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Cu-Doped Carbon Nanodots as a Promising Contrast Agent for MRI

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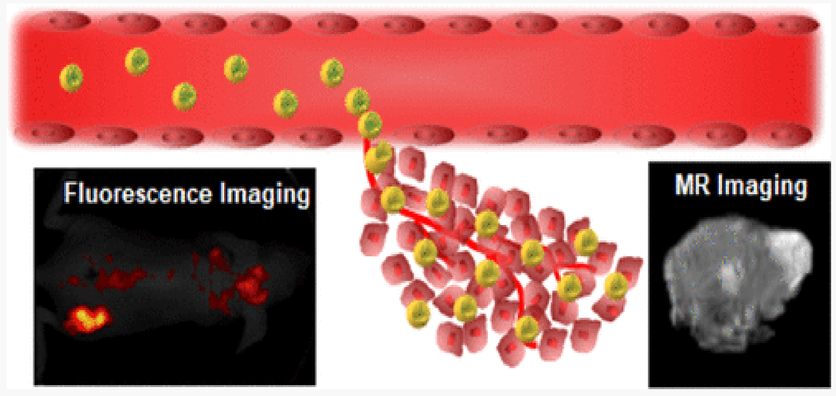
Introduction

Luminescent carbon dots (**CDs**) are biocompatible, low toxic, photostable and can be used as luminescent nanoprobes for bioimaging. By the doping of CDs by various heteroatoms it is possible to control morphology and optoelectronic transitions of CDs. Doping of CDs with paramagnetic metals allows formation of new contrast agent (**CA**) for magnetic resonance imaging (**MRI**) with a better performance than well-known commercial CAs. Such CDs are perspective as dual-modal nanoprobes for both MR- and PL-bioimaging for noninvasive diagnosis. In this work, carbon nanoparticles doped with copper ions (Cu^{2+}) with emission in a wide spectral range were developed. A high value of relaxivity r1 = 0.92 mM-1·s-1 was obtained, which is higher than the values known to us for Cu-nanoparticles.



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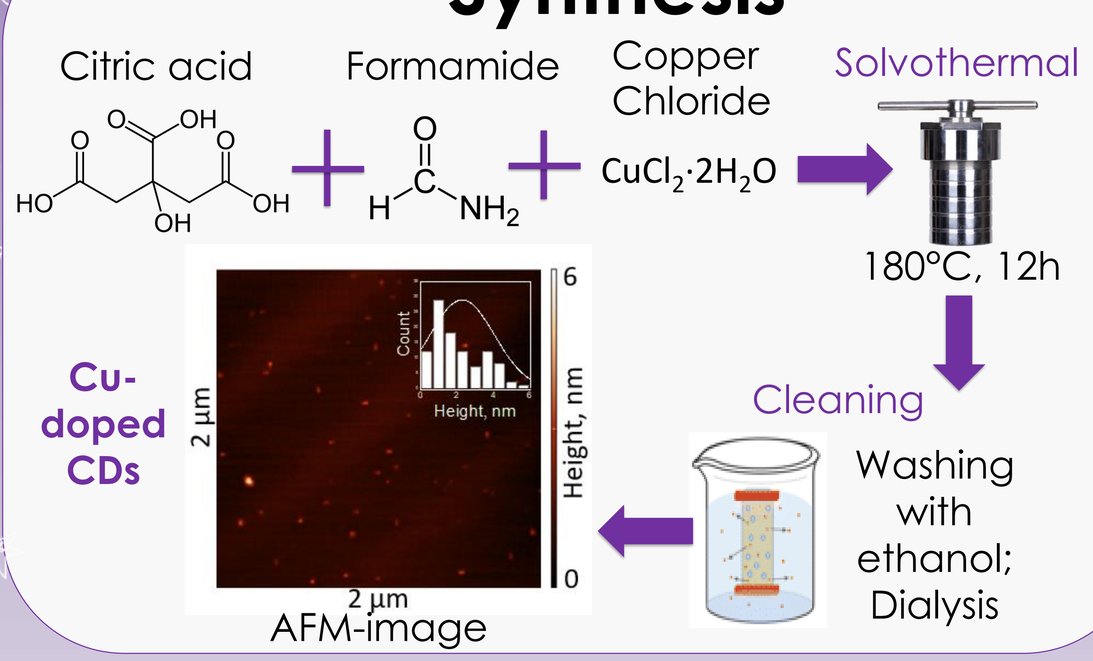
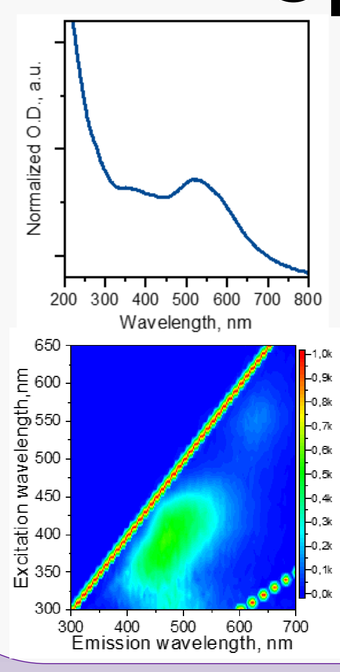
Synthesis



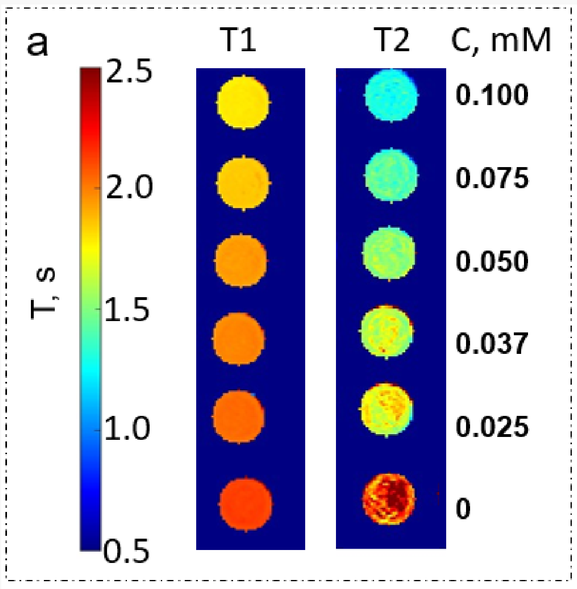
Optical properties



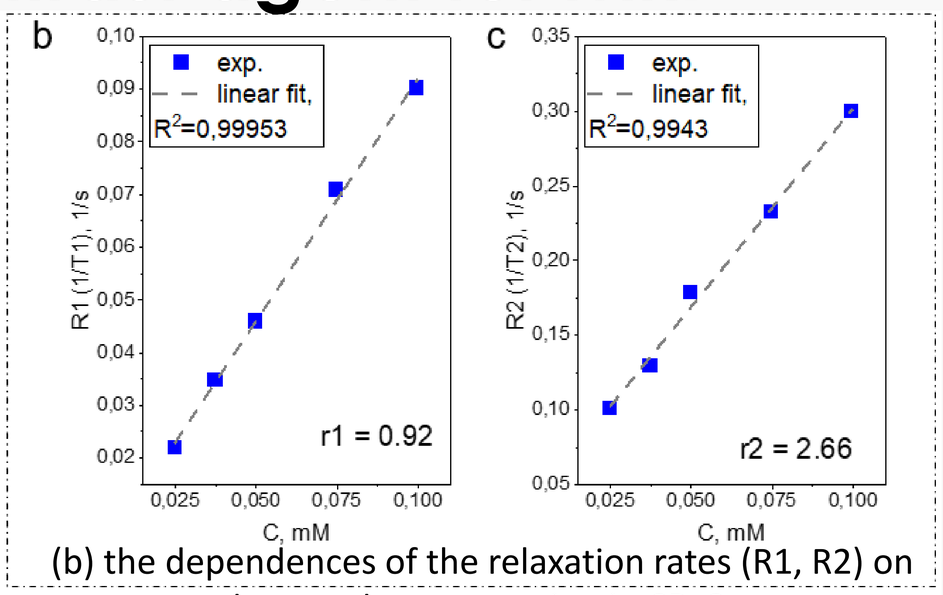
Absorption:
1) 200–300 nm – C=C bonds and optical transitions of CD's "core";
2) 300–450 nm and 500–600 nm with max. at 520 nm – optical centers similar to N-/O-doped *polycyclic aromatic hydro-carbons (PAHs)* in the CDs' core and on their surface;
3) 600–700 nm – optical n–π* transitions of surface molecular groups bonded to sp2-domains.

Emission: 1) 420–530 nm due to different doped PAHs within CDs;
2) red PL band at 620 nm is caused by CDs' surface groups

CDs as contrast agent for MRI



(a) the MR maps of the T1 and T2



(b) the dependences of the relaxation rates (R1, R2) on the metal concentration in CD-Cu

T1 & T2 – the times of longitudinal and transverse relaxation of protons, correspondingly

Cu-CDs act as a contrast agent and reduce T1 and T2. The values of the corresponding relaxivities r1 and r2, calculated as the slope of the dependence of the relaxation rate on the metal concentration, are **0.92** and **2.66 mM-1·s-1**, respectively. The ratio r2 / r1 determines the type of contrast agent: if r2 / r1 ≤ 5, then the test substance is classified as a positive or T1 contrast agent, if the ratio is above 10, it is referred to as a negative or T2 contrast agent [*DOI:10.3390/ma13112586*]. For the CDs synthesized in this work, the ratio **r2 / r1 = 2.9**, which indicates the prospect of using these nanoparticles as **T1 contrast agents**.

Conclusion

Copper-doped citric acid-based CDs with luminescence in a wide spectral range, including red emission, have been successfully developed, which makes them promising luminescent nanoprobes for bioimaging. It was also found that the obtained CDs are able to change the relaxation times of water protons during MRI, and the calculated relaxivity r1 reached 0.92 mM-1 s-1, which is the highest value for copper-based contrast agents, to the best of our knowledge. The proposed CDs can be a safe, non-expensive and effective replacement for existing CAs. Thus, the data obtained make an important contribution to the development of multifunctional nanoprobes based on CDs.

Ref.: Optics and spectroscopy, 2023 – just accepted

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