Preparation of Highly Catalytic N-Doped Carbon Dots and Their Application in SERS Sulfate Sensing

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Received: 10 August 2018; Accepted: 3 September 2018; Published: 7 September 2018

Abstract: Carbon dots (CD) have excellent stability and fluorescence activity, and have been widely used in fluorescence methods. However, there are no reports about using CD as catalysts to amplify SERS signals to detect trace sulfate. Thus, preparing CD catalysts and their application in SERS sulfate-sensing are significant. In this article, highly catalytic N-doped carbon dots (CDN) were prepared by a hydrothermal procedure. CDN exhibited strong catalysis of the gold nanoparticle (AuNP) reaction between HAuCl4 and H2O2. Vitoria blue 4R (VB4R) has a strong SERS peak at 1614 cm−1 in the formed AuNP sol substrate. When Ba2+ ions were added, they were adsorbed on a CDN surface to inhibit the CDN catalytic activity that caused the SERS peak decreasing. Upon addition of analyte SO42−, a reaction with Ba2+ produced stable BaSO4 precipitate and CDN, and its catalysis recovered to cause SERS intensity increasing linearly. Thus, an SERS method was developed for the detection of 0.02–1.7 µmol/L SO42−, with a detection limit of 0.007 µmol/L.

Keywords: N-doped carbon dots; catalysis; gold nanoreaction; SERS

1. Introduction

Because carbon dots (CD) have excellent stability, excellent chemical properties, high fluorescence activity, anti-photobleaching abilities and low cell toxicity [1–5], they are of interest to scientists. Based on the redox, complex, enzyme and immune reactions, CD have been used to determine chlorine ion, phosphate, ATP, ferric ion, hydrogen peroxide, glucose, immunoglobulin G, biological thiols, deoxyribonucleic acid, trypsin and so on [6–11]. Freire et al. [12] used polyvinyleimine to prepare carbon quantum dots (CQDs/BPEI) to detect proteins. The nitrogen-doped carbon dots with high fluorescence efficiency have attracted much attention. Liu et al. [13] prepared nitrogen-doped graphene quantum dots and a photoelectrochemical aptasensor for chloramphenicol determination. Gu et al. [14] used 2-azidoimidazole and ammonia as reactants to prepare a fluorescent quantum dots by a thermal procedure, and to determine cysteine (Cys) by the reaction of CD-Cu2+-Cys. An aptamer has good electivity and has been combined with CD. Feng et al. [15] reported a graphene quantum dots-aptamer fluorescent probe to detect lead (II) ions (as low as 0.6 nmol/L). However, there are no reports about preparation of highly catalytic N-doped carbon dots and their application to SERS quantitative analysis.

SERS is a highly sensitive and selective molecular spectral technique; it has been used in biomedical, environmental monitoring, and analytical chemistry [16–18]. Liang et al. [19] prepared silver nanorods/reduced graphene oxide (AgNR/rGO) nanosol as SERS substrate to determine
8–1500 nmol/L iodide. Yang et al. [20] prepared silver nanosol SERS substrate to determine 2–191.0 mg/L thiocyanate. Luo et al. [21] prepared triangular nanosilver based on graphene oxide catalysis, and the nanosilver was used to analysis of 0.7–72 nmol/L nitrite by SERS. Jiang et al. [22] examined the catalytic reduction of HAuCl$_4$ by cysteine with AuNP nanoenzyme to prepare gold nanosol substrate with high SERS activity to determine surfactants. Zhang et al. [23] developed a SERS method for detection of SO$_2$ with a detection limit of 1 mg/L, based on the Raman peak at 630 cm$^{-1}$ of S atom. Shang et al. [24] prepared silver nanochain (AgNC) sol substrate to analyze 0.00725–0.3 µmol/L hexametaphosphate. Sulfate is one of the important anions in water science, food science, soil chemistry, biology, mineralogy and related disciplines. For analysis of trace SO$_4^{2-}$, there are visible–ultraviolet spectrophotometry, turbidimetry, fluorescence spectrophotometry, electrochemical analysis, radiochemical analysis, resonance Rayleigh scattering, ion chromatography, and so on [25–30].

In this experiment, highly catalytic N-doped carbon dots were prepared for the HAuCl$_4$-H$_2$O$_2$ reaction, and a new and sensitive SERS quantitative analysis method was proposed for the determination of sulfate in water and beer samples, based on the CD catalysis.

2. Materials and Methods

2.1. Apparatus and Reagents

The SERS spectra were recorded by a model of DXR smart Raman spectrometer (Thermo, Waltham, MA, USA) with laser wavelength of 633 nm, power of 3.5 mW, slit of 50 µm and acquisition time of 5 s. A model of 3K-15 high-speed refrigerated centrifuge (Sigma Co., Darmstadt, Germany) and a model of 79-1 magnetic stirrer with heating (Zhongda Instrumental Plant, Jiangsu, China) were used. A model of S-4800 field emission scanning electron microscope (Hitachi High-Technologies Corporation, Japan/Oxford Company, Oxford, UK) was used to record the graphs.

A 2.9 mmol/L HAuCl$_4$ (National Pharmaceutical Group Chemical Reagents Company, Shanghai, China), 10 µmol/L VB4R (Shanghai Reagent Three Factory, Shanghai, China) stock solution, 1 mmol/L BaCl$_2$ (Hunan Reagent Factory, Changsha, China), 1.00 mmol/L Na$_2$SO$_4$ (Xilong Science Co., Ltd., Shantou, China) and 3.4 mmoL/L trisodium citrate (Xilong Chemical Plant, Shantou, China) were prepared.

Preparation of N-doped carbon dot solution (CD$_N$): A 1 g of citric acid and 0, 0.5, 1.0 and 2.0 g urea were dissolved respectively in 30 mL water, and the brown yellow transparent solution was transferred to a polytetrafluoroethylene autoclave. After sealing, the autoclave was heated at 180 °C for 5 h. It was cooled to room temperature with tap water and was dialysis a night with dialysis bag of 3500 Da, and neutralized with NaOH solution to pH 7.0 to get a 0.021 g/mL CD$_N$ that was named as CD$_{0N}$, CD$_{0.5N}$, CD$_{1N}$ and CD$_{2N}$ respectively.

2.2. Procedure

In a 5 mL graduated test tube, an appropriate amount of Na$_2$SO$_4$, 80 µL 1 mmol/L BaCl$_2$ and 75 µL 100 µg/mL CD were added and mixed well. Then 100 µL 0.1% HAuCl$_4$ and 50 µL 0.10 mol/L H$_2$O$_2$ solution were added and diluted to 1.5 mL. The tube was heated at 50 °C water bath for 20 min, cooled with ice-water, and 50 µL10 µmol/L VB4R molecular probe was added. The SERS spectrum was recorded by the spectrometer. The SERS peak intensity at 1614 cm$^{-1}$ ($I_{1614cm^{-1}}$) and a blank ($I_{1614cm^{-1}}$)$_0$ without SO$_4^{2-}$ were recorded. The value of $\Delta I = I_{1614cm^{-1}} - (I_{1614cm^{-1}})_0$ was obtained.

3. Results and Discussions

3.1. Principle

The AuNP reaction was very slow, and the CD$_{1N}$ surface contained more surface electrons that enhanced the electron transfer of the HAuCl$_4$-H$_2$O$_2$ redox reaction, and displayed strong catalytic activity on the AuNP reaction. The Ba$^{2+}$ ions adsorb on the CD$_{1N}$ surface and repress the catalysis.
When $SO_4^{2-}$ was added, stable $BaSO_4$ formed and $CD_{1N}$ was released which caused the SERS peak to increase due to formation of more SERS active gold nanoparticles. The more $SO_4^{2-}$ was added, the more CD was released, the more Au nanoparticles formed, and the SERS signal enhanced greatly after addition of probe VB4R. Accordingly, a new SERS quantitative analysis method was proposed for trace sulfate, based on the regulation of $CD_{1N}$ catalysis (Figure 1).

3.2. SERS Spectra

Compared to common carbon nanomaterials such as graphene and C$_{60}$, CD are very stable and dissolved in water, and were chosen for use. The $CD_{0N}$, $CD_{0.5N}$, $CD_{1N}$ and $CD_{2N}$ analytical systems were studied by an SERS technique with VB4R molecular probes. There are nine SERS peaks at 240, 432, 675, 800, 1175, 1202, 1290, 1394 and 1614 cm$^{-1}$ (Figure 2). With the $SO_4^{2-}$ concentration increasing, the SERS signal increased greatly. Among the four systems, the $CD_{1N}$ analytical system at 1614 cm$^{-1}$ SERS peak is the most sensitive. Thus, it was chosen to detect $SO_4^{2-}$.

3.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM, Hitachi High-Technologies Corporation, Japan/Oxford Company, Oxford, UK) and energy spectra of $CD_{1N}$ show that the small CD particles are spherical.
with an average size of 20 nm (Figure 3a) and the large aggregate may be the salt crystallization on the silicon wafer of SEM. There is a spectral peak at 0.25 keV for C, N and O elements. The SEM of HAuCl$_4$-H$_2$O$_2$-CD$_{1N}$-Na$_2$SO$_4$-BaCl$_2$-VB4R was recorded. When there is no Na$_2$SO$_4$, the HAuCl$_4$-H$_2$O$_2$ reaction is very slow to produce few quasi spherical AuNPs with an average size of 50 nm (Figure 3b); the morphology is not like the CD$_{1N}$, and there is a spectral peak at 1.7 keV for Au. When Na$_2$SO$_4$ was added (Figure 3c), there were more AuNPs with an average size of 40 nm owing to CD$_{1N}$ catalysis recovering and enhancing the SERS peak. This also indicated that the particles are AuNPs in the analytical system.

![Figure 3a](image-a.png)

(a)

![Figure 3b](image-b.png)

(b)

![Figure 3c](image-c.png)

(c)

**Figure 3.** Scanning electron microscopy of the CD$_{1N}$ analytical system. (a): 50 µg/mL CD$_{1N}$; (b): 4.2 µmol/L HAuCl$_4$ + 0.33 µmol/L VB4R + 5 µg/mL CD$_{1N}$ + 2.5 mmol/L H$_2$O$_2$ + 53 mol/L BaCl$_2$; (c): b + 1.67 µmol/L Na$_2$SO$_4$. 
3.4. Catalysis and Inhibition

Under the conditions as in the procedure, the AuNP reaction of H$_2$O$_2$-HAuCl$_4$ is slow. The CDN exhibited catalysis of the AuNP reaction, and the SERS intensity increased with increasing CD concentration (Table 1, Figure 4). The CD without N element exhibited weak catalysis of the AuNP reaction of H$_2$O$_2$-HAuCl$_4$, with a slope of 55.8. After doping N element such as CD$_{1N}$ with a slope of 249, the CD$_{1N}$ surface electrons were enhanced; the CD$_{1N}$ surface electrons accelerated the redox electron transfer so that the gold nanoreaction was greatly enhanced to produce more AuNPs which caused the SERS intensity to increase (Figure 5).

| System   | Linear Range | Regress Equation | Coefficient |
|----------|--------------|------------------|-------------|
| CD$_{0N}$ | 1.0–60 µg/mL | $\Delta I = 55.8x + 30$ | 0.9898 |
| CD$_{0.5N}$ | 6.0–20 µg/mL | $\Delta I = 89.2x + 130$ | 0.9869 |
| CD$_{1N}$ | 0.79–8 µg/mL | $\Delta I = 249.0x - 8.6$ | 0.993 |
| CD$_{2N}$ | 0.79–10 µg/mL | $\Delta I = 197.4x + 13$ | 0.9633 |

Figure 4. Relationship between the SERS intensity and CD catalyst concentration. 4.2 µmol/L HAuCl$_4$ + 2.5 mmol/L H$_2$O$_2$ + CD$_{0N-2N}$ + 0.33 µmol/L VB4R. (a) CD$_{0N}$; (b) CD$_{0.5N}$; (c) CD$_{1N}$; (d) CD$_{2N}$. 
3.5. Optimization of Analytical Conditions

The effect of reagent concentration such as HAuCl₄, H₂O₂, CD₁N, BaCl₂ and VB₄R, reaction temperature and time were optimized, respectively (Figure 6). When HAuCl₄ is 4.2 μmol/L, most AuNPs formed in analytical systems with large ΔI. With increasing H₂O₂, the ΔI increased due to the formed AuNPs increasing, and a 2.5 mmol/L H₂O₂ gives the largest ΔI. CD₁N is the catalyst of the AuNP reaction, when the catalyst concentration increased, the ΔI enhanced, a 5 μg/mL CD₁N gives the largest ΔI. BaCl₂ can inhibit the CD catalysis, when its concentration increased the ΔI was enhanced due to the blank decreasing, a 53 μmol/L BaCl₂ gives the largest ΔI. VB₄R is a sensitive molecular probe; when the concentration increased the ΔI enhanced due to more VB₄R adsorption on the AuNP surface, a 0.33 μmol/L VB₄R gives biggest ΔI. Reaction temperature and time were considered; 50 °C for 20 min gives biggest ΔI. Thus, a 4.2 μmol/L HAuCl₄, 2.5 mmol/L H₂O₂, 5 μg/mL CD₁N, 53 μmol/L BaCl₂ and 0.33 μmol/L VB₄R, and a reaction temperature of 50 °C for 20 min was selected in this SERS method.

![Figure 5](image_url)  Enhancement of the doped N element.

![Figure 6](image_url)  Cont.
The C60 catalytic SERS method was used to detect sulfate, but the preparation of C60 is complex, the C60 nanosol is unstable [25], and the CD1N analytical system overcomes the disadvantages.

3.6. Performance Curve

The working curve of the system was drawn according to the experimental method. In the four systems (Table 2, Figure 7), the CD1N was most sensitive, with a linear range (LR) of 0.02–1.7 µmol/L and a detection limit (DL) of 0.007 µmol/L, and was selected for detection of sulfate. Comparison of the reported methods for detection of sulfate [25–30] showed the SERS method was more sensitive.

Figure 6. Effect of reagent concentration, reaction temperature and time. (a): HAuCl4 + 2.5 mmol/L H2O2 + 5 µg/mL CD1N + 0.67 µmol/L Na2SO4 + 53 µmol/L BaCl2 + 0.33 µmol/L VB4R; (b): 4.2 µmol/L HAuCl4 + 0.33 µmol/L VB4R + 5 µg/mL CD1N + 0.67 µmol/L Na2SO4 + 53 µmol/L BaCl2; (c): 4.2 µmol/L HAuCl4 + 2.5 mmol/L H2O2 + CD1N + 0.67 µmol/L Na2SO4 + 53 µmol/L BaCl2 + 0.33 µmol/L VB4R; (d): 4.2 µmol/L HAuCl4 + 2.5 mmol/L H2O2 + 5 µg/mL CD1N + 0.67 µmol/L Na2SO4 + BaCl2 + 0.33 µmol/L VB4R; (e): 4.2 µmol/L HAuCl4 + 2.5 mmol/L H2O2 + 5 µg/mL CD1N + 0.67 µmol/L Na2SO4 + 53 µmol/L BaCl2 + 0.33 µmol/L VB4R; (f): Reaction temperature, 4.2 µmol/L HAuCl4 + 2.5 mmol/L H2O2 + 5 µg/mL CD1N + 0.67 µmol/L Na2SO4 + 53 µmol/L BaCl2 + 0.33 µmol/L VB4R; (g): Reaction time, 4.2 µmol/L HAuCl4 + 2.5 mmol/L H2O2 + 5 µg/mL CD1N + 0.67 µmol/L Na2SO4 + 53 µmol/L BaCl2 + 0.33 µmol/L VB4R.
with the SERS detection. Table 3 shows that the SERS quantitative analysis method has good selectivity.

\[ \text{Mg}^{2+} \]

according to the experimental method. When the relative error is within 10\%, results show that

\[ \Delta I = 66.9C + 20.4 \]

0.9283 1.0–6.0 0.50

Table 2. Analytical features of CD-catalytic SERS determination of sulfate.

| CD      | Linear Equation | Coefficient | LR (μmol/L) | DL(μmol/L) |
|---------|-----------------|-------------|-------------|------------|
| CD\(_{0.5N}\) | \( \Delta I = 166.4C + 48.8 \) | 0.9463      | 0.5–2.31    | 0.20       |
| CD\(_{1N}\)  | \( \Delta I = 348.8C + 18.0 \) | 0.9384      | 0.02–1.7    | 0.007      |
| CD\(_{2N}\)  | \( \Delta I = 268.6C–73.9 \)  | 0.9403      | 0.06–2.66   | 0.02       |

\[ \text{Zn}^{2+}, \text{Ca}^{2+}, \text{ethanol}, \text{Pb}^{2+}, \text{NH}_4^+, \text{K}^+, \text{SO}_3^{2-}, \text{Mg}^{2+}, 16.5 \text{ μmol/L ethylene glycol}, 6.6 \text{ μmol/L Cr}^{6+}, \text{Fe}^{3+}, \text{NO}_2^- \]

and glycolic acid did not interfere with the SERS detection. Table 3 shows that the SERS quantitative analysis method has good selectivity.

3.7. Influence of Foreign Substances

The influence of foreign substance on the determination of 0.66 μmol/L \( \text{SO}_4^{2-} \) was investigated according to the experimental method. When the relative error is within 10\%, results show that 33 μmol/L Na\(^+\), Zn\(^{2+}\), Ca\(^{2+}\), ethanol, Pb\(^{2+}\), NH\(_4^+\), K\(^+\), SO\(_3^{2-}\), Bi\(^{3+}\) and Cu\(^{2+}\), 26.4 μmol/L HCO\(_3^-\), Mg\(^{2+}\), 16.5 μmol/L ethylene glycol, 6.6 μmol/L Cr\(^{6+}\), Fe\(^{3+}\), NO\(_2^-\) and glycolic acid did not interfere with the SERS detection. Table 3 shows that the SERS quantitative analysis method has good selectivity.

Table 3. Effect of interfering substances on the SERS detection of 0.66 μmol/L \( \text{SO}_4^{2-} \).

| Foreign Substance | Tolerance Concentration (μmol/L) | Relative Error (%) | Foreign Substance | Tolerance Concentration (μmol/L) | Relative Error (%) |
|-------------------|---------------------------------|--------------------|-------------------|---------------------------------|--------------------|
| Na\(^+\)          | 33                              | 5.0                | Cu\(^{2+}\)      | 33                              | 7.6                |
| Zn\(^{2+}\)      | 33                              | 6.4                | HCO\(_3^-\)      | 26.4                            | 8.6                |
| Ca\(^{2+}\)      | 33                              | –6.7               | Mg\(^{2+}\)      | 26.4                            | 6.0                |
| ethanol           | 33                              | –5.6               | ethylene glycol   | 16.5                            | 5.8                |
| Pb\(^{2+}\)      | 33                              | 7.0                | Cr\(^{6+}\)      | 6.6                             | –6.0               |
| NH\(_4^+\)       | 33                              | 3.9                | Fe\(^{3+}\)      | 6.6                             | –4.5               |
| K\(^+\)          | 33                              | 6.0                | NO\(_2^-\)       | 6.6                             | 6.2                |
| SO\(_3^{2-}\)    | 33                              | –7.9               | glycolic acid     | 6.6                             | 5.0                |
| Bi\(^{3+}\)      | 33                              | 6.4                |                   |                                 |                    |
3.8. Analysis of Samples

The water samples including tap water, Rong lake water and Shan lake water were taken into sample bottles. The lake water was filtered with filter paper, and then a 2.0 mL water sample was removed in a centrifuge tube. Three beer samples were purchased supermarkets. Samples were centrifuged at 7000 r/min for 10 min, to obtain a sample solution. The sulfate content was determined according to the SERS detection procedure. The SERS results were in agreement with that of ion chromatography (IC), the relative standard deviation was in the range of 0.90–4.77% and the recovery was between 92.3% and 105% (Table 4).

Table 4. Analytical results of sulfate in water samples.

| Sample           | Single Value (µmol/L) | Average (µmol/L) | Added (µmol/L) | Found (µmol/L) | Recovery (%) | RSD (%) | Content (µmol/L) | IC Results (µmol/L) |
|------------------|-----------------------|------------------|----------------|----------------|--------------|---------|------------------|---------------------|
| Running water    | 0.39, 0.41, 0.38, 0.40, 0.43 | 0.40            | 0.13           | 0.52           | 92.3         | 4.77    | 0.40             | 0.38                |
| Rong lake water  | 1.12, 1.17, 1.11, 1.17, 1.17 | 1.15            | 0.13           | 1.274          | 95           | 2.6     | 1.15             | 1.22                |
| Shan lake water  | 0.70, 0.71, 0.71, 0.72, 0.71 | 0.71            | 0.13           | 0.839          | 99.2         | 0.90    | 0.71             | 0.68                |
| Beer 1           | 1.22, 1.26, 1.30, 1.28, 1.32 | 1.28            | 0.20           | 1.47           | 95           | 3.0     | 1.28             | 1.20                |
| Beer 2           | 1.30, 1.35, 1.38, 1.39, 1.33 | 1.35            | 0.20           | 1.56           | 105          | 2.7     | 1.35             | 1.38                |
| Beer 3           | 1.39, 1.30, 1.39, 1.32, 1.25 | 1.33            | 0.20           | 1.52           | 95           | 4.3     | 1.33             | 1.28                |

4. Conclusions

Highly catalytic CD_N was prepared by a hydrothermal procedure, and it was used to catalyze the reduction of chlorauric acid by H_2O_2 to produce AuNP sol substrate with high SERS activity. Ba(II) ions can combine with CD_N to inhibit the catalysis of CD_N. Upon addition of sulfate ions, stable barium sulfate precipitates formed, and CD_N was released, which causes CD_N catalysis to be activated and the SERS signal to be enhanced. Based on this principle, a new, simple and selective SERS quantitative analysis method was established for the detection of trace sulfate.

Author Contributions: C.L. and L.W. finished the work, acquired data, plotted Figures 1–7 and drafted the manuscript. Y.L. and Z.J. designed the work, analyzed data, and revised the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China [grant number 21667006, 21767004, 21465006, 21477025].

Conflicts of Interest: All authors declare no conflict of interest.

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