Surface/Deep Defects manipulated Fluorescence Properties and LED application of Copper Nanoclusters

Lin Ai¹,², Ji Li², Min Tang², Hsiaohsien Chen² and Hong Meng¹*

¹School of Advanced Materials, Peking University Shenzhen Graduate School, Guangdong Shenzhen 518055, CHN
²Shenzhen China Star Optoelectronics Technology Co., Ltd. Guangdong Shenzhen 518132, CHN

*Corresponding author’s e-mail: chaofenzi2015@163.com

Abstract. The contribution of metal defects to the emission enhancement of Cu nanoclusters has been proposed. But the insufficient understanding of the defects luminescence mechanism limits its further effective adjustment and control to the emission color. In this work, the surface metal defects of the assembled fluorescent materials are deliberately engineered. Metal defects have effects on luminescent energy levels, which are relative to the dynamic process of exciton radiation transition and regulate the photophysical properties of the materials. Further studies demonstrate the surface metal defects possess shallow energy level and multi sublevels, broaden the emission colors. Moreover, the continuous alteration of emission color is achieved by simply adjusting the relative ratio of the surface and deep metal defects. Based on the full-color emission of copper clusters, the white light emitting diodes (WLEDs) with different color temperatures (warm, cold, and pure white) are prepared for illumination application.

1. Introduction

As new generation fluorescent nanomaterials, ultra-small copper nanoclusters have attracted enormous interests in the applications of illumination and display on account of their non-poisonous, large amount of storage in earth, simple synthetic route, and relative low cost[1-4]. Recent 3 years, thanks to the self-assembly induced emission enhancement (SAIEE), the fluorescent quantum yields (QYs) of the copper clusters are greatly improved to 37%, comparing to previous 1%-10%. However, as the fluorescence mechanism is still an open topic, the confused mechanism makes it difficult to systematically regulate the emission color. In addition, the methods to control the emission color are finite and complicated, always involving varying size of the metal core by utilizing the quantum size effect[5], or heterogeneous metal doping to influence the ligand to metal charge transfer or ligand to metal-metal charge transfer (LMCT/LMMCT) process[6]. The scarce regulatory methods and narrow adjustable luminous bands greatly limit the associated academic researches and practical applications comparing to the competitive alternatives of organic phosphors and quantum dots (QDs).

Lately, the contribution of the metal defects to the regulation of the fluorescent properties has been investigated by our group[7], the defects-related Cu(I) rich structures influence the LMMCT process and facilitate the radiative relaxation of excitons, which drastically heightens the emission intensity. Besides, the introduction of the defect energy level shows a bright prospect for tailoring the emitting colors. As for the ambiguous fluorescence mechanism, further control and exploration are in progress.
The defects-related emission mechanism in QDs field is very well depicted to regulate emission intensity and color, and it is inspiring to observe similar behavior for quantum-sized copper clusters. It is comparatively difficult to construct atom missing and dangling bonds as the ultrasmall clusters composed of only several to several tens atoms. Surprisingly, through deliberately altering the capping ligands, the partly modified coordination environment of Cu atoms alters the surface properties of Cu NCs. The induced surface defects possess shallow defects energy level and multi sublevels, which is differing from the previous reported deep defects emission, making the emission color show significant bathochromic-shift. Remarkably, the emission color experience continuous variation by intentionally adjusting the relative ratio of the surface and deep metal defects.

In this work, solely altering the capping ligands of the copper nanoclusters, we can engineer the deep and surface defects-rich materials by renovating the coordination condition of Cu atoms. Further studies corroborate the metal defects make correlated radiative transition energy levels, which arouses the additional electron relaxation process from the intrinsic LMMCT-determined triplet state to the metal defects-related intermediate state. This process interferes the luminescence properties of copper clusters, making a substantial change in the emitting color. Additionally, the relative proportion of the two kinds of defects can be adjusted, resulting in the continuously changed emitting colors. Based on the obtained manifold color-emitting of fluorescent powders, the white light emitting diodes (WLED) by composition of pure copper clusters are prepared with tunable color temperature.

2. Materials and methods

2.1. Chemicals and reagents
Copper(II) chloride (CuCl₂, 99.0%, A. R.) was purchased from Alfa Aesar. Hexanethiol, hexanedithiol, and mercapto-1-hexanol were purchased from TCI. Alcohol, acetone and chloroform were all commercially available products and used as received without further purification.

2.2. Instrument and characterization
Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope. Photoluminescence (PL) spectroscopy was performed using a Shimadzu RF-5301 PC spectrophotometer. The spectra of the LEDs were measured under ambient conditions at room temperature by combining a Spectrascan PR-650 spectrophotometer with an integrating sphere and a computer-controlled direct-current power. The color of the light was identified using the CIE (Commission Internationale de L’Eclairage 1931) calorimeter system. Any color could be described by the chromaticity (x, y) coordinates on the CIE diagram.

2.3. Preparation of copper clusters fluorescent nanomaterials
CuCl₂ 100 mg was dissolved in 20 mL alcohol at room temperature. Different kinds of thiols capping ligands (10 mmol), which acted as a ligand cum reductant, were added and stirred at room temperature for 10 min. After reaction finished, 1 mL reaction suspension of the products was washed and precipitated by adding 2 mL chloroform and 4 mL acetone. Then, the products were centrifuged by 4500 rpm for 8 min. The purification process was repeated twice. Finally, the products were redispersed in 2 mL chloroform.

3. Results and discussion
Cu NCs were prepared in alcohol as the solvent, using different kinds of thiols as the capping ligand at 30 °C. Interestingly, we get three emission colors, corresponding to blue, yellow and red (Figure 1d). To investigate such fluorescent materials thoroughly, transmission electron microscopy (TEM) shows that the fluorescent materials are as-assemblies of Cu NCs (Figure 1a-c). High magnification TEM image confirms that the assemblies are composed of ultrasmall Cu NCs with the average diameter of <2 nm (Figure 2).
Figure 1. TEM images for blue emission (a), yellow emission (b) and red emission (c) assemblies of copper clusters, the corresponding photo images and capping ligands structures are shown inset. The fluorescence spectrum of assemblies.

Figure 2. (a) High magnification TEM images of assemblies composed of copper clusters. (b) The corresponding size calculated by 200 spots of Cu clusters in (a).

The fluorescence mechanism of tremendously disparate emitting colors is explored. Obviously, the employed capping ligands structures are key points. The capping ligands can alter the coordinate micro environment of copper source. The over reducing power of ligands makes imperfect clusters, thus facilitating to form metal defects. So, the hexanedithiol ligands easily makes deep defect. In contrast, the OH group in mercapto-1-hexanol can adsorb on the copper atom, it prefers to form surface defects at the interface where the ligands contact with the copper core. In consideration of previous work and theoretical calculation[7], besides the contribution to the relaxation of excited electrons via a radiative pathway as of the increased Cu(I), the metal defects also can generate additional energy level and narrow the emission band gap, inducing bathochromic-shift of the emission color (Figure 3).
Figure 3. Energy level of materials with blue, yellow and red emitting, where S0, T1, and S1 represent ground state, excited triplet state, and singlet state. I, II, III, and IV represent the sublevels of defect state. ISC represents the intersystem crossing process. The dotted arrow represents the luminous excitons relax to the defect state from the intrinsic triplet state.

Next the deep and surface defects should be proved further. As the surface defects are generally more sensitive to the environment, when raising the reaction temperature, due to the instability of the defects, the higher reaction temperature will gradually remove the defects, the defects luminescence will gradually quench out. The fluorescence of the metal triplet states completely replaces the one from metal defects, making the blue fluorescence appear. When reaction is conducted at high temperature of 120 °C, the red emitting materials need only 20 min while the yellow one needs nearly 1 h for the restoration of the intrinsic emitting color. That is the effect of temperature on shallow defects is greater, so the light color changes more rapidly (Figure 4).

Figure 4. PL emission spectra (a, b) and the corresponding fluorescent images (c, d) of the yellow-emitting (a, c) and red-emitting (b, d) assemblies prepared at 120 °C at different reaction time. 365 nm excitation is adopted.

Here, the continuous adjustment of emission colors is also achieved in this work by adjusting the two kinds of defects. Found that just simply alter the varieties and proportion of capping ligands, the continuous changes of emission color from yellow to red are present. From Figure 5, various proportions between hexanediithiol and mercapto-1-hexanol bring gradient changing of the fluorescent colors. When the ratio of the mercapto-1-hexanol rises, it is easier to form surface defects relatively, consequentially, more red shift of the emission color appears, demonstrating the construction of defects has reached a certain degree of controllability.
Figure 5. PL emission spectra (a) and the corresponding fluorescent images (b) of the assemblies prepared in hexanedithiol: mercapto-1-hexanol = 1:1, 1:3, 1:5 and 1:7 as capping ligands with 365 nm excitation.

As the simple synthesis, no fluorescence resonance energy transfer (FRET) and excellent stability, the obtained fluorescent powders are suitable for preparing WLED with mixed corresponding emission color. As of the well manipulative emission colors, these powders are mixed by the ratio of 2.5/0.5/1.2/1, 2/0.7/1.3/1.2 and 1.7/0.6/1.5/1.3, the high-performance WLED are constructed with cold (9587 K), natural (5122 K) and warm (3214 K) color temperature for illumination application (Figure 6).

Figure 6. Photographs of the working WLED prototypes with different color temperature (a–c). Insets in (a–c) are the corresponding emission spectra of WLEDs.

4. Conclusion
In summary, the emission color is well manipulated by intentionally inducing the metal defects. The defects energy levels can influence the radiation transition photodynamic process, which is greatly related to the emission property. The surface/deep defects of metal clusters are constructed by means of utilizing different reducing power of capping ligands. Simultaneously, through controlling the defects, the continuous change of emission color is realized, providing a new method for the adjustment of emission color, which facilitates to devise high performance WLED architectures.

Acknowledgments
This work was supported by the National key research and development program of China (2016YFB0401701), NSFC (51425303, 11674123), the 973 Program of China (2014CB643503), and the Special Project from MOST of China.

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