Defects Dominated Regulation of Fluorescence Properties of Copper Nanoclusters

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Abstract. At present, many studies have suggested that during the luminescence process of Cu nanoclusters, the increase of metal defects can further enhance the emission, but the lack of understanding of the defect luminescence principle makes it tough to further adjust the emissions of luminescence and achieve multicolor luminescence. Herein, the 2D assembled sheet materials are modified with surface or deep defects. Metal defects affect the luminous energy level by regulating the optical properties of 2D assembled materials and regulating the detailed progress of exciton radiation action. Further more, research shows that continuous adjustment of the emission color can be achieved by only regulating the ingredient of surface defects and deep metal defects, and such surface metal defects have a lighter level and multiple sub-levels, which broadens the luminescent color. Finally, white light emitting diodes (WLEDs) with warm, cool and pure white color temperatures were achieved for illuminating applications used the full-color luminescence of Cu clusters.

1. Introduction
Small size Cu clusters, used as a new-style fluorescent nanomaterials, have aroused widespread interest in the field of display and lighting due to their relatively low cost, large amounts of storage in soil, simple synthesis routes, and non-toxicity[1-4]. The fluorescence quantum yield (QYs) of common copper clusters is generally 1% to 10%, and in recent years, the quantum yields of some Cu clusters have been enormously enhanced to 37.7% due to assembly induced emission enhancement (AIE). However, it is difficult to adjust the emission color systematically and the fluorescence mechanism is still an open topic. Besides, the ways to adjust the emission colors are few and time-consuming, always involve ligands to metal charge transfer (LMCT) transitions [5]. It always involves changing scales of the Cu core by employing quantum size effect and heteroatom adulteration to make effect on the ligands to metal charge transfer process [5]. Compared with competing alternatives to organic micromolecules and semiconductor nanodots, the sparse adjustment method and narrow tunable luminescence band greatly limit related academic research and practical applications.

Recently, our team studied the influence of defects to the regulation of fluorescence performance [4]. The defect-involved Cu defect-rich structure affects the LMCT transition and promotes the radiation delay of excitons, thereby greatly increasing the fluorescence intensity. In addition, the trap energy levels raise a promising future for regulating emission colours. Further control and exploration are in progress in order to resolve the confused emission mechanism.

The emission mechanisms associated with defects in the field of quantum dots are well described to adjust color and emission intensity, and inspire people to observe analogical phenomenon of nano-sized Cu clusters. Due to ultra-small clusters consisting of only a few to dozens of atoms, it is
relatively hard to introduce atom deletions or dangling bonds. Surprisingly, by intentionally changing the end-capping ligand, the partially modified copper atom coordination environment changed the surface properties of the copper nanotubes. Unlike the previously reported deeper defect emission, the induced surface defects have multiple sub-levels and lighter defect levels, thereby causing the emission color to show a significant red shift. Remarkably, by intentionally regulating the involved ratio of shallow defects and deep defects, the emission color undergoes continuous changes.

In this work, only by changing the circumambient ligands of Cu nanoclusters, we can design materials with rich surface and deep defects by updating the coordination conditions of Cu atoms. Further research confirms that metal defects will produce related radiation transition energy levels, thereby causing an extra electron transition process from the triplet state controlled by intrinsic LMMCT to the intermediate state related to metal defects. This process interferes the luminescence properties of copper clusters, making a substantial change in the emitting colors. In addition, the relative ratio of the two defects can be adjusted so that the color of the light continuously changes. Based on various colors of the obtained phosphor, a white light emitting diode (WLED) composed of pure Cu nanoclusters was obtained with an adjustable color temperatures.

2. Materials and preparation

2.1. Chemicals

CuCl$_2$, mercapto-1-hexanol, hexanedithiol, and hexanethiol were purchased from Aladdin. C$_2$H$_5$OH, (CH$_3$)$_2$CO and CHCl$_3$ were all purchased directly and without further purified.

2.2. Characterization

PL spectroscopy was conducted using Shimadzu RF-5301. TEM was performed using Hitachi H-800. The LEDs were calculated under room temperature by utilizing a Spectrascan PR-650 with an integrating sphere. The color of the light was identified using the CIE calorimeter system. The color can be described by the chromaticity (x, y) coordinates on the CIE diagram.

2.3. Preparation

CuCl$_2$ 150 mg was dissolved in 15 mL C$_2$H$_5$OH at atmosphere. Different thiols ligands (20 mmol), acted as a capping ligand and reductant, were put and stirred at atmosphere for 1 h. After reaction accomplished, 2mL reaction solution of the products was precipitated by adding 8 mL CHCl$_3$ and 8 mL (CH$_3$)$_2$CO. Then, the products were purified through centrifuging by 9000 rpm for 16 min. The purification process was repeated 3 times. The products were redispersed in 4 mL CHCl$_3$.

3. Discussion

At 30°C, Cu NCs were prepared using different types of thiols as the end-capping ligands and alcohol as the solvent. Interestingly, we get three emission colors, corresponding to blue, yellow and red (Figure 1d). In order to thoroughly study this type of fluorescent material, transmission electron microscopy (TEM) shows that the fluorescent materials are as-assembly 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).
The fluorescence mechanism of greatly different emission colors is explored. Obviously, the structure of the capped ligand used is the key. Capping ligands can change the copper source's coordination microenvironment. The excessive reducing ability of the ligand makes the cluster imperfect and thus easily forms metal defects. Therefore, hexamethylene dithiol ligands are prone to cause deep defects. In contrast, the OH group in mercapto-1-hexanol can adsorb on the copper atom, it prefers to construct shallow traps at the surface where the ligands bond with the Cu core. Considering previous theoretical calculations and work [5], in addition to increasing Cu(I) to relax excited electrons through the radiation path, metal defects can also generate extra energy levels and reduce the emission band gap, causing red emission colors shift (Figure 3).

Figure 1. TEM for blue (a), yellow (b) and red (c) emitting assemblies of Cu clusters, the photo images and ligands structures are present in the spectro.

Figure 2. (a) HRTEM images of assembled copper clusters. (b) The size calculated through 400 spots of copper clusters in (a).

Figure 3. Schematic diagram of energy level of materials with blue, yellow and red emission, where S0 represent ground state, T1 represent excited triplet state, and S1 represent singlet state. I, II, III, and IV represent the sublevels of defect state. ISC represents the intersystem crossing process.
Next, its surface and deep defects should be further proven. Since surface defects are usually more sensitive to the environment, when the reaction temperature is increased, due to the instability of the defects, the higher reaction temperature will gradually remove the defects, and the luminescence of the defects will gradually extinguish. The appearing blue fluorescence was caused by the metal triplet fluorescence completely replaces one of the metal defects. The red luminescent material takes only 20 minutes when the reaction is carried out at a high temperature of 120°C, while the yellow luminescent material needs nearly 1 hour to restore the intrinsic luminescent color. This is that temperature has a greater influence on shallow defects, so the light color changes faster (Figure 4).

Figure 4. PL spectra (a, b) and fluorescent images (c, d) of the yellow (a, c) and red (b, d) emission materials prepared at 100 ºC at different reaction delay time.

Here, by adjusting the two types of defects, the luminescence color can also be adjusted continuously. It was found that only by changing the type and ratio of the end-capping ligand, the luminescence color would change from yellow to red. It can be seen from Figure 5 that various ratios between hexamethylene dithiol and mercapto-1-hexanol will cause a gradient change in fluorescent color. When the proportion of mercapto-1-hexanol increases, it is relatively easy to form surface defects, therefore, the emission color appears more red-shifted, indicating that the defect structure can be controlled easily.

Figure 5. PL spectra (a) and the fluorescent images (b) of the materials prepared in hexanedithiol: mercapto-1-hexanol = 1:1, 1:3, 1:5 and 1:7 with 365 nm excitation.

Due to the no fluorescence resonance energy transfer (FRET), and excellent stability simple synthesis, the resulting phosphor is suitable for the preparation of WLED with corresponding emission color mixing. 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).
4. Conclusion

In conclusion, the emission color can be well controlled by intentionally causing metal defects. The defect energy level will affect the photodynamic process of the radiation transition, which is closely related to the emission characteristics. The surface/deep defects of metal clusters are constructed by means of utilizing different reducing power of capping ligands. At the same time, through the control of defects, the continuous change of the luminous color is realized, which provides a new method for the adjustment of the luminous color, which is conducive to the design of high-performance WLED architecture.

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