The Preparation of N-doped Carbon Quantum Dots from Citric Acid and *Citrus clementina* Peel – The Application in Iron(III) Detection in Herbs and Spices

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ABSTRACT

This study represents a novel investigation of N-doped CQD derived from citric acid and citrus peel for the selective response of Fe^{3+} ions in both model and real sample systems. The hydrothermal synthesis of the samples was carried out at temperature of 180° C during 9 hours. The amino acid leucine (Leu, L) has been used as nitrogen dopant in the CQD synthetic procedure, and the CQD@hybrid was obtained as a result of mixing citric acid/citrus peel and Leu before initiating the synthesis. The physico-chemical characterization (AFM, PXRD, dispersibility in water, EDS) od the prepared CQD samples was performed, while optical characterization has shown that quantum yield for the CQD@Leu sample was calculated to be QY=36.43% and for the CQD@hybrid was QY=10.04%. Also, investigation of the excitation-dependent photoluminescence (PL) and influence of the solvents on the PL intensity was also carried out. Finally, selectivity toward metal ions were studied in the presence of CQD@Leu and CQD@hybrid and it was determined that both samples were highly selective toward Fe^{3+} ions. Hence, two different models were developed for the detection of Fe^{3+} ions in model systems described by exponential functions, and the linear responses were established in the concentration ranges: 1) 0.3 μmol dm^{-3} to 30 μmol dm^{-3} (R^2=0.9982) with a determined limit of detection of LOD = 1.77 ± 0.01 μmol dm^{-3} and limit of quantification of LOQ = 5.88 ± 0.04 μmol dm^{-3} for CQD@Leu; 2) 0.5 μmol dm^{-3} to 15 μmol dm^{-3} (R^2=0.9851) with a determined limit of detection of LOD = 2.72 ± 0.39 μmol dm^{-3} and limit of quantification of LOQ = 9.06 ± 1.29 μmol dm^{-3} for CQD@hybrid. Moreover, the photoluminescent nanoprobes were successfully used for the determination of Fe^{3+} ions in herbs (nettle) and spices (oregano).

MATERIALS AND METHODS

Carbon quantum dots (CQD) are relatively new class of photoluminescent carbon nanomaterials composed of discrete and quasi-spherical carbon nanoparticles, which due to their outstanding chemical and optical properties, excellent biocompatibility and overall great sensing performance, have attracted the enormous amount of interest in the scientific community. The possibility of facile surface modifications and heteroatom doping for the properties and performance enhancement, CQD have found versatile applications in a wide range of analyses: in biomedicine and pharmacy, water monitoring and food quality control, environmental and pesticide analysis.

Citrus clementina peel and citric acids CARBON PRECURSOR

Amino Acid Leu NITROGEN DOPANTS

HYDROTHERMAL SYNTHESIS (180°C, 9 h) $CQD@Leu_{CITRIC}$

HYDROTHERMAL SYNTHESIS (200°C, 12 h) – CQD@hybrid

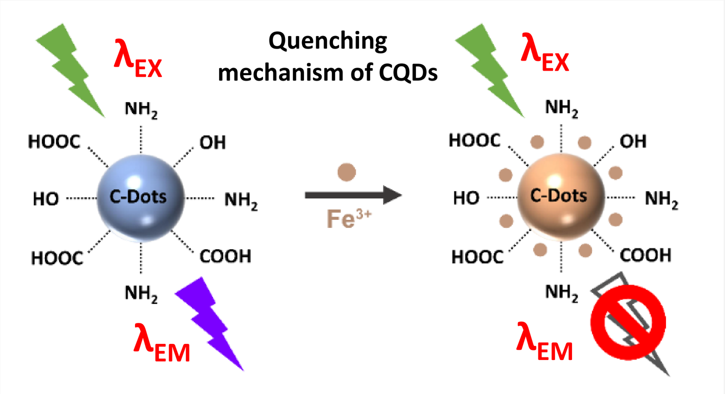
CQD@hybrid $CQD@Leu_{CITRIC}$

PURIFICATION (dialysis, MCWO 1kDa)

STORAGE AT 4°C

CHARACTERIZATION AND ANALYSIS

The calculated quantum yields of all prepared samples were as follows: 36.43 % for $CQD@Leu_{CITRIC}$, while at optimal conditions for obtaining CQD@hybrid QY = (17.52 ± 0.59) %



(A) Washing (B) Freeze-drying (C) Milling

The *Citrus clementina* peels were collected from the Dalibor Ujević family farm (Opuzen, Croatia) and were washed with water several times before use.

RESULTS AND DISCUSSION

PROCESS OPTIMIZATION OF CQD@hybrid PREPARATION

Table 1. Operating conditions for QY investigation of CQD@hybrid

Independant variables	Symbol	Level		
		Low (-1)	Center (0)	High (+1)
Temperature (°C)	X_1	130	175	220
Reaction time (hours)	X_2	5	10	15

Table 2. CCD plan for QY investigation of CQD@hybrid

Run	Variable 1	Variable 2	Response 1
	Temperature	Reaction time	QY
	°C	hours	%
1	160	9	2.03
2	180	9	12.79
3	200	9	16.30
4	180	6	7.82
5	180	9	12.47
6	200	6	14.10
7	200	12	17.04
8	160	12	2.50
9	180	9	13.14
10	180	12	13.75
11	160	6	1.54

Table 3. Analysis of variance (ANOVA) of second-order polynomial model for QY of CQD@hybrid

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F Value	*p*-Value[a]
Model	328.77	5	65.75	45.51	0.0004
X_1-Temperature	285.07	1	285.07	197.31	< 0.0001
X_2-Time	16.07	1	16.07	11.12	0.0207
X_1X_2	0.9919	1	0.9919	0.6865	0.4451
X_1^2	18.13	1	18.13	12.55	0.0165
X_2^2	2.81	1	2.81	1.95	0.2217
Residual	7.22	5	1.44		
Lack of fit	6.75	3	2.25	9.4	0.0976
Pure error	0.4783	2	0.2391		
Total	336	10			
R^2	0.9785				

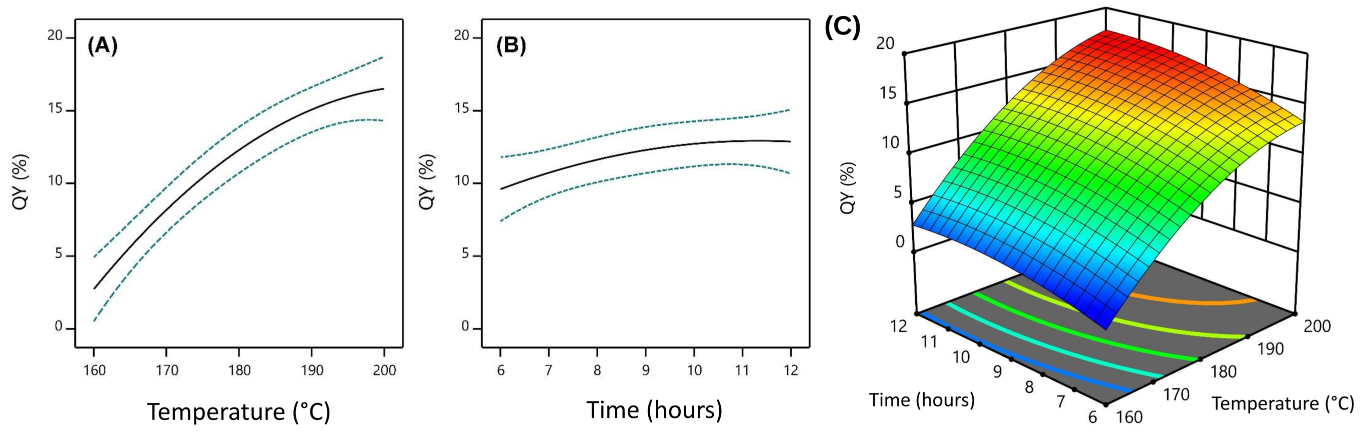


Figure 1. 2D diagrams of (A) influence of temperature and (B) infuence of reaction time on QY of CQD@hybrid sample. The illustration of 3D diagram shown in (C) shows the influence of both variables on the QY.

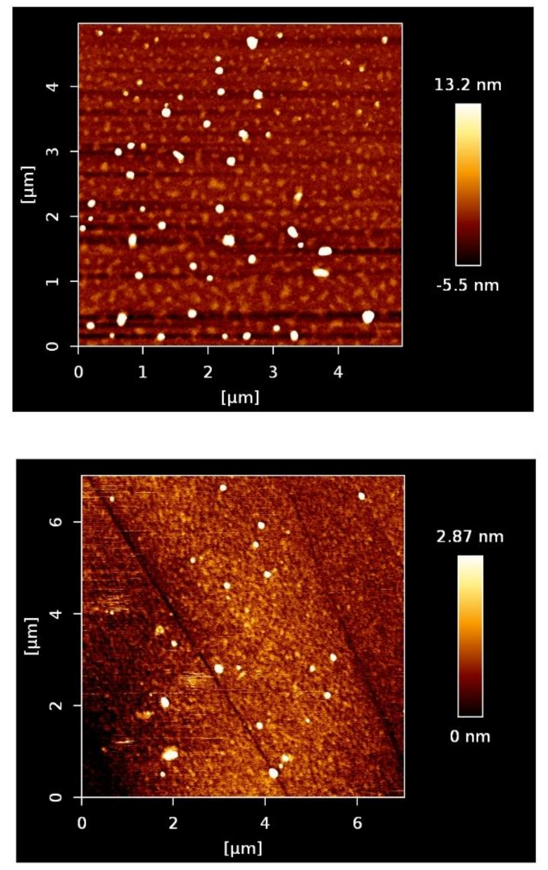


Figure 2. AFM images of (A) CQD@hybrid and (B) $CQD@Leu_{CITRIC}$

The presence of spherical nanoparticles can be seen – height of <15 nm

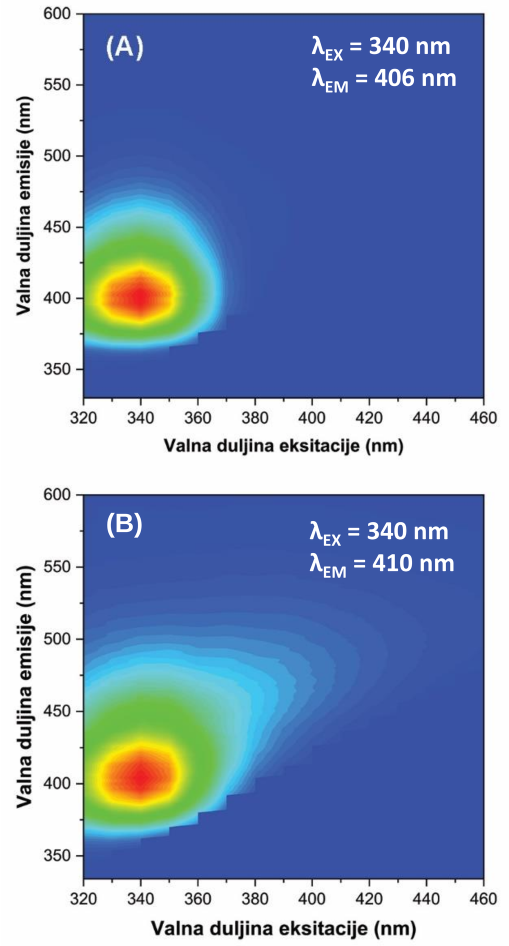


Figure 3. 2D mapping of excitation/emission (A) $CQD@Leu_{CITRIC}$ and (B) CQD@hybrid

ION SELECTIVITY

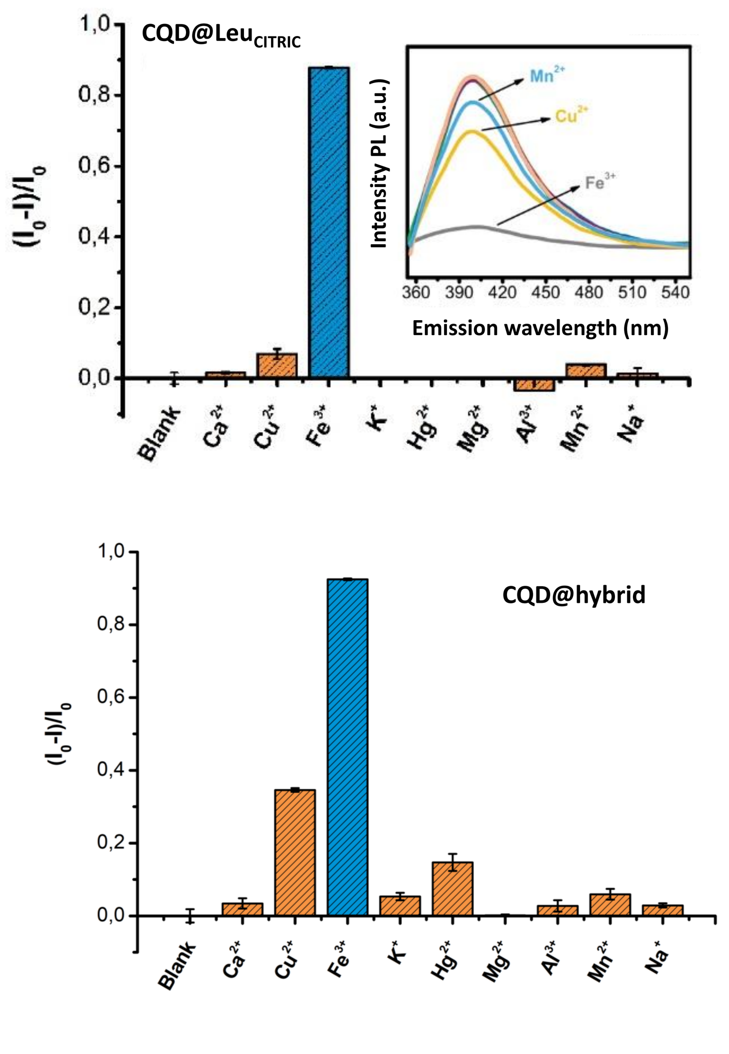


Table 4. Elemental analysis of as-prepared CQDs

Sample	Weight percentage (%)			Atomic percentage (%)		
	C (%)	O (%)	N (%)	C (%)	O (%)	N (%)
$CQD@Leu_{CITRIC}$	40.48	46.44	1.60	45.11	38.85	1.53
CQD@hybrid	88.72	38.64	13.11	63.20	20.66	8.01

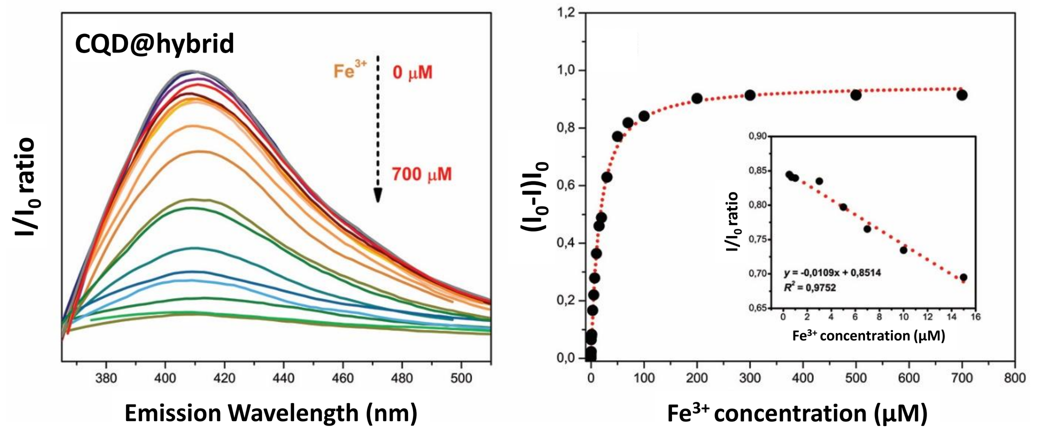
DETECTION OF Fe(III) IN NETTLE AND OREGANO

Table 5. Determination of Fe(III) in nettle and oregano samples – $CQD@Leu_{CITRIC}$

Sample	Fe(III) determined by KSCN method (mg/kg)	Experimental with CQDs (mg/kg)				Recovery (%)	RSD (%)
		1. measurement	2. measurement	Average	StDev		
Nettle sample	95.69 ± 0.04	94.62	81.04	87.83	9.60	91.80	10.93
Oregano sample	82.35 ± 0.01	119.56	111.41	115.49	5.77	140.24	4.99

Table 6. Determination of Fe(III) in nettle and oregano samples – CQD@hybrid

Sample	Fe(III) determined by KSCN method (mg/kg)	Experimental with CQDs (mg/kg)				Recovery (%)	RSD (%)
		1. measurement	2. measurement	Average	StDev		
Nettle sample	95.69 ± 0.04	69.65	78.96	74.31	6.58	77.67	8.86
Oregano sample	82.35 ± 0.01	75.48	82.80	79.14	5.18	96.10	6.54



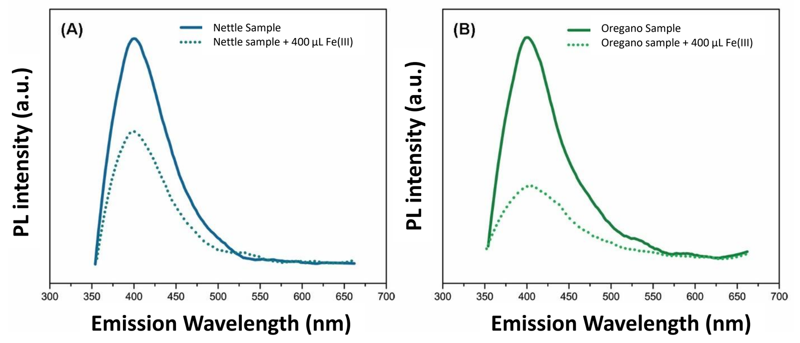
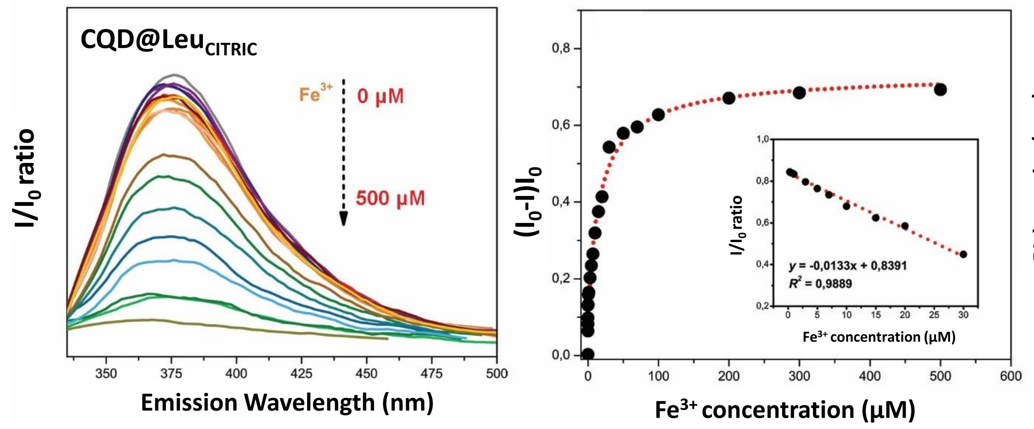


Figure 4. The PL spectra of (A) nettle and (B) oregano sample while using CQD@hybrid as fluorescent nanoprobe



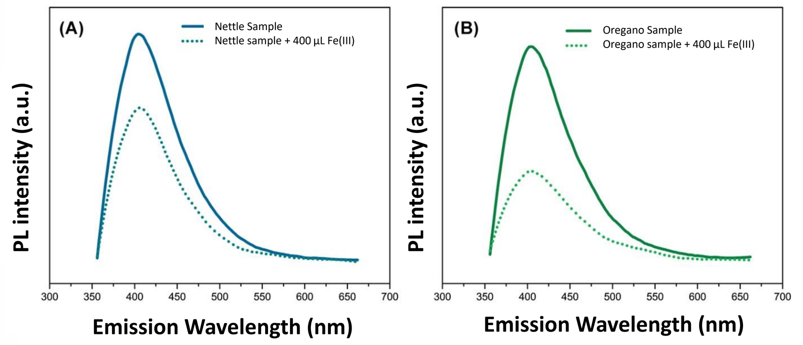


Figure 5. The PL spectra of (A) nettle and (B) oregano sample while using $CQD@Leu_{CITRIC}$ as fluorescent nanoprobe

ACKNOWLEDGEMENT

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