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Microplasma-Assisted Rapid Synthesis of Luminescence Nitrogen-Doped Carbon Dots and Its Application in pH Sensing and Uranium Detection

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Developing simple synthesis method and expanding the application of carbon dots have attracted increasing attention. In this report, we have developed a facile method to synthesis fluorescence carbon dots (CDs) with the assistance of atmosphere-pressure microplasma. The CDs could be produced within a few minutes with no need of high temperature, external energy input, and multistep procedures. The as-prepared CDs had a relatively uniform size of approximately 2.3 nm. The FTIR spectrum and the XPS analysis showed that carbonyl groups and amide groups exist on the surface of CDs. The CDs showed bright blue luminescence and high stability in high salt concentration and low pH without further modification. A pH-dependent PL behavior was observed and could be applied for pH sensing in the range of 3–14. Moreover, the CDs could be utilized as a reagent capable of detecting of U(V) with low detection limit and high selectivity.

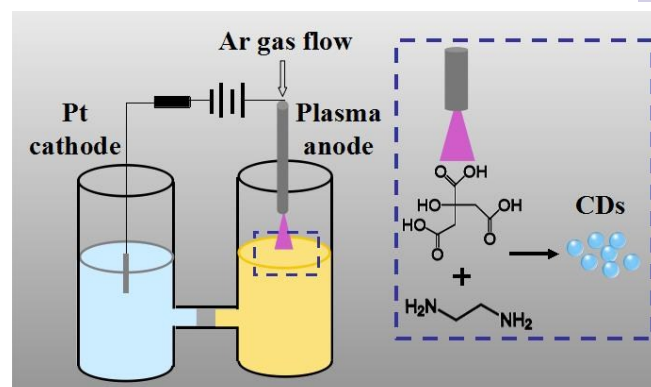
Introduction

Carbon dots (CDs) as a fascinating class of carbon nanomaterials have attracted tremendous attention, owing to their tuneable fluorescence emission properties, chemical inertness, low toxicity, and good biocompatibility.^{1, 2} These attractive merits make CDs a new kind of versatile materials with increasing applications in bioimaging,³ fluorescence ink,^{4, 5} catalysis,^{6, 7} fluorescence sensors,^{8–11} etc. However, many of the conventional synthesis methods often need high temperature, long reaction time and further modification¹². The preparation of carbon dots should be simple, low-cost and environmentally friendly as far as possible, and finding new methods that eliminate the use of rigid reaction conditions is highly desired.

Recently, the research of plasma-liquid system and using microplasma as gaseous electrodes is of great interest for both fundamental studies and technological applications. By utilizing the electrochemical reactions at the plasma-liquid interface, atmosphere-pressure microplasma-assisted method has shown unique advantages in nanomaterials synthesis such as rapid synthesis, mild reaction condition and low energy consumption.^{13–15} However, most of the researches mainly focused on preparing metal nanoparticles by the reduction reactions at plasma cathode, while the research and application of reactions at plasma anode have been rarely reported.¹⁶ Compared to plasma cathode, the condition at the plasma anode is more complex. In our former work,^{17, 18} we have

demonstrated that a plasma anode was capable of transferring positive charges and inducing electrochemical reactions in solution. Recently, we have used the charge transfer reaction between plasma anode and ionic solution for electrodeposition of copper and cuprous oxide nanostructures on solid cathode. The research of directly utilizing plasma anode to synthesize nanomaterials is still needed for further extending the application area of microplasma electrodes.

Herein, we have developed a facile and fast method for the fabrication of CDs with the assistant of atmospheric-pressure microplasma anode (**Scheme 1**). The CDs can be produced within a few minutes with no need of high temperature, external energy input, and multistep procedures.¹⁶ The as-prepared CDs showed bright blue luminescence and high stability in high salt concentration. A pH-dependent PL behaviour was observed and could be applied for pH sensing in the range of 3–14. Moreover, the CDs could be applied as reagent for the detection of uranium with good sensitivity and



Scheme 1. Schematic of preparing carbon dots with the atmospheric pressure microplasma anode electrode and Pt cathode electrode.

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selectivity. To the best of our knowledge, this is the first report of CDs-based luminescent probe for sensing of actinide elements. Our work will give a new direction for the green synthesis of carbon dots and extend the application area of carbon dots and atmospheric-pressure microplasma.

Experimental

Materials and Reagents

Citric acid was purchased from Alfa Aesar. Ethylenediamine was obtained from Aladdin. Sodium hydroxide, ammonium citrate, urea, ammonia, nitric acid and all the metal salts including AgNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, CsNO_3 , $\text{Ni}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, RbNO_3 , $\text{Sr}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ were bought from Beijing Chemical Works. De-ionized water was used for the preparation of all aqueous solutions. All reagents were of analytical grade and were used with no further purification.

Apparatus and Characterizations

The schematic diagram of the atmospheric-pressure microplasma set-up (**Scheme 1**) consists of a current source (DW-P503-1AC), a Pt cathode (purchased from Tianjin Aidahengsheng Technology CO.), and a hollow stainless steel tube with an inner diameter of 180mm which was connected to the current source via a 300 k Ω resistor. The application of the CDs for pH sensor was evaluated using pH meter. Transmission electron microscope (TEM) was recorded on JEM-2010 (JEOL). UV-vis absorption spectra were taken on a Cary 6000i UV-vis-NIR spectrophotometer (Agilent Technologies). Atomic force microscope (AFM) was analysed on SPM-960 (Shimadzu Corporation). Fluorescence spectroscopy was measured with a FluoroMax-4 spectrophotometer. FT-IR spectra were obtained using a Nicolet NEXUS 470 FT-IR spectrophotometer. X-ray Photoelectron Spectroscopy (XPS) was investigated by using 250XI spectrometer with a mono X-Ray source Al K α excitation (1361 eV). Binding energy calibration was based on C1s at 284.8 eV. X-Ray Diffraction were performed with D8 ADVANCE X-ray diffractometer.

Synthesis of Carbon Dots (CDs)

The carbon dots (CDs) were synthesized by the atmospheric-pressure microplasma method. Briefly, the method was started by dissolving citric acid (1.051 g) and ethylenediamine (335 μL) into deionized water (10 mL). Then the solution was transferred into an 'H' type glass reactor for microplasma treatment (**Scheme 1**). The nozzle of the stainless steel tube was about 2 mm above the surface of the solution at the left side with the argon gas flowing through the tube at a rate of 60 sccm (i.e., standard cubic centimeter per minute). Meanwhile, the Pt cathode was about 5 mm under the solution at the right side. The current between the two electrodes was 6 mA and the discharge voltage was around 2500 V. The microplasma treatment was continued for different periods of time, which are 5 min, 10 min, 20 min, 30 min and 60 min, thus yielding solutions with different colors. Finally, the products were dialyzed for 24 h in order to obtain the pure CDs.

Application of CDs in pH Sensing

The carbon dots that reacted for 30 min were used for pH sensing. First the dialyzed CDs (50 μL , about 0.1 mg/mL) were diluted 50 times by adding different volumes of HNO_3 or NaOH to obtain 5mL solutions of different pH measuring by a pH meter. The fluorescence spectra of different pH solution were obtained by using an excitation wavelength of 350 nm.

Application of CDs in Uranium Detection

The uranium detection experiment was taken out by using CDs that have a reaction time of 30min. The dialyzed CDs (50 μL , about 0.05 mg/mL) were diluted 100 times by adding uranium solutions with different concentrations at pH=5.0. Then the fluorescence intensity of different solutions was measured with the fluorescence spectrometer.

Results and discussion

Synthesis and Characterization.

The CDs were prepared with the assistance of microplasma. Typically, citric acid (1.051 g) and ethylenediamine (335 μL) were dissolved into 10 mL de-ionized water, and then treated by a DC atmospheric-pressure microplasma (**Scheme 1**). The microplasma was applied as an anode and the discharge current was fixed to 6 mA. During the treatment of the microplasma the solution in the anode side changed from colorless to yellow within a few minutes, indicating that microplasma method was a rapid CDs-preparing technique (**Fig. 1a**). Subsequently, the color of the solution grew darker with the accumulating reaction time, which could be attributed to the growing amount of CDs and suggested that the prepared CDs had good water

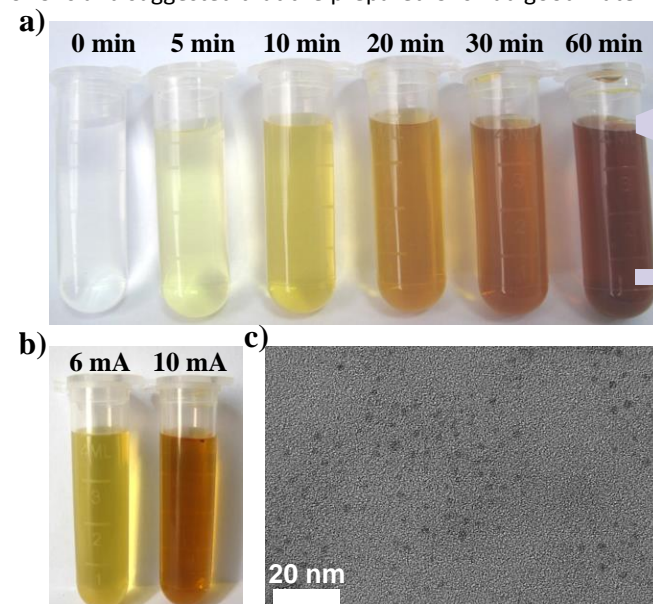


Fig. 1 a) The photographs of CDs solutions treated by microplasma anode with different reaction time b) and different discharge currents. c) TEM image of CDs.

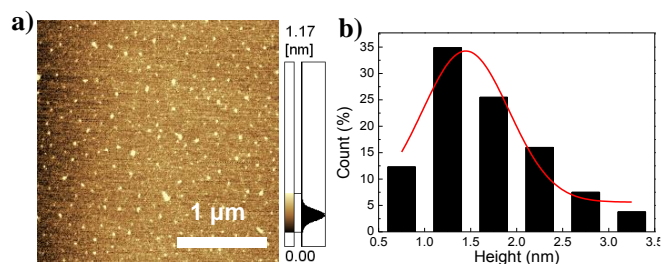


Fig. 2 a) AFM image and b) the corresponding height distribution of CDs.

solubility. Also, with the same reaction time, a higher current could prepare more CDs (**Fig. 1b**). The TEM image demonstrated that the as-prepared CDs were well separated from each other and had a relatively narrow size distribution between 1 and 3 nm with a peak at approximately 2.3 nm (**Fig. 1c, S1**). No obvious lattice fringes were observed on the CDs and the XRD patterns also displayed that the CDs had no obvious lattice structure (**Fig. S2**). **Fig. 2** showed the AFM image and the height distribution of CDs. The Gauss fitting curve revealed that the average height of CDs was 1.45 ± 0.09 nm.

The UV-vis absorption spectra in **Fig. 3a** clearly showed that the CDs solution had a very broad adsorption band in the range of 200–700 nm with two peaks at ~ 280 nm (carbonic core centre) and ~ 330 nm (surface/molecule centre).¹⁹ When excited at 350 nm, the CDs showed strong photoluminescence (PL) in the range of 400–600 nm, with the maximum at around 450 nm (**inset of Fig. 3a**). The CDs could even be utilized as fluorescence inks for writing on filter paper. Upon the irradiation of 365 nm UV light, the written words could generate a blue-green colour and be clearly recognized (**Fig. S3**). The emission spectra was sensitive to the excitation wavelength and the emission peak shifted from 416 nm to 547 nm as the excitation wavelengths increasing from 325 nm to 450 nm (**Fig. 3b**). This excitation-dependent PL behaviour is common in fluorescence CDs and may be effected by the particle size as well as the surface state.^{19, 20} Besides, with the emission peak red shift, the peak intensity gradually reduced due to the weakened interaction between the excitation source and the CDs.¹⁶ The time-resolved fluorescence decay curve was measured by the time-correlated single photon counting (TCSPC) method (**Fig. S4**). The decay curve was very well fitted to a triple-exponential function, and the mean lifetime was calculated to be 5.6 ns. The fluorescence quantum yield of the as-prepared CDs was calculated to be about 5.1% by selecting quinine sulphate as a reference and 350 nm as an excitation wavelength. The CDs also showed good stability in different ionic strengths and the fluorescence intensity showed no obvious decrease as the concentration of NaCl increasing from 0 to 2 mol/L (**Fig. S5**).

To get further information of the structure and components of the CDs, Fourier transformed infrared (FTIR) spectroscopy (**Fig. 3c**) and X-ray photoelectron spectroscopy (XPS) (**Fig. 3d**) characterizations were performed. The FTIR spectrum showed the ν (N-H) at 3420 cm^{-1} , the δ (N-H) at 1570 cm^{-1} , ν (C=O) at 1635 cm^{-1} and ν (C-O) at 1220 cm^{-1} . Meanwhile, the XPS analysis displayed that the existence of C, O, N, on the surface of the CDs and the graphitic or aliphatic (C=C and C-C), oxygenated, and

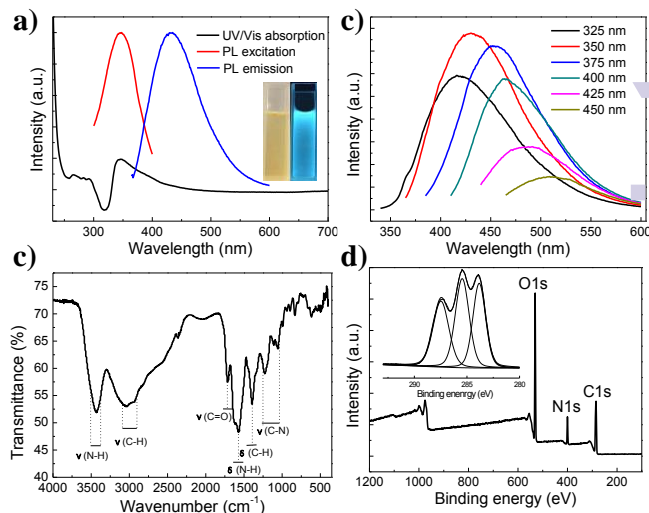


Fig. 3 a) UV-vis absorption, PL excitation and PL emission spectra (Ex=350 nm) of CDs in aqueous solution (0.05mg/mL), inset are the photos of CDs under sunlight (left) and 365nm lamp (right) b) Fluorescence spectra at excitation wavelengths from 325 nm to 450 nm of CDs c) The FTIR spectra and d) XPS analysis of CDs.

nitrogenous carbon atoms (**Table S1**) were also discovered by analyzing the C1s peaks. A high oxygen content (34%) was observed (**Table S2**). These results indicated that on the surface of CDs there were plenty of functional groups such as -COOH, -OH and N-containing groups. The abundant groups gave the CDs excellent solubility in water without further modification and might bring novel properties for sensing application.

Reaction Mechanism of CDs.

To figure out the roles that microplasma played in the reaction, we compared the solutions respectively treated by plasma anode (PI-A), plasma cathode (PI-C) and platinum anode (Pt-A) with the same electric current and reaction time (**Fig. 4a**). From the color of the solution, we found that nearly no CDs were produced by Pt-A, which meant the reaction was not a simple electrochemical reaction and the presence of microplasma was necessary. Compared to PI-A, much less CDs were got from PI-C, suggesting that the reaction was related to the property of the plasma. According to the literatures^{21, 22} and our former reports^{17, 18}, both microplasma anode and cathode could transfer charges and induce electrochemical reactions in the solution. The difference is the former transfer positive charges and latter transfer electrons to the solution, thus, different electrochemical reactions occur at the plasma-liquid interface. Moreover, in a plasma, there contains complex conditions such as ultraviolet radiation, radicals, electrons and ions. The condition at the anode is even more complex than at the cathode, resulting in different non-electrochemical reactions. It is reported at the plasma anode oxide species much more than Faraday's law will be produced, which may contribute to the high oxygen content in the prepared CDs. All these results suggest that the microplasma anode provide a unique condition for preparing CDs, which is different than other reported plasma methods^{23, 24}.

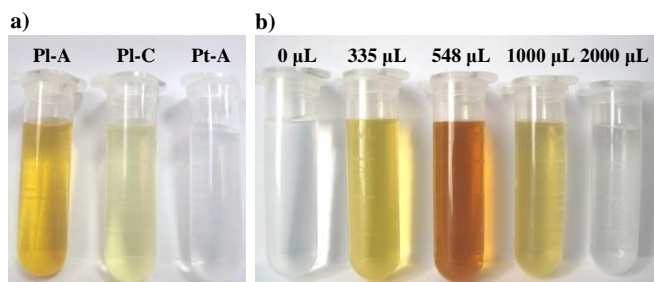


Fig. 4 a) Photographs of CDs solutions treated with different electrode: PI-A: plasma as anode, PI-C: plasma as cathode, Pt-A: Pt as anode. b) Photographs of solutions with different amount of ethylenediamine: 0, 335 μL , 548 μL , 1000 μL , 2000 μL with the fixed amount of citric acid (1.051 g), water (10 mL) and the reaction time (10 min).

The formation mechanism of CDs was further investigated. Firstly, solutions with a fixed amount of water and citric acid but different amount of ethylenediamine (0, 335, 548, 1000 and 2000 μL) were treated with microplasma anode for 10 min respectively (**Fig. 4b**). When there was no ethylenediamine, no visible color change was observed, indicating the presence of ethylenediamine was necessary in the reaction. But excessive amount of ethylenediamine also inhibited the reaction. Most CDs were generated when the added amount of ethylenediamine was 548 μL , in which condition, the molar ratio between citric and ethylenediamine was about 2:3 and the molar ratio between $-\text{COOH}$ and $-\text{NH}_3$ was 1:1. These results suggested that the condensation reaction between citric and ethylenediamine was the origin of forming CDs and the presence of microplasma dramatically accelerated the reaction rate.¹⁵

To further confirm our hypothesis, solutions of CA and different additives were treated by microplasma for 10 minutes. Compared to the solution of CA and EDA, the addition of ammonia water, urea and NaOH to CA did not show obvious color change (**Fig. 5a**). The fluorescence spectra in **Fig. 5b** confirmed that little or none CDs was synthesized by using these materials as the emission peak was very weak. According to Sun et al.'s report²⁵ on preparing excitation-independent graphene quantum dots (GQDs), by using hydrothermal method, under basic reaction condition, the CA molecules could self-assembled into sheet structure followed by condensation reactions through intermolecular dehydroxylation, forming nanocrystalline graphene quantum dots (GQDs). When replacing NaOH with different amines to synthesize N-doped GQDs, N atom entered GQDs by forming pyrrolic structure through intramolecular dehydroxylation between neighbor carboxyl groups. While in our experiments, CA molecules could hardly form CDs by themselves. Also, with CA and EDA as origin materials, the products of both methods were different. The plasma-prepared CDs were excitation-dependent amorphous particles, while the hydrothermal-prepared GQDs were excitation-independent crystalline graphene layers. The mechanism of plasma-prepared CDs was more similar to another report on hydrothermal-prepared excitation-dependent CDs.¹⁹ In that report, the reaction was conducted by

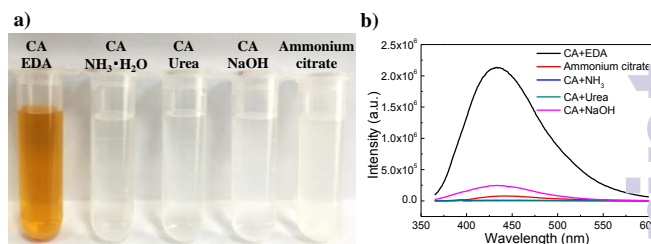


Fig. 5 a) Photographs and b) fluorescence spectra of solutions with different materials treated by microplasma anode for 10 min. CA + EDA: citric acid (0.55 μM) and ethylenediamine (0.825 μM), CA + $\text{NH}_3 \cdot \text{H}_2\text{O}$: citric acid (0.55 μM) and ammonia (1.65 μM), CA + Urea: citric acid (0.55 μM) and urea (0.825 μM), CA + NaOH: citric acid (0.55 μM) and NaOH (1.65 μM), and ammonium citrate (0.55 μM).

first condensing CA and EDA, whereupon they formed polymer-like CDs, which were then carbonized to form the CDs. These results suggested that the low-temperature microplasma only provided a mild reaction condition that allowed the condensation of CA and EDA to form polymer-like CDs. After plasma treating, ammonium citrate solution showed a slightly color change and relative weak emission. The formation of small amount of CDs might be caused by a different and more complicate mechanism.²⁶

Application of CDs in pH sensing.

For further applications, we firstly studied the effect of pH on the fluorescence intensities of our plasma-prepared CDs and compared with CDs prepared by hydrothermal method (HCDs) with the same amount of reactant but different reaction condition (200 $^\circ\text{C}$, 5 h). The intensity of plasma-prepared CDs decreased with the pH increasing from 1-14 (**Fig. 6a**), while the intensity of HCDs is stable in the pH range of 5-9 and decrease at both lower and higher pH (**Fig. S8**). At low pH condition (≤ 5), the intensity of HCDs decreases fast with the decrease of pH and the intensity drops more than 90% in the presence of 1 mol/L HNO_3 . For plasma-prepared CDs, the intensity peak appears at pH=1 and the intensity only decrease about 20% at the presence of 3 mol/L HNO_3 . These results showed that plasma-prepared CDs were more suitable for sensing application in low pH. This may be a consequence of the difference of chemical structure and functional group between CDs prepared by these two methods.

More interestingly, it was found that in a broad range of pH (3.0-13.6), the fluorescent intensity of CDs displayed good linearity with pH variation (**Fig. 6a**). And the fluorescent intensities kept constant with the pH changed from 5 to 11 for about 4 cycles (**Fig. 6b**), which also indicated that the structure and surface state of CDs were not destroyed with the decrease of fluorescence intensity. Thus the plasma-prepared CDs could be served as a potential pH sensor.

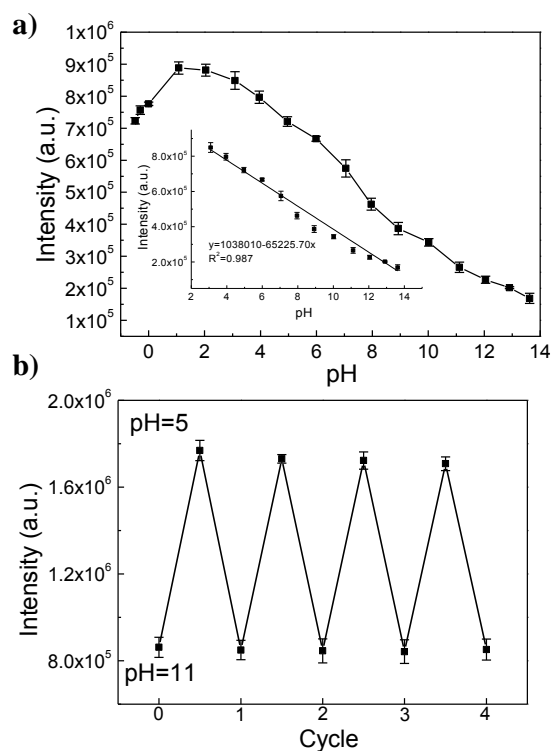


Fig. 6 a) Effect of pH on the fluorescence intensity of plasma-prepared CDs (CDs) inset is the linear fitting line of CDs from pH 3.0 to 13.6. b) Fluorescence intensity upon the cyclic switching of CDs under alternating conditions of pH =5 and pH =11.

Application of CDs in Uranium Detection.

As a predominant fuel of nuclear energy, the consumption of uranium is increasing with the growing demand for nuclear power. During the mining process and the reprocessing of nuclear spent fuel, monitoring uranium concentration in waste water attracts intense concern for both safety and separation demand²⁷. As shown in **Fig. 7a**, with the increasing concentration of U(V), the fluorescence intensity of CDs decreased. A good linear relationship between the concentration of U(V) and the fluorescence intensity was observed in the range of 0 to 75 ppm with the R^2 of 0.996 (insert of **Fig. 7b**). The detection limit for U(V) was measured to be about 0.71 ppm.

To validate the selectivity of CDs for U(V), the fluorescence quenching effect of a series of competing metal ions on CDs were investigated. The metal ions, including Ag^+ , Ba^{2+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Cs^{2+} , Mg^{2+} , Ni^{2+} , Rb^{2+} , Sr^{2+} and Zn^{2+} , were studied at a concentration of 1 mM, respectively. As shown in **Fig. 7c**, U(V) ions caused a dramatic fluorescence quenching comparing to other metal ions. This may be attributed to the special coordination interaction between U(V) ions and the amino groups as well as the hydroxyl groups of CDs. Besides, the slight fluorescence quenching for other metal ions may be a result of the nonspecific interactions between the carboxylic groups and the metal ions.¹⁹ The result showed that, the CDs had a desirable selectivity for U(V) over a series of metal ions, which suggested that the CDs might act as a potential material for U(V) detection.

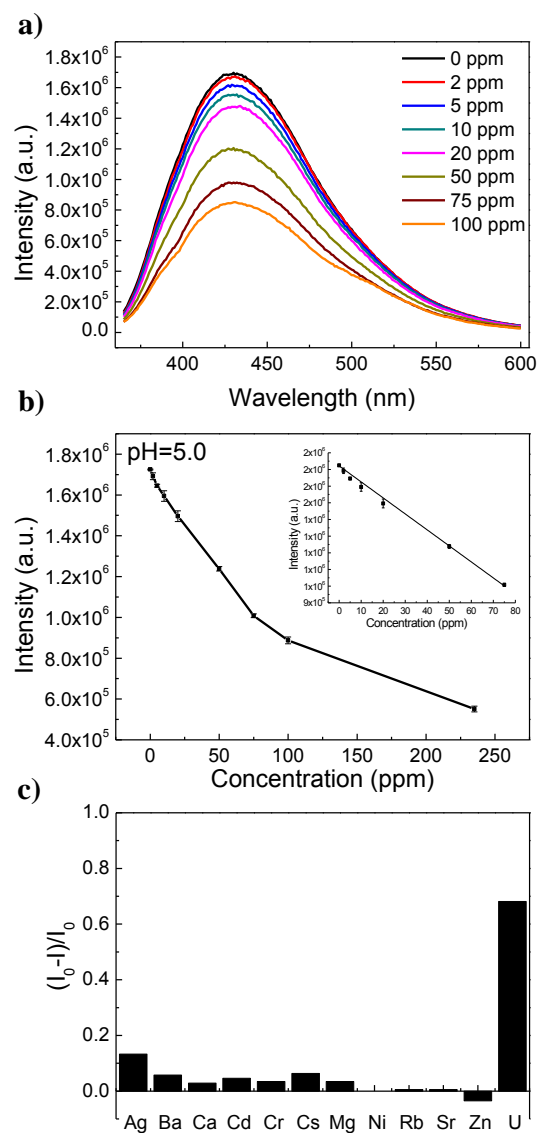


Fig. 7 a) The PL spectra of CDs in U (V) aqueous solution at different concentrations (excited at 350 nm). b) The detecting trend between the fluorescence intensity and the concentration of U (V). Insert: the linear fitting line from the range of 0 to 75 ppm. c) Selectivity of microplasma CDs for U (V) detection after the addition of different metal ions. Metal ions: 1mM, pH: 5.0, CDs: around 0.05mg/mL.

Conclusions

In summary, we have developed a facile method to synthesize fluorescence carbon dots with the assistance of atmospheric pressure microplasma. The as-prepared CDs have a relatively uniform size of approximately 2.3 nm with a blue fluorescence. The FTIR spectrum and the XPS analysis show that carbonyl groups and amide groups exist on the surface of CDs. The as-prepared CDs have fantastic PL properties which are dependent on excitation wavelength and pH. The pH-dependent PL behaviour could be applied as a pH sensor. Moreover, the CDs could be utilized as a reagent capable of detecting of U(V). The low detection limit and the high selectivity for U(V) compa...

to a series of competing metal ions make CDs a new candidate for U(V) detection. Our work provided a new direction for the green synthesis of carbon dots and may extend the application area of carbon dots and atmospheric-pressure microplasma.

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