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Preparation of Amino Acid-Functionalized Carbon Quantum Dots from Citric Acid – Efficient Fluorescent Nanoprobe for Selective Detection of Fe^{3+} Ions in Model Systems and in Well Water Samples

Silvija Šafranko[1,*], Kristina Janđel [2], Monika Kovačević [2], Maja Dutour Sikirić [3], Šimun Mandić [4], Aleksandar Széchenyi 5, Ivica Strelec [1], Stela Jokić [1]

[1]Faculty of Food Technology Osijek, University of Osijek, Franje Kuhača 18, 31000 Osijek, Croatia; tel. +385 31 224 348, e-mail: **silvija.safranko@ptfos.hr**; [2]Department of Chemistry, University of Osijek, Ulica cara Hadrijana 8/A, 31000 Osijek, Croatia; [3]Division of Physical Chemistry, Ruđer Bošković Institute, 10000 Zagreb, Croatia; [4]Center of Excellence for Advanced Materials and Sensing Devices, Institute of Physics, Bijenička Cesta 46, 10000 Zagreb, Croatia; [5]Institute of Pharmaceutical Technology and Biopharmacy, Faculty of Pharmacy, University of Pécs, H-7624 Pécs, Hungary

INTRODUCTION

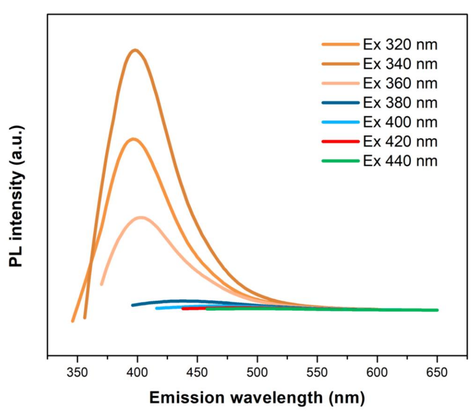
Carbon quantum dots (CQDs) belong to a group of new and efficient carbon photoluminescent nanomaterials that have attracted the attention of many scientists over the past decade, especially due to their excellent chemical and optical properties. Their chemical stability, biocompatibility/low toxicity, water solubility and optical efficiency represent a huge potential for a wide range of applications in biomedical research and nanotechnology. This study presents a simple, inexpensive, environmentally friendly and green synthesis of N-doped carbon quantum dots from citric acid, and six different amino acids (Leu, Trp, Arg, Lys, Ala, His). Firstly, the differences between the chemical, structural and optical properties were studied. The incorporation of nitrogen into the CQDs obtained from citric acid and amino acids has led to an increase in quantum yield (QY) and in general, improvement in the performance and sensitivity of nanoprobes, compared to the blank system (without the addition of amino acids). The prepared N-doped CQDs demonstrated selectivity toward Fe^{3+} ions, showed great stability in aqueous/high ionic media and similar optical properties, and were used as nanoprobe for Fe^{3+} ion detection in model systems, as well as in well water samples.

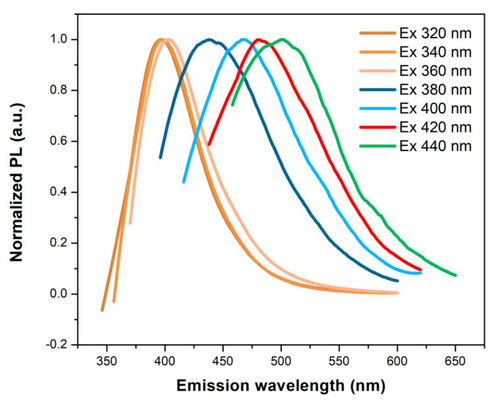
MATERIALS AND METHODS

Parameters	Conditions
Temperature	180 °C
Time	9 hours
Procedure for CQDs preparation	Hydrothermal synthesis; 825 mg of citric acid was dissolved in 15 mL of Milli-Q water, then 175 mg of AA was dissloved in 5 mL Milli-Q water – overall 20 mL of mixture
Prepared samples	Blank + [citric acid + Amino acid (Ala, Arg, His, Leu, Lys, Trp)]

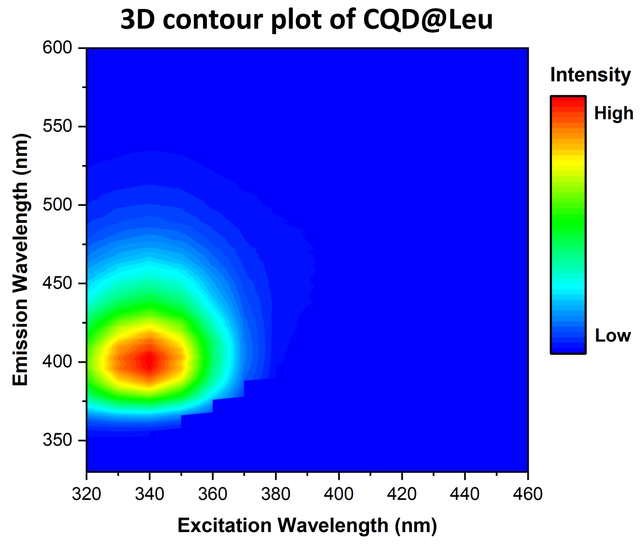
CHEMICAL/STRUCTURAL/OPTICAL CHARACTERIZATION

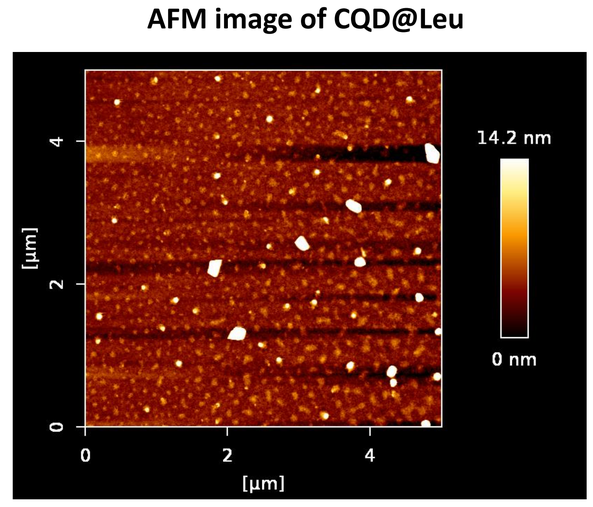
Prepared sample	Quantum yield (QY; %)	Maximum excitation wavelength (nm)	Maximum emission wavelength (nm)
Blank	2.02	340	430
Leucin	36.43	343	406
Triptofan	33.17	367	423
Arginin	23.92	335	415
Lizin	16.94	340	408
Alanin	16.42	340	398
Histidin	12.97	335	401





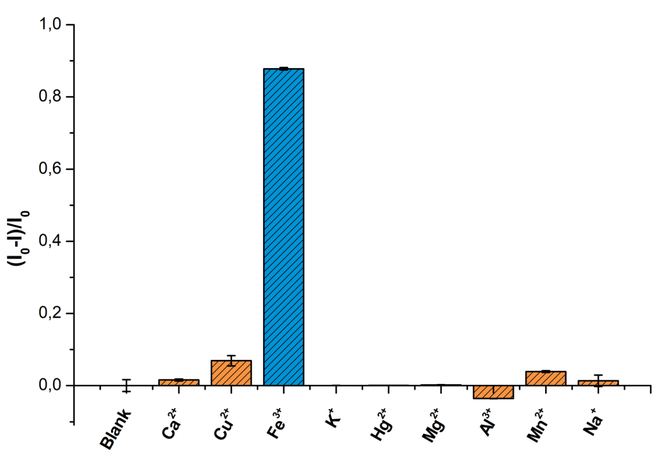
Prepared CQD@Leu nanoparticles showed great stability in aqueous/high ionic media and good optical properties – maximum emission wavelength of 406 nm with excitation wavelength of 343 nm. With the excellent QY of 36.43%, CQD@Leu showed good potential in sensing of different chemical species.

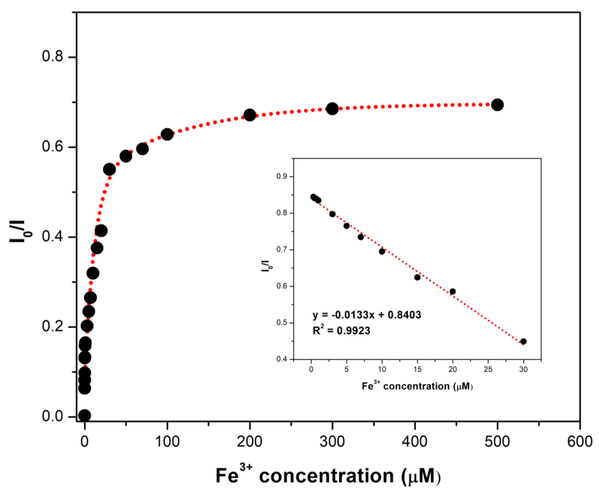


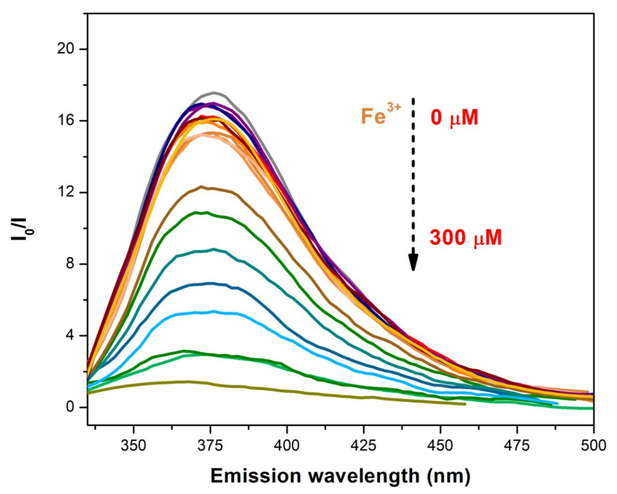


Sample	Standard method – determined Fe^{3+}		Determined Fe^{3+} with CQDs nanoprobe		Average ± Standard Deviation	Recovery %	RSD %
			1	2			
16	1338	µg/L	1449.24	1391.08	1420.16 ± 41.12	106.14	2.90
17	2036	µg/L	1965.73	1989.54	1977.63 ± 16.84	97.13	0.85
18	4960	µg/L	5121.44	5048.87	5085.15 ± 51.31	102-52	1.00

APPLICATION OF CQD@Leu IN METAL ION SENSING







The developed model was described by an exponential function with a suitable coefficient of determination of R^2 = 0.9810, while the linear range was determined in the concentration range from 0.3 µmol dm^{-3} to 30 µmol dm^{-3} with a determined limit of detection of LOD = 1.76 ± 0.01 µmol dm^{-3} and limit of quantification of LOQ = 5.89 ± 0.04 µmol dm^{-3}. The satiscatory results were obtained for the Fe^{3+} ion detection in well water samples (compared to the standard methods).

CONCLUSIONS

<u>This work reports carbon quantum dots (CQDs) from citric acid modified with different amino acids, resulting in a successful nitrogen doping of CQDs.</u>

1. Prepared amino acid-funtionalized CQDs possessed good sensing properties, satisfactory optical and chemical properties.
2. The samples of CQDs were prepared at temperature of 180°C during 9 hours.
3. The highest determined quantum yield was achieved with the CQD@Leu (QY=36.43%). The Blank sample demonstrated the lowest quantum yield (QY=2.02%).
4. The maximum emission wavelength of CQD@Leu is determined at 406 nm, when excited at 340 nm.
5. The CQD@Leu showed outstanding selectivity toward Fe^{3+} ions, among the all tested metal ions and prepared samples.
6. The developed model was described by an exponential function with a suitable coefficient of determination of R^2 = 0.9810.
7. The model was tested with well water samples and were compared with standard methods of Fe^{3+} ions detection in water monitoring industry.

The presented study may represent a novel and useful approach for efficient utilization of the waste for practical applications, including those in analytical chemistry and environmental monitoring.

ACKNOWLEDGEMENT

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