Fast synthesis and size separation of thiolated/ water soluble copper clusters

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Fluorescent nanomaterials have drowned extensive attention in biological labelling and imaging due to their controllable physical and chemical properties. Recently, lots of efforts have been devoted to prepare various ultra-small and functional copper nanoclusters (CuNCs) with different emissions from blue to red [1], [2]. Herein, we discuss the synthesis of water soluble and highly stable glutathione (GSH) protected clusters, their characterization and to date, the first size-separation by chromatography (HPLC) and electrophoresis (PAGE).

In a typical procedure, GSH and $Cu(NO_3)_2*3H_2O$ were taken in an agate mortar and ground well for 5min. The homogeneous powder was dispersed in Milli-Q water and the formed hydrogel was heated up to 80°C for 10 min. 1M NaOH was added drop wise until transparent and clear solution formed. The main results are summarized in Fig.1:

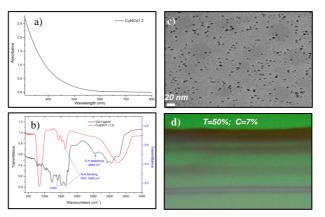


Fig.1 a) UV-vis and b) FTIR spectra, c) HRTEM image, and d) PAGE separation of CuNCs

Based on the obtained results, the crude mixture of 6.7 < x < 9.6 nm particle size has no obvious optical fingerprints in the visible range. The surface properties of CuNCs were exploited by FTIR measurements. The absent of S-H stretching vibrational mode suggests the cleavage of the S-H bond and binding of the GSH molecules onto the surface of CuNCs through Cu-S bonding.

Polyacrylamide gel electrophoresis (PAGE) separation of the crude sample enabled the separation of 5-well defined fractions. Moreover, the last two bands (from bottom) were only visible under UV irradiation. It is worthwhile mentioning that the crude sample shows very weak NIR emission with a peaking centered at 740nm.

We have furthermore been able to separate different sizes via HPLC using ProSwift[®]WAX-1S Monolith column. Preliminarily results were in a good agreement with PAGE separation, showing that it is possible to isolate well-defined copper clusters.

References

- [1] C. Wang and Y. Huang, *Nano*, vol. 08, no. 05, p. 1350054, 2013.
- [2] C. Wang, L. Ling, Y. Yao, and Q. Song, *Nano Res.*, vol. 8, no. 6, pp. 1975–1986, 2015.