Variability and improvement of optical and antimicrobial performances for CQDs/mesoporous SiO$_2$/Ag NPs composites via *in situ* synthesis

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Abstract: To change the optical properties and improve the antibacterial performances of carbon quantum dots (CQDs) and Ag NPs, mesoporous SiO$_2$ spheres were combined with them to form the composites. In this paper, CQDs with a uniform size of about 3.74 nm were synthesized using glucose as carbon source. Then, CQDs/mesoporous SiO$_2$/Ag NPs composites were obtained *in situ* under UV light irradiating by using mesoporous SiO$_2$ and Ag NO$_3$ as the carrier and silver resource, respectively. The diameter of CQDs/mesoporous SiO$_2$/Ag NPs particles was in the range of 200–250 nm. With the increase in irradiating time, the red-shift in the UV-Vis spectrum for as-prepared CQDs/mesoporous SiO$_2$/Ag NPs composites was found, and the adsorption peak was widened. In addition, the composites showed a high antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* via disc diffusion method. These results indicated that inhibition circles for Ag NPs/mesoporous SiO$_2$/CQDs and mesoporous SiO$_2$/Ag NPs were similar in diameter. Furthermore, the two composites had a better bactericidal performance compared with other particles. Therefore, as-prepared CQDs/mesoporous SiO$_2$/Ag NPs composites in this paper have great potential applications for fluorescent materials and antimicrobial materials.

Keywords: silver nanoparticles, carbon quantum dots, mesoporous silicon dioxide, antimicrobial performances

1 Introduction

Raw materials of carbon quantum dots (CQDs) are very rich, and they showed low toxicity, good biocompatibility, multicolor fluorescence, excellent conductivity, and catalytic performances [1–6]. Compared with conventional semiconductor quantum dots, CQDs also had large specific surface area and exhibited strong fluorescence [7–10]. Moreover, CQDs, acting as both electron donors and electron acceptors, can be used as the oxidizer and reductant. Interestingly, the fluorescence for the system quenched when electron donor and acceptor were concurrent in the composites containing CQDs [11–13].

Ag NPs had excellent electrical and thermal conductivity, catalytic performances, antibacterial performances, and so on [14]. To the best of our knowledge, CQDs/Ag NPs composites are effective antibacterial materials in food packaging by using the synergistic effect of CQDs and Ag NPs. Besides, they can be applied in environmental protection and anti-counterfeiting [15]. Wang and coworkers synthesized core-shell structured CQDs/Ag NPs composites with the size of 40–80 nm, having a good monodispersity [16]. Zhao and coworkers prepared CQDs/Ag NPs composites consisting of CQDs well dispersed on the surface of Ag NPs [7]. For synthesizing CQDs/Ag NPs composites, reductants were essential, and surfactants were often used. As far as we know, the utilization efficiency would decrease drastically if materials had a poor stability [9]. Therefore, it is the key to control the stability of composites containing Ag NPs for building antibacterial materials [17].

Mesoporous SiO$_2$ particles had good optical transparency, biocompatibility, and high chemical inertness; thus, they were frequently used in preparing core-shell structured materials. Ge and coworkers synthesized mesoporous SiO$_2$ supported by Ag NPs and graphene quantum dots (GQDs), providing a highly reactive surface enhanced Raman scattering substrate [18]. Importantly, the solution
of GQDs prepared by the electrochemical method can be used as the reductant for in situ synthesis of Ag NPs/GQDs composites under UV irradiating.

Inspired by aforementioned studies, mesoporous SiO$_2$ spheres were used to improve the stability of as-prepared CQDs in this paper. Meanwhile, CQDs/mesoporous SiO$_2$/Ag NPs composites were prepared by using CQDs as the reductant. Interestingly, compared with Ag NPs and CQDs, CQDs/mesoporous SiO$_2$/Ag NPs composites showed variable optical properties and excellent antibacterial performances.

2 Experimental

2.1 Materials

Glucose was purchased from Kemio (Tianjin) Chemical Reagent Co., Ltd. Ag NO$_3$ particles were obtained from North China Petrochemical Co., Ltd. CTAB was purchased from Tianjin Windward Chemical Reagent Co., Ltd. Urea was purchased from Tianjin Yongsheng Fine Chemical Co., Ltd. Glycerol was purchased from Tianjin Fuchen Chemical Reagent Factory. Tetraethyl orthosilicate (TEOS) was purchased in a photochemical reactor. Brieﬂy, 0.6 g of glucose was dissolved in 90 mL of deionized water, and the mixture was transferred to a 100 mL teflon-lined autoclave and heated at 180°C for 24 h. Then, the reactor was cooled to room temperature naturally. Finally, obtained mixtures were centrifuged at 6,000 rpm for 15 min, and the precipitate was washed thrice with ethanol and once with deionized water. The white product was dried at 80°C for 5 h and then calcined at 540°C for 4 h to obtain mesoporous SiO$_2$ spheres.

For synthesizing CQDs/mesoporous SiO$_2$ composites, 0.075 g of as-prepared mesoporous SiO$_2$ was added to 5 mL of above CQDs solution with stirring for 2 h. The mixtures were centrifuged and then dried in a vacuum oven at 80°C for 12 h to obtain CQDs/mesoporous SiO$_2$ composites.

2.4 Synthesis of CQDs/mesoporous SiO$_2$/Ag NPs

CQDs/mesoporous SiO$_2$/Ag NPs composites were prepared in a photochemical reactor. Brieﬂy, 5 mg of AgNO$_3$, 10 mL of CQDs solution, and 10 mL of deionized water were mixed with stirring for 20 min, and then placed in the photochemical reactor under UV irradiating with the power of 200 W. The irradiating time was set as 10, 20, and 30 min, respectively, and different samples of CQDs/mesoporous SiO$_2$/Ag NPs composites were obtained.

2.5 Characterization

Morphologies of CQDs, CQDs/mesoporous SiO$_2$, and CQDs/mesoporous SiO$_2$/Ag NPs were observed by transmission electron microscope (TEM, JEOL-2010, Japan). The specimens for TEM were prepared by dropping the solution containing samples on a copper grid and dried under an infrared lamp. The structure of CQDs was investigated by an X-ray diffractometer (Shimadzu XRD-7000, Japan) in the scanning range of 10–80°. Functional groups for CQDs were characterized by a Fourier infrared spectrometer (FTIR, SHIMADZU 8400S, Japan) using potassium bromide as the matrix in the range of 500–4,000 cm$^{-1}$. Optical performances were investigated by using an UV-Vis spectrometer (SHIMADZU UV-1800, Japan) and a ﬂuorescence spectrometer (HITACHI, F-4600, Japan), and the samples were diluted before testing. All measurements were performed at room temperature.
2.6 Antimicrobial test

Antibacterial effects of CQDs/mesoporous SiO$_2$/Ag NPs against *E. coli* and *S. aureus* were verified by the inhibition zone method. Briefly, 16.5 g of agar was dissolved in 500 mL deionized water at 100$^\circ$C, and then 10–15 mL of agar solution was taken to drop to the petri dish. Meanwhile, *E. coli* and *S. aureus* were dissolved in sterile deionized water and diluted to make sure that the bacteria concentration was in the range of 10$^6$–10$^8$ cfu/mL. After the agar was solidified, an inoculating loop was used to scrape as-prepared *E. coli* and *S. aureus* solution and spread them on the solidified agar petri dish. Then, filter papers (the diameter of 6 mm) containing samples were placed on agar petri dishes. Finally, as-prepared petri dishes were put in a box (the temperature of 37$^\circ$C and the humidity of 70%) for 24 h to observe the growth of bacteria around filter papers. All equipment in the experiment was sterilized and the whole process was operated under aseptic conditions.

3 Results and discussion

3.1 Morphologies and optical performances of CQDs and CQDs/mesoporous SiO$_2$ composites

TEM image of as-prepared CQDs is shown in Figure 1a, and they were near-spherical particles. In addition, the lattice spacing of (020) for CQDs (upper right inset in Figure 1a) was about 0.275 nm. According to Figure 1a, we counted the diameter of about 500 CQDs using Nano Measure software, and the size distribution is shown in Figure 1b. According to the result in Figure 1b, the particle size of most CQDs was in the range of 3–4 nm and the average diameter was about 3.74 nm. Thus, these results indicated that as-prepared CQDs with graphite like microcrystal had a small and relatively uniform size.

To further characterize the synthesized CQDs, as-prepared solution containing CQDs was freeze-dried, and
obtained solids were characterized by XRD. As shown in Figure 1c, there was a broad peak in the range of 2θ = 20–30°, indicating (002) lattice plane for synthesized CQDs. The wide peak at 3,450 cm⁻¹ was ascribed to the stretching vibration of –OH. In addition, the peaks at 1,600 and 1,100 cm⁻¹ were attributed to the stretching vibration of C=O and the stretching vibration of C–H, respectively. These peaks corresponded to the characteristic functional groups for CQDs.

As shown in Figure 2a, as-prepared mesoporous SiO₂ spheres had a uniform size of about 200 nm. According to TEM image of CQDs/mesoporous SiO₂ composites (as shown in Figure 2b), we observed that CQDs were wrapped around SiO₂ by electrostatic interaction [19]. The illustration of the synthesis of CQDs/mesoporous SiO₂ composites is shown in Scheme 1.

To the best of our knowledge, CQDs usually exhibited characteristic absorption peaks in the range of 250–390 nm in UV-Vis spectra. As shown in Figure 3a, the UV-Vis absorption peak for CQDs located at around 260 nm because of the π–π* transition of C=C, while there were two peaks at around 290 and 400 nm for CQDs/mesoporous SiO₂ composites. The absorption peak at about 290 nm was because of the n–π* transition of C=O for CQDs in composites [20]. In addition, CQDs/mesoporous SiO₂ composites had a broad absorption line near 400 nm, which may be caused by the optical effect of mesoporous SiO₂ spheres [21,22].

According to the previous report, the fluorescence emission peak in the range of 300–500 nm belonged to the characteristic emission of CQDs [23]. As shown in Figure 3b, the strongest peak for CQDs was 375 nm at the excitation wavelength of 300 nm, and that for CQDs/mesoporous SiO₂ composites located at 365 nm. The latter containing CQDs with smaller size had a blue-shift, which was mainly attributed to the quantum size effect [24–26]. On the contrary, the intensity of fluorescence emission for the composites was greatly enhanced, which may be because of the reduction of surface defects for CQDs/mesoporous SiO₂, and the non-radiative transition also had less probability [27–30].

3.2 Morphologies and optical performances of CQDs/mesoporous SiO₂/Ag NPs

TEM images of CQDs/mesoporous SiO₂/Ag NPs obtained in photochemical reactor for different UV irradiating time are shown in Figure 4a–c. We found that the diameter of as-prepared Ag NPs was about 10 nm, and Ag NPs and CQDs mainly distributed on the surface of mesoporous

![Figure 2](image-url)  
**Figure 2:** TEM images of (a) as-prepared mesoporous SiO₂ particles and (b) CQDs/mesoporous SiO₂ composites.

![Scheme 1](image-url)  
**Scheme 1:** Schematic diagram for the synthesis of CQDs/mesoporous SiO₂.
SiO$_2$ spheres. Compared with Figure 4a, the particle size of Ag NPs as shown in Figure 4b and c was more uniform, and the amount changed to be more inferring that the concentration of obtained Ag NPs was higher under a longer UV irradiating time. These results indicated that the irradiation time plays an important role in the formation and the morphology of CQDs/mesoporous SiO$_2$/Ag NPs composites. The illustration of the formation of CQDs/mesoporous SiO$_2$/Ag NPs composites is shown in Scheme 2.

As shown in Figure 5a, the absorption peak of CQDs/mesoporous SiO$_2$/Ag NPs composites showed gradual blue-shift, and the absorption band was narrowed with the increase in UV irradiating time. This may be because of more uniform size and higher concentration of Ag NPs in the composite solution consistent with the result of TEM analysis [31].

Figure 5b shows that the wavelength for the fluorescence emission peak of composites basically remained constant. To the best of our knowledge, the wavelength of fluorescence emission for Ag nano clusters (Ag NCs) was around 530 nm, and the intensity was proportional to the concentration of Ag NCs in composites [32,33], similar to that obtained in this paper. In addition, there was a fluorescence emission peak at about 375 nm under the excitation wavelength of 300 nm, corresponding to the fluorescence emission peak of CQDs. This result was basically consistent with that in Figure 3b. As-prepared CQDs/mesoporous SiO$_2$/Ag NPs composites under UV irradiating for 30 min were selected as the specific sample for the antibacterial test because of the excellent optical performances.

### 3.3 Antibacterial performances of CQDs/mesoporous SiO$_2$/Ag NPs

The inhibition zones for as-prepared five antibacterial agents against *E. coli* and *S. aureus* are presented in Figure 6a and b, respectively. The initial concentration

![Figure 3](image)

**Figure 3**: (a) UV-Vis spectra of CQDs and CQDs/mesoporous SiO$_2$, and (b) fluorescence emission spectra of CQDs and CQDs/mesoporous SiO$_2$.

![Figure 4](image)

**Figure 4**: TEM images of CQDs/mesoporous SiO$_2$/Ag NPs composites in photochemical reactor for different UV irradiating time: (a) 1 h, (b) 2 h, and (c) 3 h.
Scheme 2: Schematic diagram for the synthesis of CQDs/mesoporous SiO$_2$/Ag NPs.

Figure 5: (a) UV-Vis spectra and (b) fluorescence emission spectra of as-prepared CQDs/mesoporous SiO$_2$/Ag NPs composites in photochemical reactor for different UV irradiating time.

Figure 6: Representative images of agar plates containing (1) CQDs/mesoporous SiO$_2$/Ag NPs, (2) Ag NPs, (3) mesoporous SiO$_2$/Ag NPs, (4) CQDs/mesoporous SiO$_2$, and (5) CQDs, and inhibition zones for (a) E. coli and (b) S. aureus (diluted 10 times (I), 10$^2$ times (II), and 10$^3$ times (III), respectively).
of E. coli and S. aureus was diluted 10 times (I), 10² times (II), and 10⁵ times (III), respectively. Antibacterial performances for these antibacterial agents were estimated by the size of inhibition zone. We found that CQDs/mesoporous SiO₂/Ag NPs and mesoporous SiO₂/Ag NPs composites showed excellent antibacterial performances against E. coli and S. aureus. To the best of our knowledge, sole Ag NPs possessed good antibacterial properties without any modification. The antibacterial mechanism for Ag NPs may be that Ag⁺ on the surface of nanoparticles can interact with sulfhydryl and amino groups of DNA molecules; thus, bacteria cells failed to divide and proliferate and eventually die [34,35]. In addition, Ag NPs can be freely diffused into the culture medium and act as fungicides. In previous reports, CQDs have been used to synthesize the composites containing metal NPs and also can improve the stability of Ag NPs [36–39]. Ag⁺ attached on mesoporous SiO₂ microspheres easily interacted with bacterial cells; therefore, CQDs/mesoporous SiO₂/Ag NPs and mesoporous SiO₂/Ag NPs composites also exhibited excellent antibacterial performances [40–42].

Compared with other samples, the antibacterial performance for solo CQDs was poor. However, that for CQDs/mesoporous SiO₂ was significantly improved by loading CQDs. According to the characteristics of composites, many –OH groups on the surface of mesoporous SiO₂ spheres have a strong activity. Therefore, they were used as carriers to adsorb antibacterial ions to achieve the sterilization [42,44]. Interestingly, the antibacterial activity of CQDs/mesoporous SiO₂/Ag NPs composites against E. coli was greater than that against S. aureus. This result may be because of the fact that Ag NPs eliminated the random distribution of DNA in E. coli, and the degradation of total DNA in E. coli was better than that in S. aureus [33,34]. According to the antibacterial effects against different dilutions of E. coli and S. aureus, we inferred that as-prepared composites can possess stable and effective antibacterial activity for E. coli and S. aureus.

4 Conclusion

In this work, glucose was used as the carbon source to synthesize CQDs via a hydrothermal method, and then mesoporous SiO₂ microspheres were used as carriers to prepare CQDs/mesoporous SiO₂/Ag NPs composites in a photochemical reactor. Compared with CQDs, optical properties of CQDs/mesoporous SiO₂/Ag NPs composites changed significantly, and the fluorescence intensity increased with the increase in UV irradiating time. In addition, mesoporous SiO₂/Ag NPs and CQDs/mesoporous SiO₂/Ag NPs composites showed a high stability and a strong antibacterial activity against both E. coli and S. aureus, which were similar to that for Ag NPs. Therefore, as-prepared CQDs/mesoporous SiO₂/Ag NPs composites in this paper can be used as potential candidate materials for antibacterial packaging.

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