C-H)
(C=O)
(C=C)
(C-O)
4000
3500
3000
2500
2000
1500
Wavenumber (cm^{-1})

Fig.2

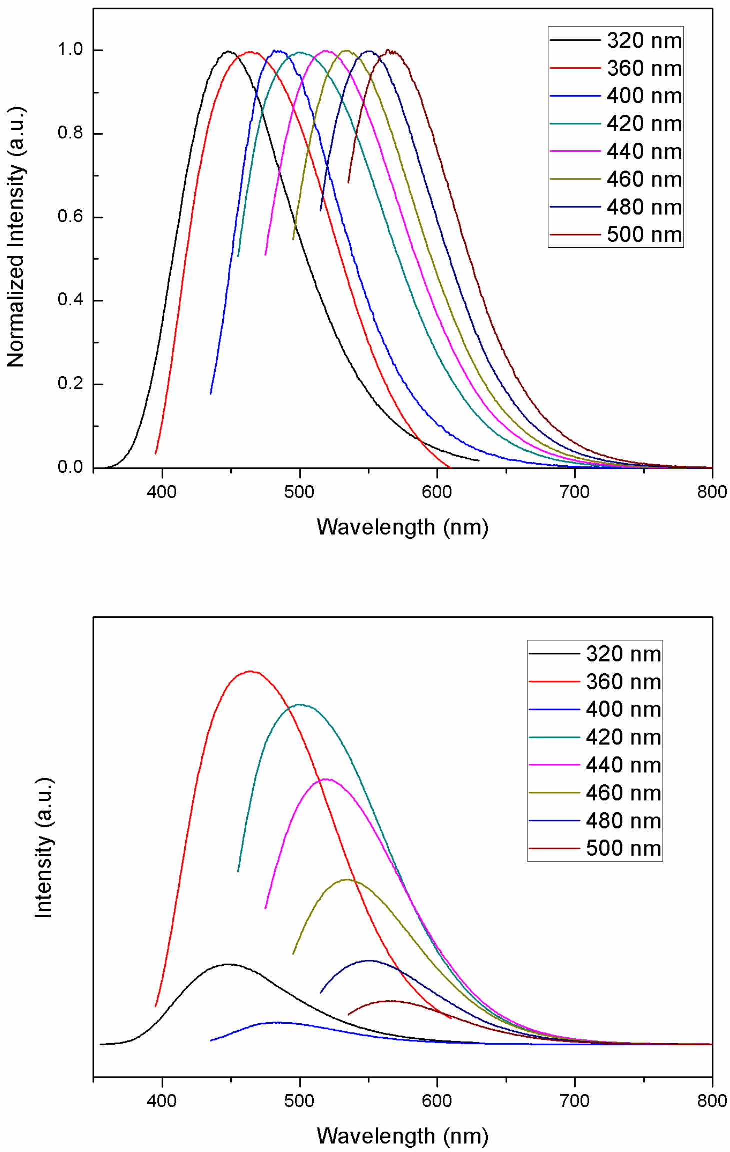
Normalized Intensity (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
Wavelength (nm)
320 nm
360 nm
400 nm
420 nm
440 nm
460 nm
480 nm
500 nm
Intensity (a.u.)
400
500
600
700
800
Wavelength (nm)
320 nm
360 nm
400 nm
420 nm
440 nm
460 nm
480 nm
500 nm

Fig.3

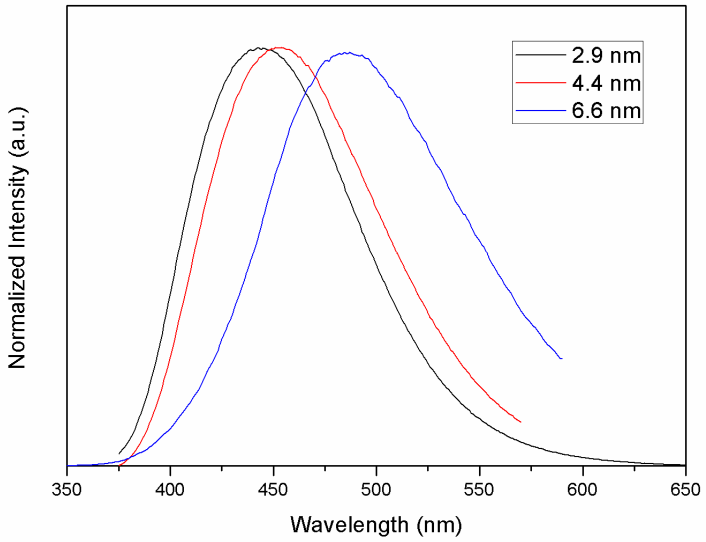
2.9 nm
4.4 nm
6.6 nm
Normalized Intensity (a.u.)
Wavelength (nm)
350
400
450
500
550
600
650

Fig.4

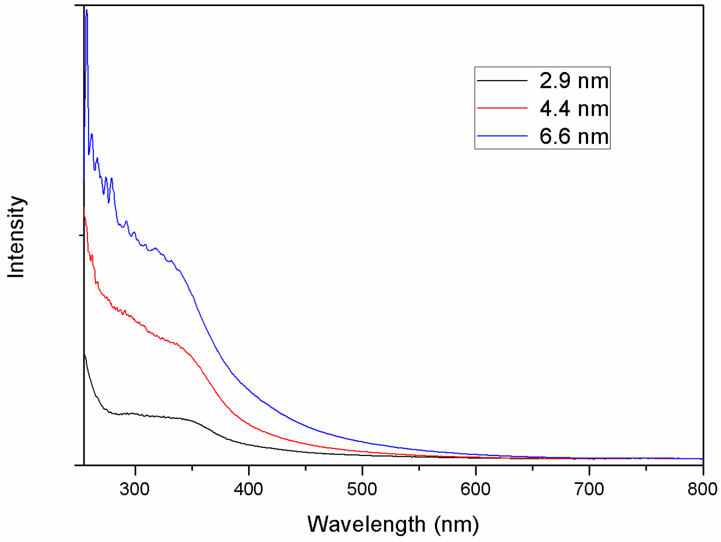
2.9 nm
4.4 nm
6.6 nm
Intensity
300
400
500
600
700
800
Wavelength (nm)

Fig.5

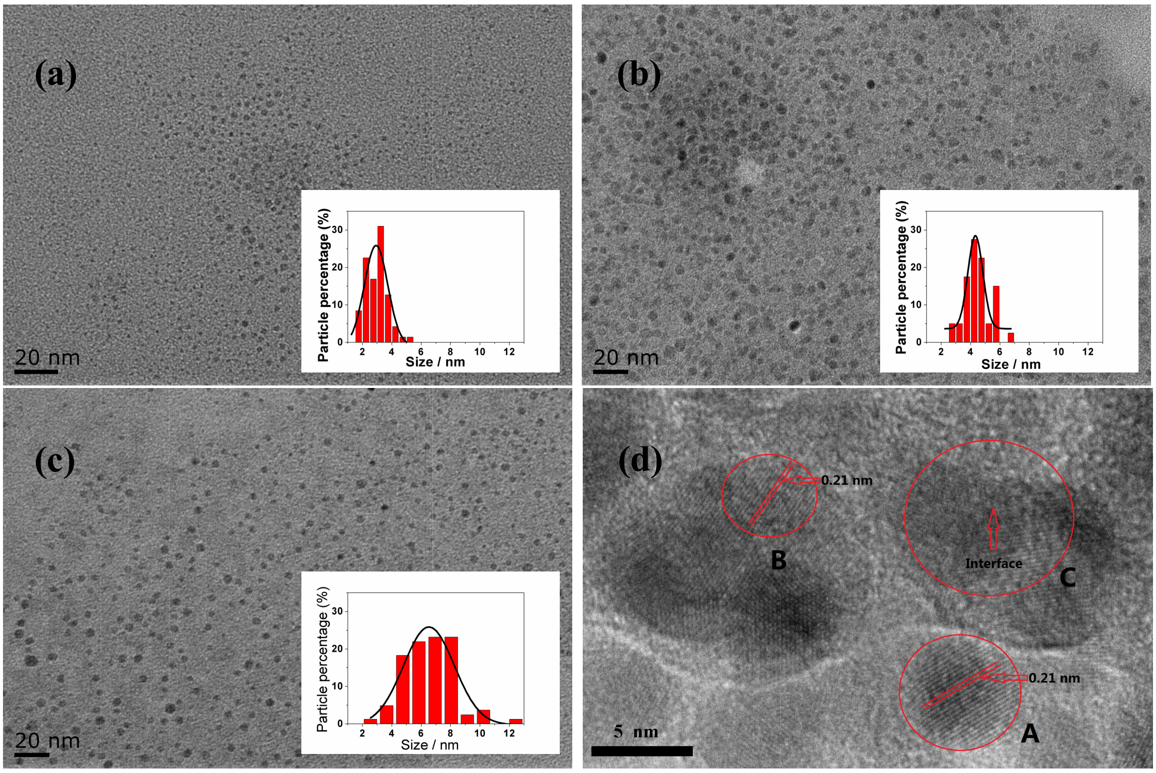
(a)
20 nm
Particle percentage (%)
Size / nm
0
10
20
30
2
4
6
8
10
12
(b)
20 nm
Particle percentage (%)
Size / nm
(c)
20 nm
Particle percentage (%)
Size / nm
(d)
0.21 nm
B
Interface
C
0.21 nm
A
5 nm

Fig.1

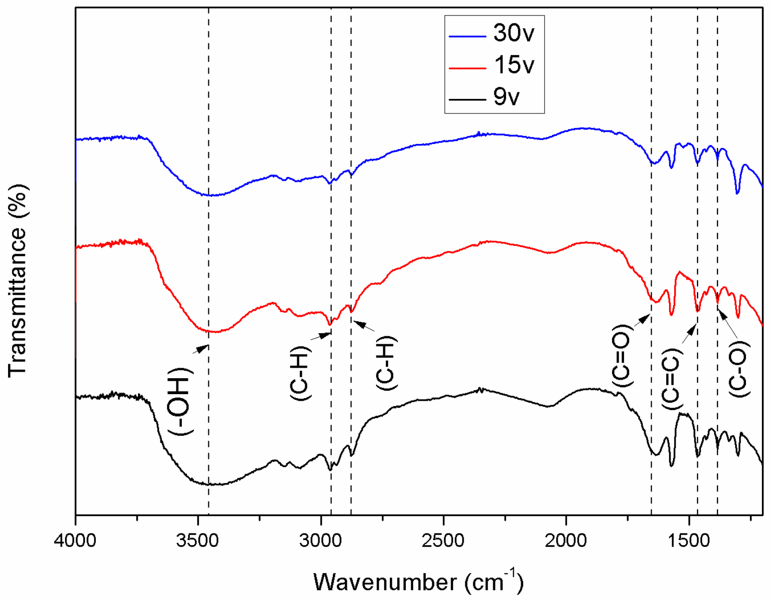
30v
15v
9v
Transmittance (%)
(-OH)
(C-H)
(C-H)
(C=O)
(C=C)
(C-O)
4000
3500
3000
2500
2000
1500
Wavenumber (cm^{-1})

Fig.2

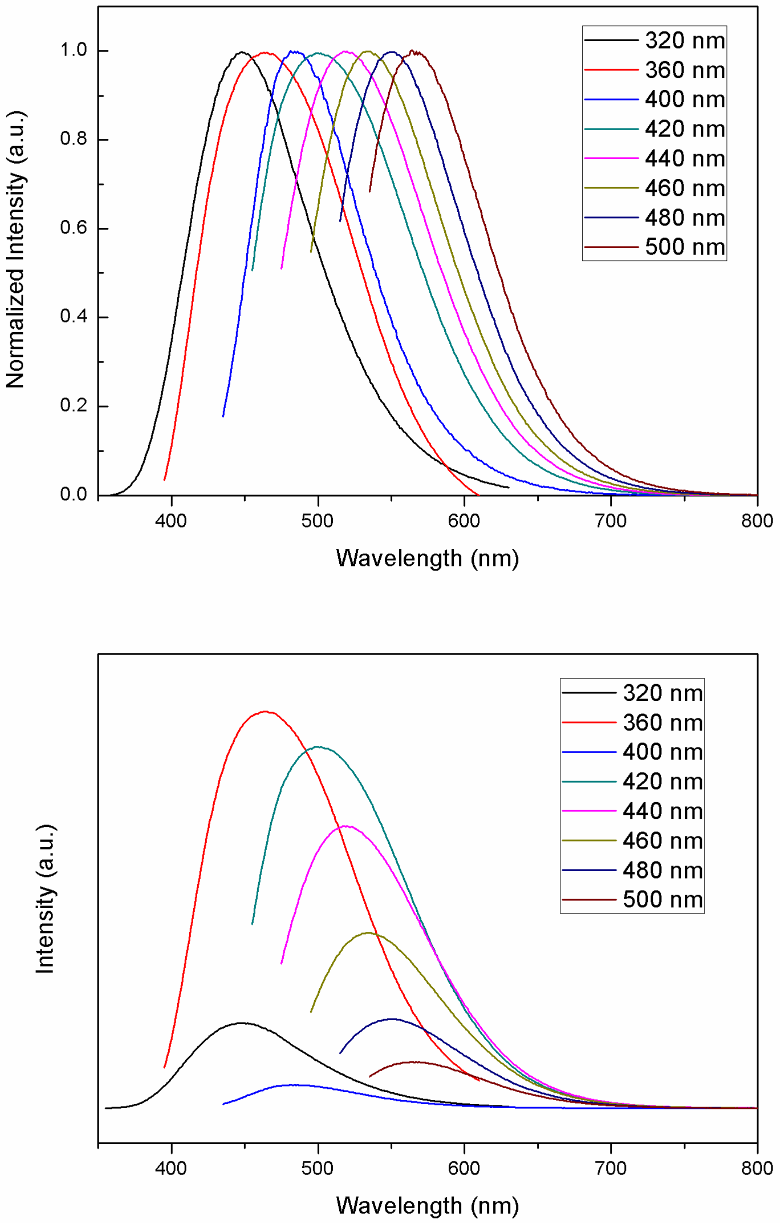
Normalized Intensity (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
400
500
600
700
800
Wavelength (nm)
320 nm
360 nm
400 nm
420 nm
440 nm
460 nm
480 nm
500 nm
Intensity (a.u.)
400
500
600
700
800
Wavelength (nm)
320 nm
360 nm
400 nm
420 nm
440 nm
460 nm
480 nm
500 nm

Fig.3

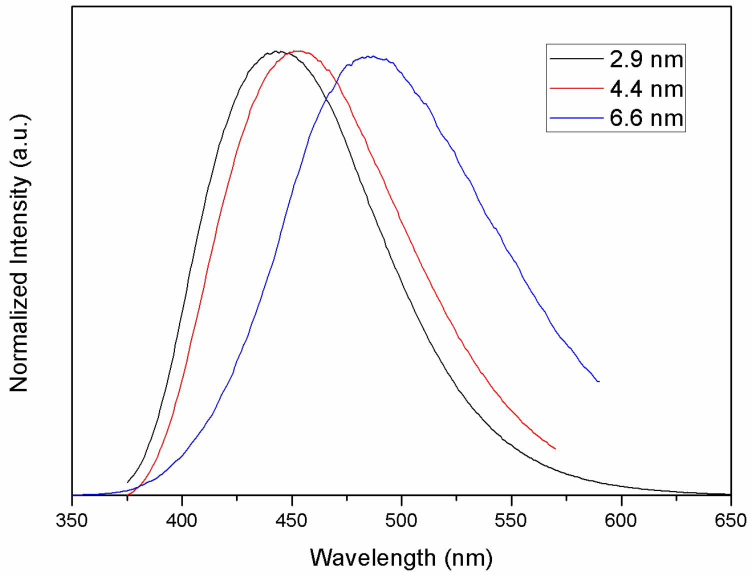
Normalized Intensity (a.u.)
Wavelength (nm)
350
400
450
500
550
600
650
2.9 nm
4.4 nm
6.6 nm

Fig.4

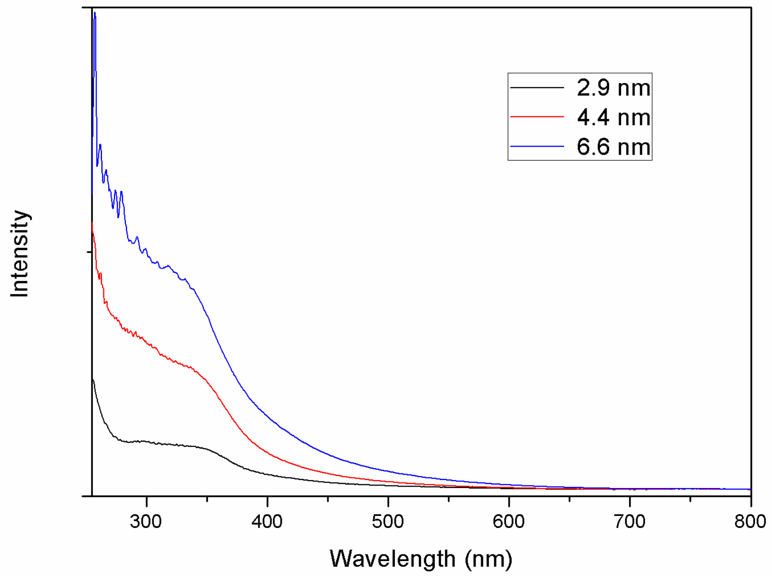
Intensity
2.9 nm
4.4 nm
6.6 nm
300
400
500
600
700
800
Wavelength (nm)

Fig.5