

Simple and Cost-Effective Synthesis of Carbon Nanodots and Their Application as Luminescent Probes

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Abstract

Research on photoluminescent compounds have experienced a fast development in the last decades, due to their promising and diverse applications ranging from optoelectronics to biology, especially in the rapidly growing field on bionanotechnology [1]. Carbon nanodots (C-dots), as a new type of fluorescent nanomaterial have shown superior properties compared with conventional organic dyes and high-cost fluorophores [2-3]. Carbon-based nanodots may offer substantial advantages such as: (i) lower toxicity in comparison to other semiconductor quantum dots; (ii) high stability and limited blinking effects; (iii) abundance and low-cost production; (iv) wide emission spectrum within the UV-Visible range; (v) flexible surface chemistry to attach biomedical markers.

In the present work, we report a simple and cost-effective approach for the preparation of carbon nanoparticles under hydrothermal conditions with excellent luminescent properties in a wide spectrum range. We have evaluated different parameters such as reaction time, temperature of synthesis, organic compounds used as carbon sources and other co-reactants as additives. Several characterization techniques such as TEM, FT-IR, XPS and UV-Vis spectroscopy have shown the production of carbon nanoparticles with different size and emission ranges from UV to green with high quantum yields and long-term stability (see Figure 1-A for a representative example).

We have evaluated the influence of pH on the luminescence properties of these C-dots. The results show a clear influence on the final PL emission wavelengths and their relative luminescence intensities (Figure 1B). The maximum fluorescence activity of the C-dots was observed within the range of pH 4-9. Nevertheless, the presence of highly alkaline media partially quenches the overall PL intensity and favors a progressive shift of the emission wavelengths (Figure 1C). This optical behavior is tunable and reversible upon pH variations, thereby providing the C-Dots with a potential capacity as pH-nanosensor (Figure 1C). Moreover, the enhanced luminescent exhibited at physiological pH values makes them good candidates for biological labeling and imaging applications.

Further investigations have also shown the potential application of these C-Dots as selective nanosensors of metal ions [4-5]. It is especially remarkable the high selectivity shown in the presence of Cu²⁺ cations. The PL emission is progressively quenched even in the presence of ppb amounts. The selectivity detection limit in the presence of additional metal ions remains stable and reproducible in the micromolar range (ppm) (Figure 1D). These preliminary results suggest that sensor platforms based on C-dot can in principle respond to complex environments, serving as probes for the detection of analytically important metals of vital importance for biological monitoring and wastewater management.

References

- [1] Z. Kang, Y. Liu, S. Lee et al. *J. Mater. Chem.* **22** (2012) 24175-24175.
- [2] S.N. Baker and G.A. Baker, *Angew. Chem. Int. Ed.* **49** (2010) 6726.
- [3] M.J. Krysmann, A. Kellarakis, P. Dallas, E.P. Giannelis, *J. Am. Chem. Soc.* **134** (2012) 747.
- [4] Y. Liu, C.Y. Liu, Z.Y. Zhang. *Applied Surface Science.* **263** (2012) 481.
- [5] A. Salinas-Castillo, M. Ariza-Avidad, C. Pritz, M. Camprubi-Robles, B. Fernandez, M.J. Ruedas-Rama, A. Megia-Fernandez, A. Lapresta-Fernandez, F. Santoyo-Gonzalez, A. Schrott-Fischer, L.F. Capitan-Vallvey. *Chemical Communications*, **49** (2013) 1103.

Figures

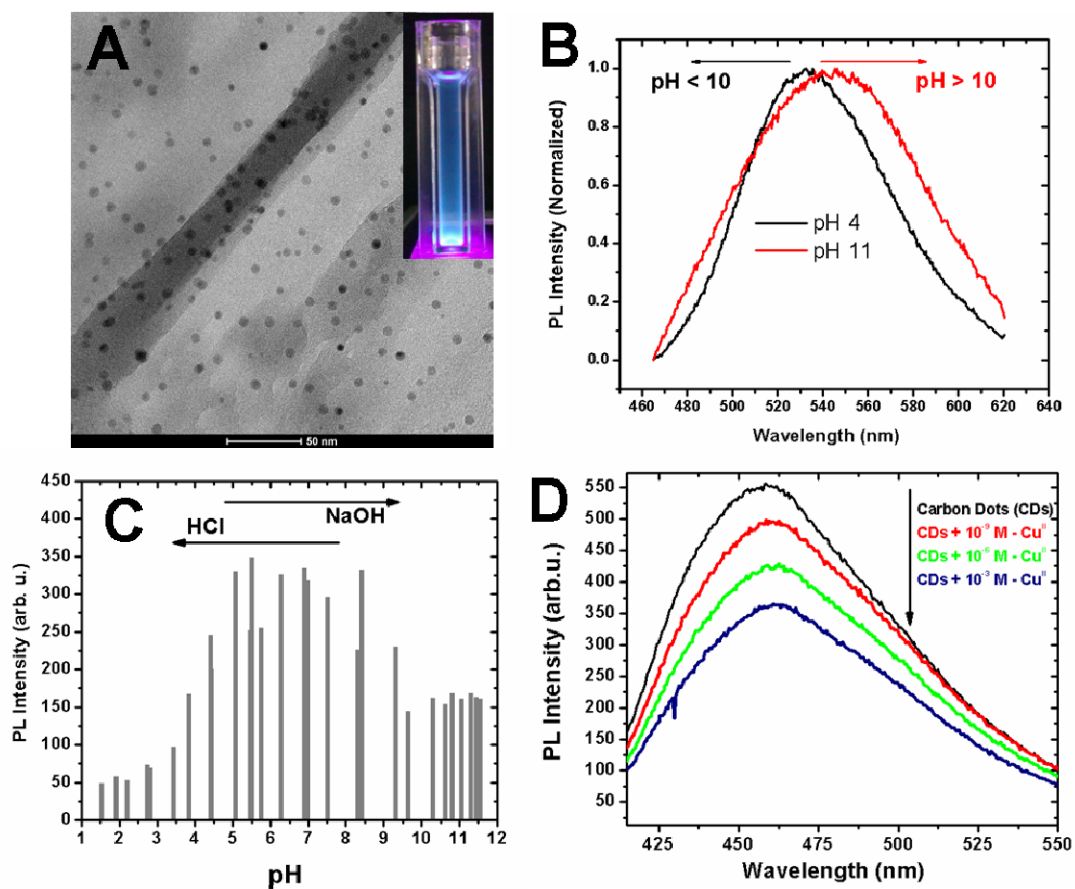


Figure 1. (A) Representative TEM image of carbon nanodots obtained by hydrothermal synthesis; (B) Photoluminescence emission spectra at different pH values ($\lambda_{\text{exc}} = 450 \text{ nm}$); (C) Photoluminescence emission intensities evolution upon the variation of pH conditions; (D) Photoluminescence quenching effect induced by increasing concentrations of copper ions; Inset: digital photograph of a colloidal solution containing C-dots and excited under an UV lamp ($\lambda_{\text{exc}} = 400 \text{ nm}$).