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Quantum Yield Optimization of Hybrid Carbon Quantum Dots and Their Application as Sensing Nanomaterials

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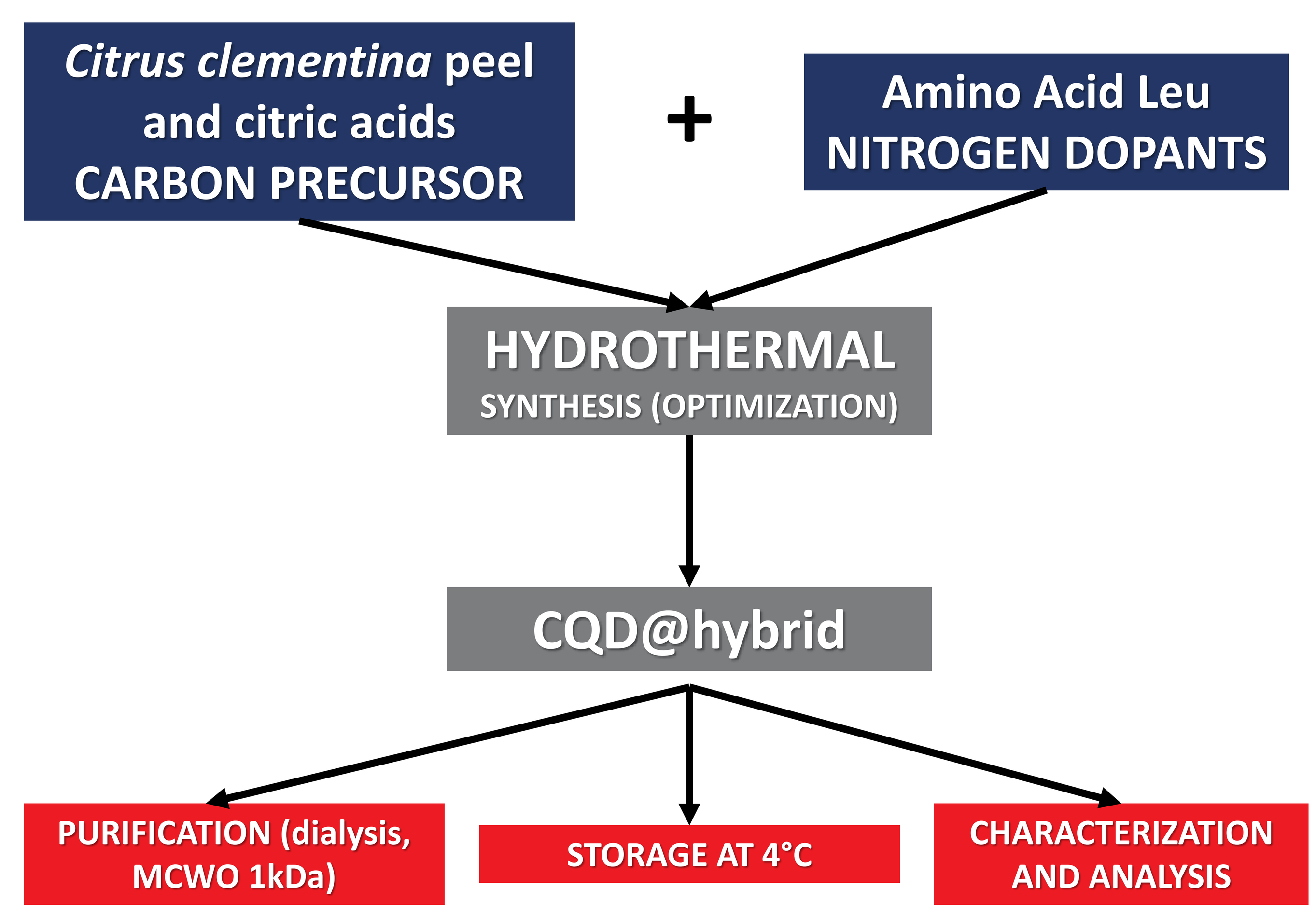
INTRODUCTION

Carbon quantum dots (CQDs), as a new type of zero-dimensional carbon-based nanomaterials, represent an emerging class of fluorescent materials for potential applications in biosensing, chemical sensing, and in theranostics. Also, CQDs have attracted an enormous attention due to their outstanding physico-chemical and tunable optical properties, water dispersity, high photostability and biocompatibility. In this study, hybrid carbon quantum dots (CQD@hybrid) have been prepared by hydrothermal procedure and quantum yield was optimized using response surface methodology (RSM). The process was analyzed and optimized with a central composite face-centered design (CCFD) model in a quadratic function consisting of 11 experimental runs with included three replicates at the central point. The effects of temperature (160–200 ° C; X_1), and preparation time (6–12 h; X_2) was investigated on the quantum yield (y) obtained by CQD@hybrid sample. The sample of CQD@hybrid obtained under optimal conditions exhibited high quantum yield of 17.52 ± 0.59 %, and was studied in details regarding physical (FTIR, PXRD), and optical (spectrofluorimetry). Furthermore, the sample CQD@hybrid were applied as fluorescent nanoprobe toward Fe^{3+} ion detection in model systems, and also for the detection of Fe^{3+} ions in real samples of well-water. The presented results are indicative of a good preparative approach toward obtaining highly fluorescent CQDs with a great potential for the studies in water monitoring, food analysis and quality control.

MATERIALS AND METHODS



RESULTS AND DISCUSSION

Table 1. Pre-optimization process for CQD@hybrid

CP extract (1:30) / mL	Citric Acid amount (mg) in 5 mL	Leucine mass / mg	Arginine mass / mg	QY / %
15	250	-	-	1.25
15	500	-	-	2.05
Poslije određivanja kvantnog prinosa Blank sustava				
15	500	175	-	10.04
15	500	-	175	7.36

The highest QY has been determined with the addition of 500 mg of citric acid and with amino acid Leu

PROCESS OPTIMIZATION

Table 2. Coded and actual levels of the independent variable for the CCFD design for the QY investigation for CQD@hybrid.

Independant variables	Symbol	Levels		
		Low (-1)	Center (0)	High (+1)
Temperature (°C)	X_1	160	180	200
Reaction time (hours)	X_2	6	9	12

Table 3. CCFD experiments for QY investigation of CQD@hybrid

	Variable 1	Variable 2	Response 1
Run	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

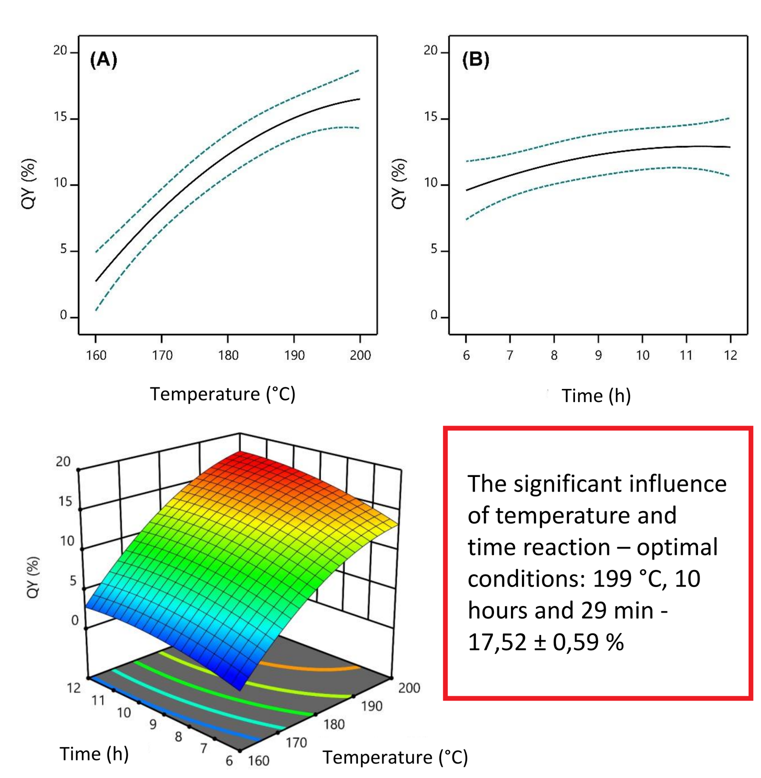
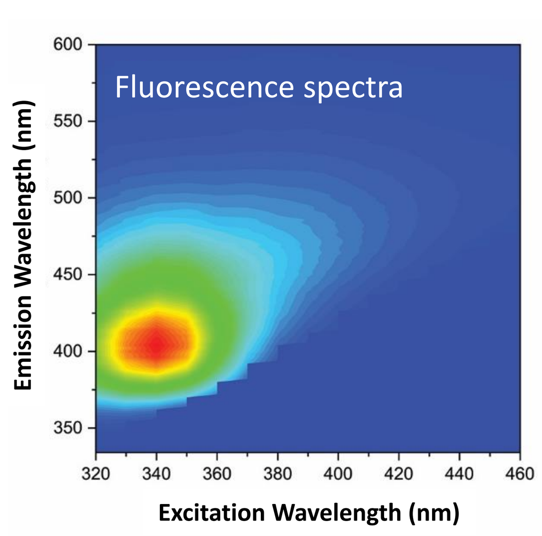
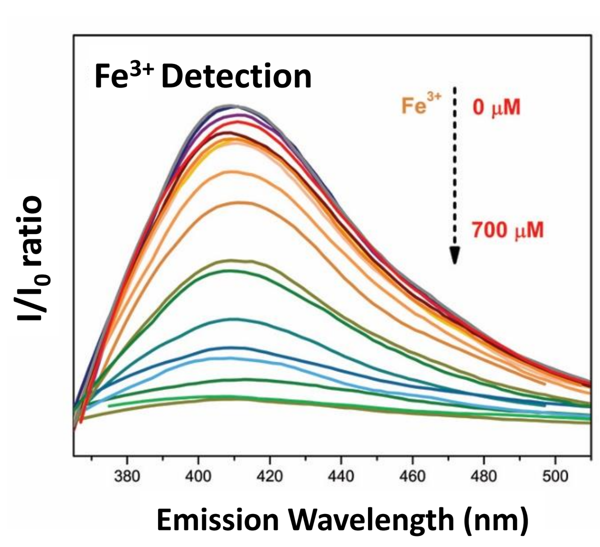


Table 4. Analysis of variance (ANOVA) of quatratic model for QY - CQD@hybrid

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				

[a] ** $p < 0.01$ highly significant; * $0.01 \le p < 0.05$ significant; $p \ge 0.05$ not significant.





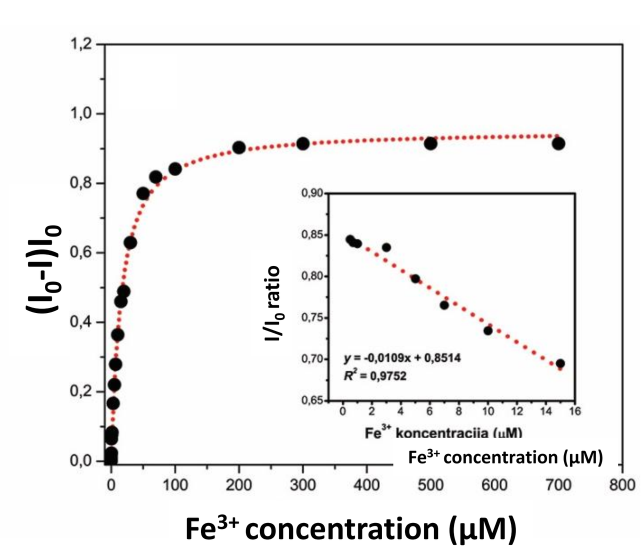
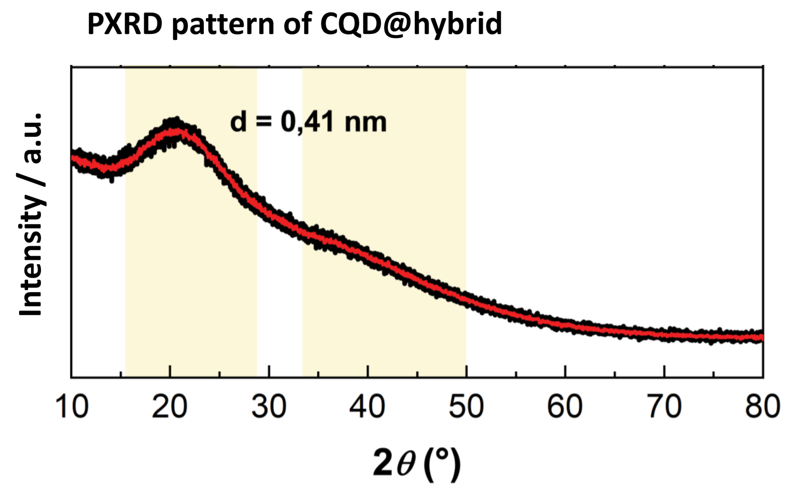


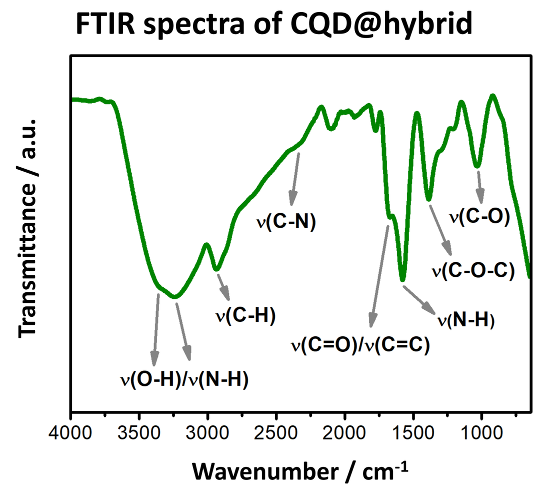
Table 5. Determination of Fe(III) in well-water analysis - CQD@hybrid

Sample	Fe^{3+} determined with standard method / µg/L	$\gamma_{experimental}$ (Fe^{3+}) with CQD method / µg/L			Recovery / %	RSD / %
		1	2	Average ± StDev		
16	1338.00	1443.47	1484.29	1463.88 ± 28.86	109.41	1.97
17	2036.00	2042.05	2106.26	2074.16 ± 45.40	101.87	2.19
18	4960.00	5027.48	4616.77	4822.12 ± 290.42	97.22	6.02

PXRD pattern of CQD@hybrid



FTIR spectra of CQD@hybrid



CONCLUSIONS

1. Central composite experimental design (CCFD) was used to investigate the influence of the parameters on the QY for the samples CQD@hybrid; process optimization was also performed.
2. The sample of CQD@hybrid obtained under optimal conditions exhibited a high quantum yield of 17.52 ± 0.59 %;
3. The sample characterization showed good physico-chemical and optical properties;
4. The detection of Fe^{3+} ions in real samples of well-water - a great potential for the studies in water monitoring and food quality control.

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