Effects of Coal Rank and High Organic Sulfur on the Structure and Optical Properties of Coal-based Graphene Quantum Dots

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Abstract: Coal-based graphene quantum dots (GQDs) were successfully produced via a one-step chemical synthesis from six different coal ranks, from which two superhigh organic sulfur (SHOS) coals were selected as natural S-doped carbon sources for the preparation of S-doped GQDs. The effects of coal properties on coal-based GQDs were analyzed by means of high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), ultraviolet-visible (UV-Vis) absorption spectroscopy, and fluorescence emission spectra. It was shown that all coal samples can be used to prepare GQDs, which emit blue-green and blue fluorescence under ultraviolet light. Anthracite-based GQDs have a hexagonal crystal structure without defects, the largest size, and densely arranged carbon rings in their lamellae; the high-rank bituminous coal-based GQDs are relatively reduced in size, with their hexagonal crystal structure being only faintly visible; the low-rank bituminous coal-based GQDs are the smallest, with sparse lattice fringes and visible internal defects. As the metamorphism of raw coals increases, the yield decreases and the fluorescence quantum yield (QY) initially increases and then decreases. Additionally, the surface of GQDs that were prepared using high-rank SHOS coal (high-rank bituminous coal) preserves rich sulfur content even after strong oxidation, which effectively adjusts the bandgap and improves the fluorescence QY. Thus, high-rank bituminous coal with SHOS content can be used as a natural S-doped carbon source to prepare S-doped GQDs, extending the clean utilization of low-grade coal.

Key words: coal, graphene quantum dots, coal rank, organic sulfur, China

1 Introduction

Graphene quantum dots (GQDs) are nanocarbonaceous materials of the smallest known diameter (≤ 2–10 nm) (Bacon et al., 2014), and have recently garnered worldwide attention. As the newest member of the graphene family, GQDs have been synthesized from glucose (Tang et al., 2013), graphite or fullerene, and other new carbonaceous materials (Lu et al., 2011; Peng et al., 2012; Sun et al., 2013). Compared with inorganic quantum dots, the new carbon-based quantum dots combine the excellent performance of graphene with nontoxicity, biocompatibility, fluorescence stability, size-dependent photoluminescence, and better surface grafting properties. GQDs may replace inorganic quantum dots to play important roles in many fields (Liu et al., 2012; Liu and Kim, 2015; Salam et al., 2015).

Coal is a carbon-rich material and has been applied to the development of new nanostructured carbon materials because of its lower price in recent years (Ye et al., 2013; Xu et al., 2014; Zhang et al., 2014; Powell and Beall, 2015; Wang et al., 2015). Coal-based GQDs were also successfully prepared (Ye et al., 2013; Singamaneni et al., 2015). A simplified model of coal contains angstrom-scale or nanocrystalline graphite crystallites with defects connected by aliphatic amorphous carbon chains (Lu et al., 2001), which can be easier to oxidatively displace than pure $sp^2$-carbon structures (Hu et al., 2014). The unique structure of coal is inherently ideal for producing quantum dots with amorphous carbon at the edges (Ye et al., 2013). The number and size of graphite crystallites differ in coals with different degrees of coalification, which facilitates the size-controllable synthesis of GQDs.

Coal is different from graphite; its organic structure is complex and irregular and contains single-layer, double-
layer, and multilayer aromatic sheets combined through cross-linked bonds, with varying degrees of disorder. Affected by the coal-forming plants and diversified coal-accumulating environment, from lignite to bituminous coal to anthracite, there is a significant difference in the degree of condensation of aromatic rings (Cheng Aiguo, 2008). Research on coal as a carbon source for preparing new carbon nanomaterials is still in its initial stage. Researchers often lack an understanding of coal structures, while coal-type selection to improve the product quality and yield requires thorough research. While preparing fullerences, carbon nanotubes, GQDs, and other carbon nanomaterials, academics have noted that the formation mechanism of coal as a carbon source may be different from that of graphite (Moothi et al., 2012; Ye et al., 2013). The influence of coal characteristics on the quality of products has been researched (Qiu et al., 2002 and 2004; Yu et al., 2003), but the focus is seldom on coal-based GQDs. Furthermore, doping GQDs with heteroatoms could effectively regulate the bandgap and electronic density, improving the chemical reactivity and fluorescence quantum yield (QY) of GQDs (Li et al., 2014). Sulfur has a much larger atomic size than carbon, but the difference in electronegativity between sulfur (2.58) and carbon (2.55) appears to be insufficient, offering extremely weak charge transfer in C-S composites (Gao et al., 2012; Zhou et al., 2017); thus, chemical doping of sulfur into the frameworks of GQDs may be difficult (Gao et al., 2012; Li et al., 2014). The choice of SHOS coals as carbon sources was primarily based on recent research on the preparation of S-doped GQDs (Li et al., 2014). The organic sulfur content in natural SHOS coals can reach 4%-11% (Chou, 1997), primarily because of thiophene. Thiophene is particularly prevalent in coal (Baroah and Barua, 1996), and thus these coals can be regarded as natural S-doped carbon sources for the preparation of S-doped GQDs. Here, we report the production of GQDs from six different coal ranks (including two SHOS coals) to determine the characteristics of GQDs produced using different types of coal, to provide a theoretical basis for quality control, material selection, and other aspects of coal-based GQDs toward industrialization, as well as innovative ideas for clean and efficient utilization of low-grade coal.

### 2 Experiment

#### 2.1 Samples and sampling sites

Six Late Permian and Pennsylvania coal samples with various ranks from different regions of China were selected, for which the average maximum vitrinite reflection (R_{o,max}) was 0.72% to 3.93%, with corresponding coal ranks ranging from low-rank bituminous coal to anthracite, respectively (Table 1). These coal samples were collected from Chenxi (CX), Hunan Province; Fenxi (FX), Shanxi Province; Heshan (HS), Guangxi Province; Ximeng (XM), Shanxi Province; Xiaofalu (XFL), Yunnan Province; and Jincheng (JC), Shanxi Province. Among them, CX and FX are low rank bituminous coal, HS and XM are high-rank bituminous coal, and XFL and JC are anthracite. Notably, CX and HS are typical superhigh organic sulfur (SHOS) coals of China. Bright and semibright coals were preferred in this study. Table 1 shows that the vitrinite changes from 62.5% to 89.7%, the inertinite content changes from 8.9% to 25.2%, and low liptinite contain. Sample collection sites are shown in Fig. 1.

#### 2.2 Preparation of GQDs from coals

**Demineralization.** To minimize the influence of minerals and inorganic sulfur on the coal-based GQDs, the six samples were demineralized by blending with acids. The details of the demineralization procedures can be found elsewhere (Bishop and Ward, 1958; Nyathi et al., 2013). The native anthracites were treated with HCl, HF and HNO₃ successively in PTFE beakers (soaked in water at 60°C for 24 h) to form demineralized coals; the residual slurries were washed with ultrapure water until pH=7 and then dried in a vacuum oven at 70°C to constant mass.

**GQD preparation.** A one-step chemical synthesis was used to generate coal-based GQDs (Ye et al., 2015). The main synthetic procedure was as follows: 0.3 g of demineralized coal was added to a mixed solvent of 60 mL.

### Table 1 Basic characteristics of coal samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lithotype</th>
<th>R_{o,max} (%)</th>
<th>Proximate analysis (%)</th>
<th>Forms of sulfur and Ultimate analyses (%)</th>
<th>Maceral composition (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M₄d</td>
<td>A₄d</td>
<td>V₄d</td>
</tr>
<tr>
<td>Jicheng (JC)</td>
<td>bright</td>
<td>3.93</td>
<td>3.26</td>
<td>13.41</td>
<td>5.63</td>
</tr>
<tr>
<td>Xiaofalu (XFL)</td>
<td>bright</td>
<td>3.41</td>
<td>0.34</td>
<td>1.58</td>
<td>5.01</td>
</tr>
<tr>
<td>Ximeng (XM)</td>
<td>bright</td>
<td>1.99</td>
<td>0.70</td>
<td>8.24</td>
<td>15.18</td>
</tr>
<tr>
<td>Heshan (HS)</td>
<td>semibright</td>
<td>1.86</td>
<td>0.68</td>
<td>24.97</td>
<td>15.04</td>
</tr>
<tr>
<td>Fenxi (FX)</td>
<td>semibright</td>
<td>0.96</td>
<td>0.35</td>
<td>10.66</td>
<td>36.87</td>
</tr>
<tr>
<td>Chenxi (CX)</td>
<td>semibright</td>
<td>0.72</td>
<td>0.21</td>
<td>8.44</td>
<td>37.15</td>
</tr>
</tbody>
</table>

**Note:** R_{o,max}, the maximum reflectance of vitrinite; M, moisture; A, ash yield; V, volatile matter; F, fixed carbon; S₄, total sulfur; S, organic sulfur, by difference; C, carbon; H, hydrogen; N, nitrogen; O, oxygen, by difference; d, air-dry basis; d, dry basis; daf, dry ash-free basis; V, Vitrinite; I, Inertinite; L: Liptinite; M, Mineral.
sulfuric acid and 40 mL nitric acid. The mixture was sonicated (30°C) for 2 h and then placed in an oil bath for 24 h at 100°C. After oxidation, the mixture was cooled to room temperature and 5 mol/L sodium carbonate solution was added to adjust the pH to 7, resulting in a clarified brownish-red solution. The solution was dialyzed in 3500 Dalton dialysis bags against ultrapure water for 3 d. During dialysis, the water was changed every 12 hours.

2.3 Characterization

The demineralized coal samples were analyzed using high-resolution transmission electron microscopy (HRTEM). Microgram amounts of coal samples (<200 mesh) were transferred to a mortar, ground for 15 min to a fine powder, and diluted with ethanol under ultrasonic conditions. The samples were deposited on a copper microgrid, and the ethanol was evaporated. HRTEM was performed using a JEM-2100F microscope equipped with a computerized imaging system, operated at 200 kV, with a dot resolution of 0.19 nm and a line resolution of 0.14 nm.

The demineralized coals were scanned with a Rigaku D/max 2500 VK/PC X-ray diffractometer, using Cu Kα radiation at 40 kV and 100 mA with a graphite monochromator. Measurements were recorded from 20 = 10–80° at a scanning speed of 2°/min. The X-ray diffraction (XRD) pattern showed (002) and (100) peaks. The interlayer spacing (d_{002}) was calculated from the (002) peak using Bragg's equation. The mean crystallite height (L_c) and average diameter (L_a) were calculated from the broadening of the Gaussian profiles for the (002) and (110) peaks using Scherrer’s equation (Okolo et al., 2015).

All Fourier transform infrared (FTIR) measurements of demineralized coals were performed using a Nicolet 6700 spectrometer (Thermo Fisher, USA), using the traditional KBr pellet method. To prepare the pellets, the coal samples (approx. 1 mg) were ground to below 200 mesh and mixed with approximately 200 mg of dry KBr. The mixture was molded into a disc. The samples were analyzed at ambient temperature, and spectra were recorded by coadding 32 scans in the range 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹. The corresponding infrared spectrum was obtained, and baseline correction was performed to eliminate scattering effects.

Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100F field emission gun operated at 120 kV with the as-prepared GQDs (in ultrapure water) directly transferred to a C-flat grid and high-resolution TEM was operated at 300 kV. Solid-state FTIR spectra were obtained using a Nicolet FTIR microscope with an MCT/B detector to analyze the functional groups. Solid quantum dot powder was obtained by freeze-drying, and the KBr pellets were prepared as for the coal samples. The scanning range was 400–4000 cm⁻¹. The chemical states of carbon, oxygen, and sulfur were investigated using X-ray photoelectron spectroscopy (XPS) with a 45° takeoff angle and a 100 nm beam size. Ultraviolet-visible (UV-Vis) absorption and fluorescence spectra were recorded using a UV-2450 spectrophotometer and an FLS980 fluorescence spectrometer, respectively, to investigate the fluorescence characteristics of the samples. Yield determination of solid coal-based GQDs by freeze-drying.

The fluorescence QY of the GQDs was determined by comparing the integrated fluorescence intensities (excited at 340 nm) and the absorbances of the GQDs with quinine sulfate in a 10 mM H₂SO₄ aqueous solution, according to the following equation:

\[
Q = Q_r \frac{I_A n_r^2}{I_r A n^2}
\]

Where Q is the QY, I is the measured integrated emission intensity, A is the optical density, and n is the refractive index (1.33 for water). The subscript r refers to the reference. \(Q_r = 0.54\) at 340 nm.

3 Results

3.1 Characterizations of coals

The HRTEM values follow the same trend as the XRD...
results and can thus be compared to investigate the development and variation of aromatic structures in coal (Sharma et al., 2000, 2001; Aso et al., 2004; Castro-Marcano et al., 2012). Origin 8.5 was used to evaluate the parameters of the fitted curves (inset in Fig. 2, using XM as an example), and lattice fringes were directly observed using HRTEM. The HRTEM images were subjected to an image analysis routine that was proposed by Sharma and Fernandez-Alós et al. (Sharma et al., 2000, 2001; Mathews et al., 2010; Nickerk and Mathews, 2010; Fernandez-Alós et al., 2011) to quantify the stacking distribution, layer size distribution, and average layer size.

Figures 3a–3f show the lattice fringes and the corresponding skeletonized images of coals (using FX and HS as examples). The average aromatic lattice parameters are shown in Table 2. Significant differences in the average diameter ($L_a$) were revealed by XRD and HRTEM. Coal is a non-crystalline solid, and the average microcrystalline parameters can be obtained using XRD, but the data obtained by HRTEM are related to local observations, so the results exhibit discrepancies; however, they follow the same trends: that is, the interlayer spacing ($d_{002}$) decreases as the maximum reflectivity of vitrinite increases, as with graphite ($d_{002} = 0.335$ nm); the crystallographic height ($L_c$), average diameter ($L_a$), and the average number of aromatic layers ($N_{av}$) increase with the metamorphism of coal. This is because, during coalification, the aromatic layers of coal become denser and more ordered, the interlayer spacing gradually decreases, and the original significant amounts of disordered amorphous carbon in the coal also gradually decrease (Lu et al., 2001). In addition, for the SHOS coal, HS, the XRD and HRTEM results showed that the decrease in $d_{002}$ and the increases in $L_c$, $L_a$ and $N_{av}$ were abnormally large, which is related to their high organic sulfur content. High concentrations of thiophene sulfur in coal with a higher degree of metamorphism promote cross-linking to join the relatively fragmented aromatic rings together (called cross-linking sulfur) (Brandtzaeg and Øye, 1988; Adjizian et al., 2013). CX coal is also SHOS coal, but because of its low degree of metamorphism, $R_{o, max}$ is only 0.72%, and it has only experienced the first coalification jump ($R_{o, max}$= 0.6%) (Stach and Murchison, 1990; Han Dexin, 1996). The coal body structure is relatively loose and contains more oxygen functional groups, side chains, bridge bonds, and hydrogen bonds and fewer stacked aromatic lamellae in the crystallite basic structural unit (BSU). Thus, organic sulfur is mostly distributed on the aliphatic carbonyl chains or on the edges of the aromatic rings and is unable to cross-link aromatic structures.

The baseline-corrected FTIR spectra of the six demineralized coal samples are shown in Fig. 4. Band assignments based on the standard patterns reported in the literature (Painter et al., 1981; Geng et al., 2009; Zhao Zhengfu et al., 2015) are shown in Table 3. Despite the different coal ranks, the FTIR spectra of all the coal samples were similar, indicating that these samples contain similar organic functional groups (He et al., 2017). Figure 4 shows that aromatic CH stretching and out-of-plane deformation signals at 870 cm$^{-1}$, 815 cm$^{-1}$ and 750 cm$^{-1}$ decrease with increasing metamorphism of coal, it is indicated that the substituents in aromatic system of coal decreases with the increase of metamorphic degree, while the aromatic layer expands continuously. Aliphatic chains at 1375–1450 cm$^{-1}$ and carbonyl/carboxyl C=O stretching at 1712 cm$^{-1}$ vary from strength to weakness until almost disappear in anthracite stage means that the oxygen functional groups and aliphatic chains in coal are unstable and are removed with increase of coal metamorphism. The structures of CX and FX are characterized by the

![Fig. 2. XRD patterns of demineralized coals. The inset shows the curve fitted of XM’s XRD from 10°–60°.](image-url)

<p>| Table 2 Comparison the structure parameters of aromatic layers with XRD and HRTEM |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Samples</th>
<th>$d_{002}$(nm)</th>
<th>$L_c$(nm)</th>
<th>$L_a$(nm)</th>
<th>$N_{av}$(nm)</th>
<th>$d_{002}$(nm)</th>
<th>$L_c$(nm)</th>
<th>$L_a$(nm)</th>
<th>$N_{av}$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JC</td>
<td>0.348</td>
<td>2.430</td>
<td>2.336</td>
<td>1.271</td>
<td>6.983</td>
<td>6.956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XFL</td>
<td>0.351</td>
<td>2.249</td>
<td>2.179</td>
<td>2.077</td>
<td>6.407</td>
<td>6.759</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XM</td>
<td>0.355</td>
<td>2.133</td>
<td>1.576</td>
<td>1.963</td>
<td>6.008</td>
<td>6.229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>0.348</td>
<td>2.846</td>
<td>1.702</td>
<td>1.182</td>
<td>8.178</td>
<td>6.968</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FX</td>
<td>0.364</td>
<td>1.755</td>
<td>1.141</td>
<td>0.776</td>
<td>4.821</td>
<td>5.062</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CX</td>
<td>0.363</td>
<td>1.452</td>
<td>1.420</td>
<td>0.803</td>
<td>4.090</td>
<td>4.651</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3. Original HRTEM micrographs, skeletonized images and lattice fringe-extracted images of FX (a, b, c) and HS (d, e, f).
enrichment of oxygenated functional groups and aliphatic compounds; the aromatic rings and degree of graphitization of HS and XM increased significantly after the strongest aromatization at \( R_{\text{max}} = 1.3\% - 2.0\% \) (Han Dexin, 1996), and the length of aliphatic chains also decreased; the heterocyclic compounds and amorphous carbon structures in XFL and JC almost completely disappeared, the size of the aromatic clusters and graphite crystallites continuously increased, and the microcrystalline structures in XFL and JC were refined, approaching a graphite structure. High concentrations of organic sulfur were also detected in CX and HS coals, such as the -SH absorption peak near 475 cm\(^{-1}\) and the disulfide -S-S- peak at 540 cm\(^{-1}\).

3.2 Characterization of graphene quantum dots

Tunable coal-based GQDs were synthesized by treatment with acids followed by dialysis separation, using different types of coal as the carbon precursor. Figures 5a–5f show typical TEM images of GQDs obtained from coal at 100°C, indicating that these can be prepared from the coals of different ranks that were used in the experiment. Although the particle sizes differ, most GQDs were irregularly round and well dispersed. The GQDs that were synthesized from different types of coal were denoted as GQDs-X, where “X” is the abbreviation for the raw coal. Figures 5a–5f show that, under the same experimental conditions, the sizes of the GQDs prepared using different types of coal were significantly different and were related to the degree of metamorphism. The higher the degree of metamorphism is, the larger the GQDs diameter is. The statistical results obtained using the Nano Measure software demonstrate that the particle size distributions of the six coal-based GQDs are significantly different (Fig. 5g). GQDs-JC and GQDs-XFL, prepared using anthracite JC and XFL, respectively, have the largest size distributions of \( \pm 3 \) to \( \pm 15 \) nm, mainly concentrated between \(-6 \) and \(-9 \) nm; the high-rank bituminous coal-based GQDs-XM and GQDs-HS were significantly smaller at approximately \( 4-6 \) nm, seldom exceeding 10 nm, and layers below 2 nm were observed. The diameters of low-rank bituminous coal-based GQDs-FX and GQDs-CX were below 5 nm; for GQDs-CX, the

### Table 3 Assignment of FT-IR spectrum bands in coal

<table>
<thead>
<tr>
<th>Peak (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>475</td>
<td>thiol -SH</td>
</tr>
<tr>
<td>540</td>
<td>disulfide S-S</td>
</tr>
<tr>
<td>700-900</td>
<td>aromatic structures</td>
</tr>
<tr>
<td>750</td>
<td>1, 2 – Substituted aromatic</td>
</tr>
<tr>
<td>810</td>
<td>Aromatic nucleus CH(_2) two adjacent H deformation</td>
</tr>
<tr>
<td>815</td>
<td>1, 2, 4 – (1, 2, 3, 4 -) Substituted aromatics CH</td>
</tr>
<tr>
<td>880-860</td>
<td>Aromatic nucleus CH(_1) one adjacent H deformation</td>
</tr>
<tr>
<td>1000-1800</td>
<td>oxygen-containing structures</td>
</tr>
<tr>
<td>1380-1375</td>
<td>Aliphatic chains CH(_2) -</td>
</tr>
<tr>
<td>1660</td>
<td>Aliphatic chains CH(_3) – CH(_2) –</td>
</tr>
<tr>
<td>1670-1690</td>
<td>Aromatic ring stretching C-O or C=C</td>
</tr>
<tr>
<td>1720-1690</td>
<td>Conjugated aromatic C=O</td>
</tr>
<tr>
<td>2800-3000</td>
<td>aliphatic structures</td>
</tr>
<tr>
<td>2920-2860</td>
<td>Aliphatic CH(_2) symmetric stretching vibration</td>
</tr>
<tr>
<td>3650-3030</td>
<td>Aromatic nucleus CH stretching vibration</td>
</tr>
<tr>
<td>3330-3800</td>
<td>-OH stretching vibration and NH groups</td>
</tr>
</tbody>
</table>
The total content of GQDs between 1 and 2 nm was above 75%. The experimental results show that, under the same preparation conditions, the degree of metamorphosis of the coal significantly influences the size of the coal-based GQDs. The lower the degree of metamorphism is, the smaller the GQD particle size is.

Single coal-based GQDs can be observed and analyzed using HRTEM. The hexagonal crystal structures of the GQDs are clearly visible in the HRTEM images (Fig. 6). These are also easily seen in the inset two-dimensional (2D) fast Fourier transform (FFT) images, indicating that the coal-based GQDs have higher crystallinity. The inset in the middle above shows the line-profile analysis of the GQDs, in which the distance between two peaks represents the in-plane lattice spacing of 0.2–0.232 nm. The lattice fringe spacing corresponds to the (100) in-plane lattice of graphene (Tang et al., 2012; Zhang et al., 2018). The lattice spacing increases slightly as the coal rank decreases, which indicates that the content of sp² clusters in the lamellae is reduced. A comparison of Fig. 6 showed that the anthracite-based GQDs are larger and the arrangement of carbon rings in their lamellae is dense with...
no defects (GQDs-JC and GQDs-XFL). The 2D FFT image clearly shows a hexagonal crystal structure and symmetrical spots. The high-rank bituminous coal-based GQDs (GQDs-XM and GQDs-IIS) are relatively smaller, and distinct crystalline domains and the lattice direction can be observed. The hexagonal crystal structure of GQDs-HS in the 2D FFT image is only faintly visible, and symmetrical spots are difficult to determine. Low-rank bituminous coal-based GQDs (GQDs-FX and GQDs-CX) are tiny and only faintly visible under HRTEM. The hexagonal crystal structures in the 2D FFT images are almost invisible. Visible internal defects remain in the highly volatile bituminous coal-based GQD layers, as indicated by the purplish-red circle in Fig. 6 (GQDs-FX and GQDs-CX). The measured lattice spacings are 0.487 nm and 0.489 nm, respectively, indicating a pentagon-heptagon pair or a monovacancy defect (Hashimoto et al., 2004; Liu Lili et al., 2015). In addition, the arrangement of the lattice fringes of GQDs-CX is sparse due to the low metamorphism of raw coal CX, so the orientability is uncertain (see the yellow line in Fig. 6).

The effectiveness of different types of coal-based GQDs was evaluated by studying their photophysical properties using UV-Vis and fluorescence spectroscopy. The UV-Vis absorption spectra are shown in Fig. 7a. The GQDs exhibit a primary emission peak at 200 nm due to the π–π* transition of sp² bonding C=C and a weak shoulder at 280 nm assigned to the n–π* transition of the heteroatom double bond (C=O) (Pan et al., 2010); these are similar to those of the reported coal-based GQDs (Hu et al., 2014) but exhibit a blue shift of about 30 nm compared with other carbon-based GQDs (Li et al., 2013). The UV-Vis spectra of GQDs were reported to reveal a size-dependent optical absorption known as the quantum size effect (Li et al., 2013). However, in Fig. 7a, the two absorption peaks are independent of the size, similar to the glucose-based GQDs (Tang et al., 2012). This is not uncommon, as the different preparation methods and carbon sources can lead to GQDs with different absorption behaviors, or the excitation energy might be transferred to nonemissive percolated sp³ carbon (Hu et al., 2014), but the mechanism is unclear. The intensity of UV-Vis absorption depends on the solution’s concentration; that is, the higher the concentration, the higher the absorption strength (Li et al., 2014); this is not discussed here. Figure 7b shows the fluorescence properties of six GQDs excited at 340 nm; the fluorescence emission peaks of GQDs-JC, GQDs-XFL, GQDs-XM, GQDs-HS, GQDs-FX, and GQDs-CX are at 550, 570, 510, 530, 455 and 465 nm, respectively, corresponding to the blue-green and blue emission shown.
in the inset photograph in Fig. 7b. Larger GQDs tend to emit at longer wavelengths, whereas the emission of smaller GQDs is blue-shifted, in accordance with the quantum confinement effect. In addition, the light emission mechanisms of GQDs are also affected by edge functionalities and defect effects (Alivisatos, 1996; Li et al., 2013). Notably, the degree of metamorphism of raw coal HS is lower than that of XM, but the fluorescence spectrum of GQDs-HS shows a slight red shift compared with that of GQDs-XM, and its intensity is higher than that of GQDs-XM, suggesting that sulfur might be present in GQDs-HS.

Figure 7c shows that the lower the degree of metamorphism of the coal-based precursor, the lower the yield of GQDs, which can be explained in terms of the
content and size of crystallites in different coal ranks. The lower graphene sheet content and smaller size in low-rank coal cause the yield to naturally decrease after decomposition into GQDs. The change in the fluorescence QY is different from that of the production yield: it first increases and then decreases as the degree of metamorphism increases, reaching the highest level for GQDs-HS. This is basically in accordance with a rule stating that the QY increases with increasing quantum dot size (Ye et al., 2015), but the QY of GQDs-HS increases more than expected. The QY of anthracite-based GQDs (GQDs-JC and GQDs-XFL) is the smallest, below 1.5%, which is attributed to larger layers, fewer surface defects (Ye et al., 2015), and an aggregation quenching effect from stacking of polyaromatic structures (Hong et al., 2009), which consequently become less emissive. The high-rank bituminous coal-based GQDs-XM exhibited a QY that is more than three times that of anthracite-based GQDs, largely because of the relatively small BSUs and degree of defects in low-volatility bituminous coal with comparably low rank, leading to enhancement of the emission from GQDs. The QY of low-volatility bituminous coal-based GQDs-HS reached 9.12%, which is comparable to that of reported S-doped GQDs (Li et al., 2014). From this, we believe that sulfur is doped in the inner layer of GQDs-HS. Sulfur is a strong electron donor and can be involved in the development of π-conjugated structures, which promote electron-hole recombination and increase the QY. Low-rank bituminous coal-based GQDs (GQDs-FX and GQDs-CX) have a QY that is lower than that of GQDs-HS but higher than that of anthracite-based GQDs, which is believed to be because low-rank coal usually contains more amorphous carbon. Even after acid oxidation, it showed no luminescence. Two points should be noted: First, CX is also a SHOS coal, but GQDs-CX shows no abnormal fluorescence effects. This is because CX is a low-rank bituminous coal with a loose and porous structure that is rich in side chains and bridge bonds (Brandzeg and Oye, 1988), and most of the organic sulfur is distributed on the aliphatic carbon chains or on the edges of aromatic rings and is easily removed by removing side chains or functional groups during acid oxidation and filtered out during the subsequent dialysis. Thus, there should be no organic sulfur on the surface of GQDs-CX. Second, although HS is a SHOS coal and its high organic sulfur content plays a role in cross-linking relatively dispersed aromatic rings (Adzijian et al., 2013; Bourrat et al., 1987), the yield of GQDs-HS appears to be normal. This shows that organic sulfur does not affect the yield of coal-based GQDs.

The differences between GQDs-HS and GQDs-CX were analyzed using XPS to verify the above analysis. The full-scan XPS spectra of GQDs-HS and GQDs-CX show a predominant graphitic C1s peak at 284 eV and an O1s peak at 532 eV (Fig. 8a). In addition, a pronounced S 2p peak was detected for GQDs-HS at 168 eV, whereas no signal was detected for GQDs-CX. This indicates that the organic sulfur in the raw coal CX was effectively removed and also shows that the sulfur in sulfurous acid was not introduced into the quantum dots during thermal oxidation. So we can draw a conclusion that the sulfur on the surface of GQDs-HS originates from the organic sulfur in the raw coal HS. The XPS survey spectrum of the GQDs-HS shows the presence of S, C, and O with atomic percentages of 3.41%, 72.45%, and 24.14%. The C1s XPS spectrum of GQDs-HS was deconvoluted into five peaks (Fig. 8b), centered at 284.5 eV (C–C), 285.5 eV (C–C–H), 286.2 eV (C–OH), 287.9 eV (C–O–C, C–S), and 288.6 eV (C–O) (Li et al., 2014). In the S 2p XPS spectra (Fig. 8c), the peaks located at 163.9 eV and 165.5 eV are 2p1/2 and 2p3/2, respectively, of thioephene sulfur because of spin-orbit coupling, and the peak located at 168.0 eV is attributed to oxide -O-S, whereas that at 169.9 eV corresponds to sulfate (Yang et al., 2012; Li et al., 2014; Li et al., 2015). Sulfate is derived from the partial oxidation of organic sulfur in coal, which remains in the solution and is incompletely removed. Excluding the sulfate, two forms of organic sulfur doped on the surface of GQDs-HS were confirmed, in which a small amount of sulfur existed as thioephene-like sulfur (green and blue, Fig. 8c), most of which was sulfone (pulpish red, Fig. 8c). This proved that the surface of GQDs-HS remained rich in sulfur after oxidation with strong acid, which could effectively adjust the bandgap and improve the fluorescence QY. Sulfone is the main component of organic sulfur in S-doped GQDs, indicating that the original organic sulfur in coal only promotes cross-linking to combine the relatively dispersed aromatic lamellae. However, after prolonged strong acid oxidation, the cross-linked aromatic lamellae were also decomposed, and the cross-linking sulfur was decomposed to sulfur oxides and distributed on the edges of GQDs or dissolved in solution and then dialyzed. Furthermore, a small amount of thioephene sulfur was preserved after acidification and existed in the GQD lamellae.

4 Discussion

These results demonstrate that GQDs can be successfully prepared with the six selected coals, as they contain BSUs made up of overlapping layers of aromatic rings. After oxidation with a strong acid, the heteroatoms, side chains, and a variety of functional groups in coal were
destroyed. Aromatic rings are stable and difficult to oxidize at low temperature, so they were reserved to form GQDs. A study on coal structure (Wang et al., 2017) revealed that low- and medium-rank coals contain more oxygen functional groups, side chains, bridge bonds and hydrogen bonds, and they have loose structures with few-layer and small aromatic rings in BSUs; the prepared GQDs are small with many defects and a loose arrangement of benzene rings due to the poor orientation of the aromatic lamellae in coal. During coalification, the coal structure undergoes carbon enrichment, hydrogen elimination and deoxidation. Molecular rearrangement, aggregation, order enhancement and BSU expansion are achieved by aromatization and condensation (Han Dexin, 1996). Therefore, in the anthracite stage, the BSU already has a higher degree of order and the prepared GQD has a larger slice size and a completely hexagonal crystal structure.

5 Conclusions

Coal-based GQDs represent a new research field. Understanding the effects of coal characteristics on the yield and QY of coal-based GQDs will facilitate process design and improvement. This paper on the effects of the degree of metamorphism and high organic sulfur on coal-based GQDs indicates the following:

(1) Coal-based GQDs can be successfully prepared with the six selected coals; most of the GQDs are irregularly round and well dispersed in aqueous solutions and can emit blue-green or blue fluorescence under UV irradiation. Under the same conditions, the sizes are closely related to the coal properties: anthracite-based GQDs have the largest size distributions of ~3 to ~15 nm, mainly concentrated in the range 6–9 nm; the high-rank bituminous coal-based GQDs are significantly smaller at approximately 4–6 nm, seldom exceeding 10 nm, and layers below ~2 nm were observed; the diameters of low-rank bituminous coal-based GQDs are below 5 nm; for GQDs-CX, the total content of GQDs between 1 and 2 nm is above 75%.

(2) As the raw coal rank decreases, the dense carbon ring arrangement of coal-based GQDs loosens, the hexagonal structure becomes obscure, and the content of sp² clusters in the lamellae is reduced, creating a pentagon-heptagon pair or a monovacancy defect. As the metamorphism of coal-based precursors increases, the yield decreases and the fluorescence QY first increases and then decreases.

(3) The SHOS coal with a higher degree of metamorphism retains its rich sulfur content after oxidation with strong acid; this effectively adjusts the bandgap and improves the fluorescence QY, which mainly exist in the aromatic rings with covalent bonds. A small fraction of the sulfur content is thiophene, most of which is sulfone. Thus, high-rank bituminous coal with SHOS content can be used as a natural S-doped carbon source to prepare S-doped GQDs, thereby extending the clean utilization of low-grade coal.

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