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Preparation method of copper nanoclusters with PVP as ligand

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Copper nanoclusters (CuNCs@PVP) with excellent luminescent properties were prepared from polyvinylpyrrolidone K30 (PVP) and anhydrous copper(II) sulfate. By optimizing the reaction conditions, the optimal conditions for the preparation of CuNCs@PVP were determined and its structural characteristics were studied using fluorescence spectrophotometer and Fourier transform infrared spectroscopy. The results showed that the optimal reaction conditions were 0.05 g/mL PVP solution 10 mL, 0.16 g/mL anhydrous copper(II) sulfate solution 2 mL, reaction temperature 200°C and reaction time 2 hours. CuNCs@PVP have intense fluorescence at 525 nm. The fluorescence excitation peak of CuNCs@PVP is located at 460 nm, PVP is both a ligand and can act as a reducing copper/ion.
Keywords: copper nanoclusters, hydrothermal synthesis, fluorescence luminescence.

Спосіб отримання нанокластерів міді з ПВП як ліганд. *Xueling Cao, Faxian Li, Xinxing Zhang, Danfeng He*

Нанокластери міді (CuNCs@PVP) з відмінними люмінесцентними властивостями були отримані з полівінілпіролідону К30 (ПВП) та безводного сульфату міді(II). Шляхом оптимізації умов реакції визначено оптимальні умови отримання CuNCs@PVP та вивчено його структурні характеристики з використанням флуоресцентного спектрофотометру та інфрачервоної спектроскопії з Фур'є-перетворенням. Результати показали, що оптимальними умовами реакції були розчин ПВП 0,05 г/мл 10 мл, розчин безводного сульфату міді (II) 0,16 г/мл 2 мл, температура реакції 200° і та час реакції 2 години. CuNCs@PVP мають інтенсивну флуоресценцію при 525 нм. Пік збудження флуоресценції CuNCs@PVP розташований при 460 нм, ПВП одночасно є лігандом і може діяти як іон міді, що відновлює.

1. Introduction

Copper nanoclusters (CuNCs) are a new type of fluorescent nanomaterials that have been widely used in various fields due to their excellent fluorescence, catalytic activity, biocompatibility, and ease of preparation due to their low cost [1–4]. The main method for preparing CuNCs currently reported is to reduce divalent copper ions to copper atoms by adding reducing agents. Common methods include template method [5], ligand method [6], reduction method [7], etching method [8], etc. These methods usually require the addition of reducing agents and ligands separately to reduce and prevent the aggregation of CuNCs into larger particle sizes, which in turn affects their fluorescence intensity [9–12]. In this paper, PVP and anhydrous copper(II) sulfate are mainly used as the main components, and the hydrothermal synthesis method is used to prepare and find the best experimental method route by controlling the reaction preparation conditions. Compared with other methods, this method has the advantages of simple operation and low experimental cost, which can be better applied to the synthesis of CuNCs. It can also

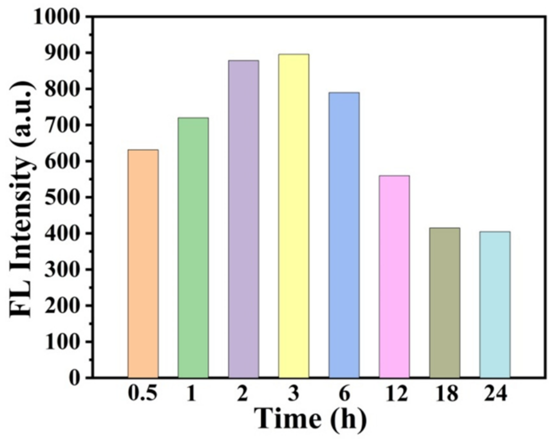

Fig. 1. Effect of reaction time on fluorescence intensity of CuNCs@PVP, the samples were synthesized at 200°C.

effectively utilize resources and fundamentally reduce the cost required for the preparation process, and can be widely applied in production.

2. Experimental

Reagents and instruments

Fourier transform infrared spectra (PerkinElmer, USA); Fluorescence spectrophotometer (Agilent Technologies Co., Ltd.). Polyvinylpyrrolidone K30 (PVP) and anhydrous copper(II) sulfate (China National Pharmaceutical Group Chemical Reagent Co., Ltd); sodium hydroxide (Tianjin Dingshengxin Chemical); hydrochloric acidsodium (Tianjin Damao Chemical Reagent Factory) and other reagents are analytically pure.

Synthesis of CuNCs@PVP

Accurately add 10 mL of 0.5 g PVP and 2 mL of 0.32 g anhydrous copper(II) sulfate in a Reactor core of high-pressure reactor. After ultrasonic treatment, the solution is completely dissolved and placed in an oven for heating reaction to obtain CuNCs@PVP. The color of the reaction solution changed to brownish red, CuNCs@PVP was obtained, and was ready for use. All solvents used in the solution are water.

3. Results and discussion

Effect of reaction time on CuNCs@PVP

In order to investigate the effect of reaction time on the reaction process, the effect of reaction time on the fluorescence intensity of CuNCs@PVP was investigated. Fig. 1 shows the fluorescence intensity spectra of CuNCs@PVP under different reaction time conditions at 200°C, followed by the fluorescence emission intensity peaks corresponding to reaction times of 0.5 h, 1 h, 2 h, 3 h, 6 h, 12 h, 18 h, and 24 h. In the figure, it can be observed that the fluorescence intensity of CuNCs@PVP showed an increasing trend before 3 hours, decreased after 3 hours, and began to stabilize at 18 hours. To save reaction costs, choose 2 h as the optimal reaction time.

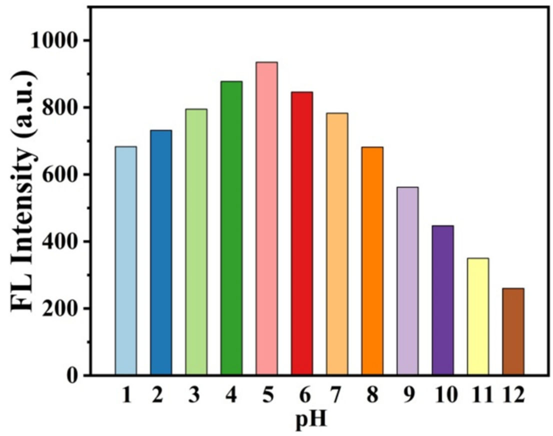

Fig. 2. Effect of reaction pH on fluorescence intensity of CuNCs@PVP, the samples were synthesized at 200°C and 2 h.

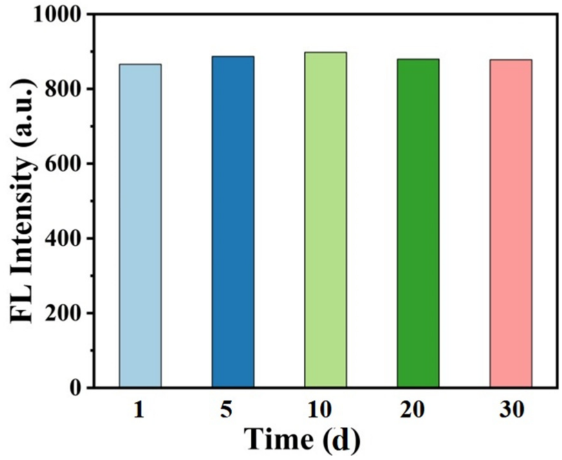

Fig.3. Stability of CuNCs@PVP placed at room temperature.

Effect of acidity and alkalinity of reaction system on CuNCs@PVP

The preparation of CuNCs@PVP is carried out at reaction temperature of 200°C and reaction time of two hours. Fig. 2 shows the fluorescence emission spectra of CuNCs@PVP under different acid-base conditions, with pH = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12. In the reaction system, only anhydrous copper(II) sulfate and PVP solutions are light blue. With the pH of the solution gradually increasing, the color of

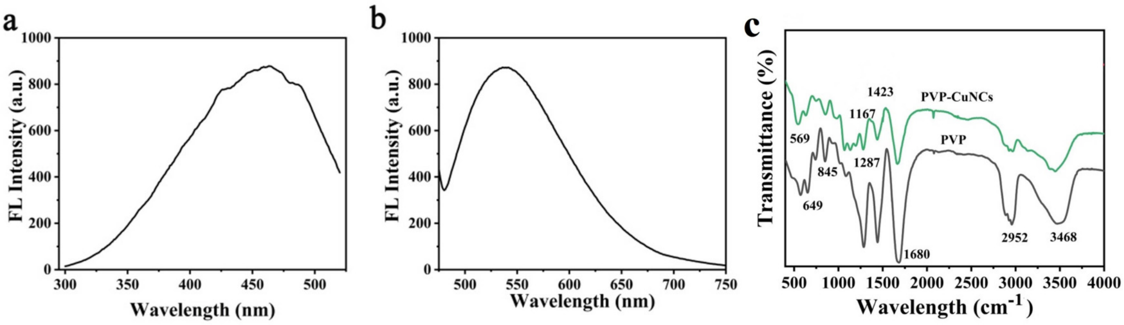

Fig. 4. a: The fluorescence excitation diagram of CuNCs@PVP; b: The fluorescence emission diagram of CuNCs@PVP; c: The infrared spectrum of PVP and CuNCs@PVP.

the solution changes from light to dark. The fluorescence emission intensity of the reacted solution is the strongest when pH = 5, so the optimal reaction condition is to adjust the pH value of the solution to 5. When the solution is 0.05 g/mL PVP solution 10 mL and 0.16 g/mL anhydrous copper(II) sulfate solution 2 mL, the pH value is 5, and no other reagents need to be added for adjustment.

Stability of CuNCs@PVP

Fig. 3 shows the stability of fluorescence intensity of CuNCs@PVP. The prepared CuNCs@PVP was placed at room temperature for 30 days to observe the stability of CuNCs@PVP. Results showed that the fluorescence intensity of CuNCs@PVP did not change significantly within 30 days. This feature of CuNCs@PVP suggests that it can be conveniently stored at room temperature for future use.

Optimization of preparation conditions of CuNCs@PVP

The reaction conditions for the preparation of CuNCs@PVP were optimized through single factor experiments. The optimal reaction conditions for the preparation of CuNCs@PVP were finally obtained as follows: 2 mL of 0.16 g/mL anhydrous copper(II) sulfate, 10 mL of 0.05 mg/mL PVP solution, 200°C reaction temperature, pH value of solution 5, and 2 h reaction in a high-pressure reactor. Fig. 4 shows the fluorescence and IR spectra of the CuNCs@PVP under optimal conditions. From Fig. 4a and b, it can be observed that the fluorescence excitation peak of the CuNCs@PVP is located at 460 nm, and the emission peak is located at 525 nm. The fluorescence quantum yield is 14.1 %. The characteristic absorption peaks of the IR spectrum can be observed in Fig. C: 3468 cm^{-1} is the O–H stretching vibration absorption peak, 2952 cm^{-1} is the C–H stretching vibration absorption peak, 1680 cm^{-1} is the C=O stretching vibration absorption peak, which coincides with the O–H bending vibration, 1423 cm^{-1} is the C–H bending vibration absorption peak, 1287 cm^{-1} is the C–N stretching vibration absorption peak, etc. Comparing the IR spectra of PVP and CuNCs@PVP, it can be seen that when PVP is used as a ligand to prepare CuNCs@PVP, the structure remains unchanged, which is consistent with the conjecture that PVP can both act as a ligand and reduce copper ions, and the structure remains unchanged.

4. Conclusions

By using a single factor experimental method, the effects of reaction time, reaction temperature, reaction pH value, and type of reducing agent on the fluorescence emission intensity of CuNCs@PVP were investigated. The optimal reaction conditions were obtained and the prepared CuNCs@PVP were characterized by fluorescence and infrared spectroscopy. The results showed that this method can easily and quickly prepare CuNCs with strong luminescent properties, providing a new fluorescent probe for practical applications.

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