Integrating fluorescent carbon nanodot synthesis and optical detection of methylmercury

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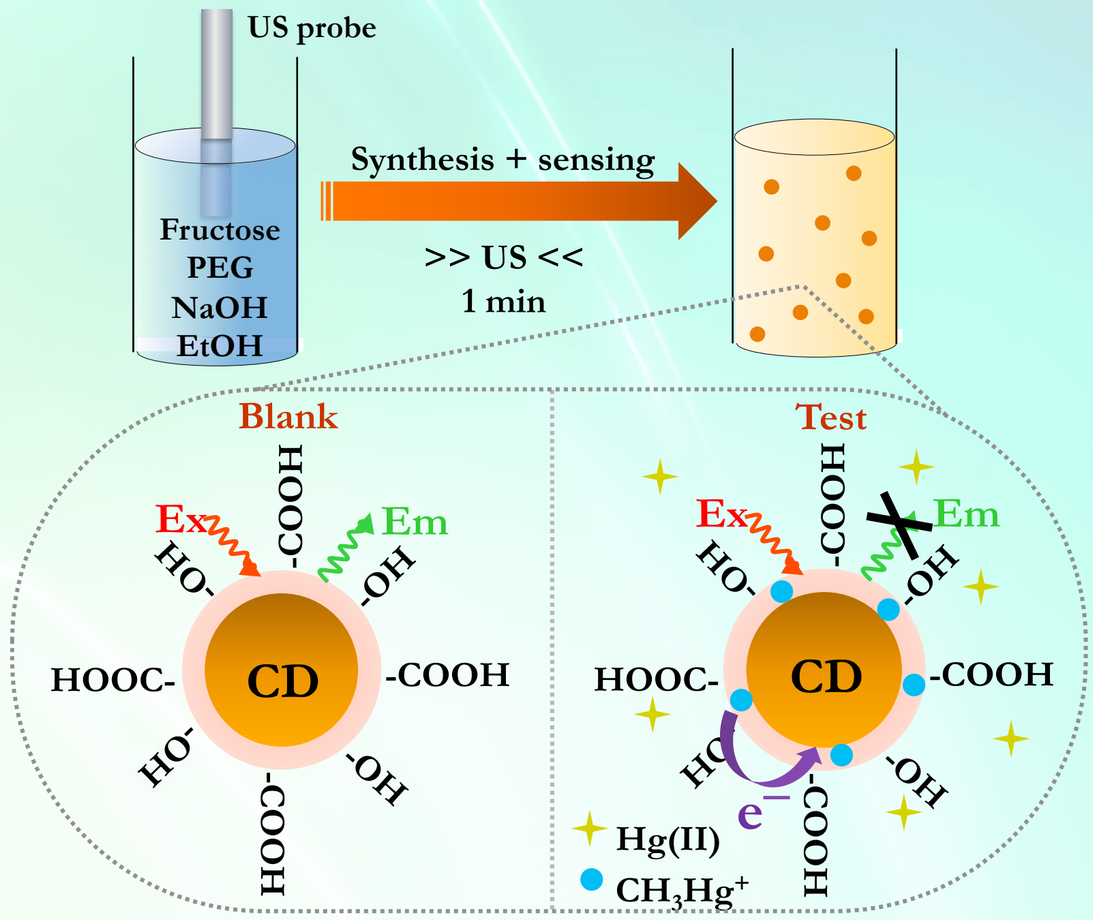
INTRODUCTION

In the last years, a great interest toward development of optical nanoprobes has arisen, so fluorescent nanomaterials have been implemented in analytical systems for the detection of several species. Recently, fluorescent carbon dots (CDs) have received much attention due to its attractive optical properties, its simplicity of synthesis, making use of natural and non-toxic precursors, and its ability for being used as fluorescent nanoprobes.

In this work, a novel assay that integrates the synthesis of fluorescent CDs and sensing within one step, for the fast, sensitive and selective detection of methylmercury is presented. To this end, high-intensity ultrasound (US) energy is exploited to synthesize CDs at the same time that facilitates the permeation of methylmercury through the passivation coating of CDs made of PEG, causing the fluorescence quenching.



Optimized conditions

Mass of CDs precursor	40 – 45 mg of fructose
Sample volume	1 mL (0.1 M HCl)
PEG volume	1.2 mL
NaOH volume	200 µL
NaOH concentration	3.5 M
Ethanol volume	200 µL
US amplitude	10%
US time	1 minute

Analytical Performance

Linearity	23 – 278 nM
Detection limit	5.9 nM
Quantification limit	19 nM
Repeatability (RSD)	2.2 % (n=7)
Reproducibility (RSD)	4.1 % (n=3)

Analysis of water and fish

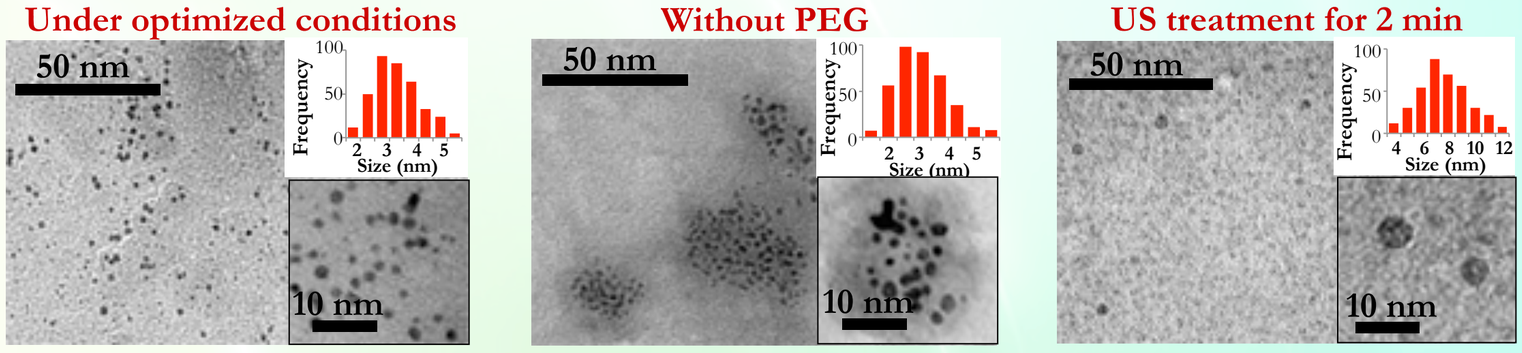
WATER SAMPLES

Sample	Added CH_3Hg^+ conc. (nM)	Recovery (%)
River water	0 – 232	94.4 – 95.7
Tap water	0 – 232	89.7 – 92.2
Sea water	0 – 232	99.3 – 101
BCR-610	23	90.9

MARINE ANIMAL TISSUES

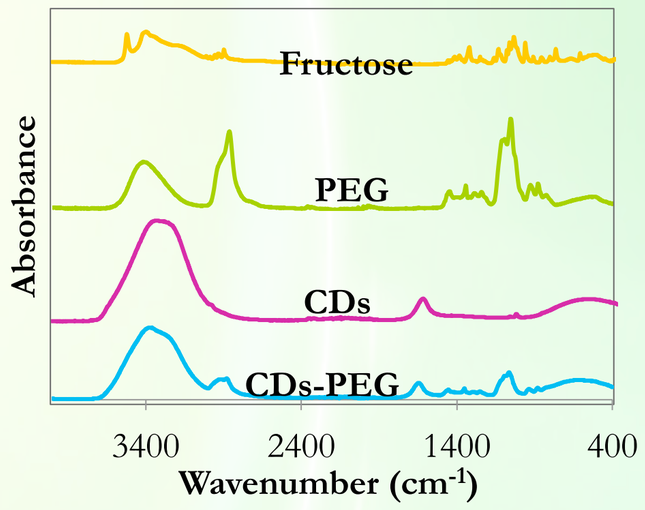
CRM	Certified value (mg/kg)	Recovery (%)
BCR 464	5.50 ± 0.17	114
DOLT-4	1.43 ± 0.13	93.7
DORM-3	0.381 ± 0.060	96.9

TEM measurements



- ✓ Under optimized conditions CDs are uniformly dispersed and its average size is 2.5 nm.
- ✓ PEG prevents CDs from aggregation.
- ✓ Application of higher US time causes the formation of larger CDs.

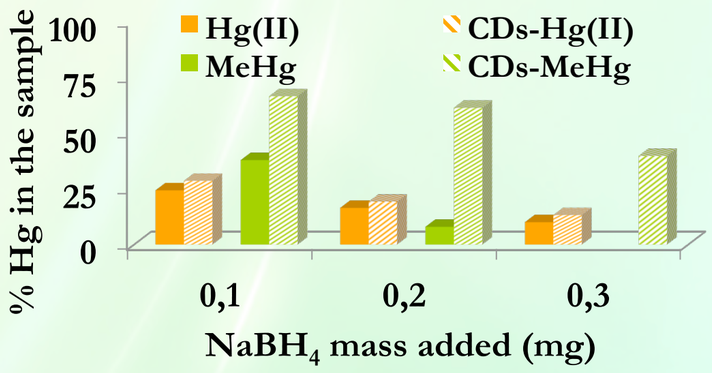
FT-IR measurements



Group	Wavenumber (cm^{-1})
O – H (stretching)	~3350
sp^3 C – H (stretching)	~2900
C – H (bending)	400 – 1450
C – O (stretching)	~1080

- ✓ CDs are surrounded by hydrophilic groups.
- ✓ New peak centered at 1643.4 cm^{-1} is found for CDs-PEG. This new peak may be attributed to the sonochemical treatment of fructose, which causes changes in its structure.

Volatilization experiments



- ✓ No interaction between CDs-PEG and Hg(II)
- ✓ Strong interaction between CH_3Hg^+ and PEG.

REFERENCES

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CONCLUSIONS

The main conclusions of the present work can be summarized as follows:

1. Integration of fluorescent CDs synthesis and CH_3Hg^+ sensing is achieved by the use of high-intensity sonication, which allows to develop a fast and simple assay in a single step.
2. This optical nanoprobe is highly selective for CH_3Hg^+. The interaction of CDs and CH_3Hg^+ is facilitated by the ultrasound treatment which causes that hydrophobic species such as CH_3Hg^+ to cross the PEG coating and interact with CDs.
3. The recognition mechanism is based on a dynamic quenching process caused by collisions between CDs and CH_3Hg^+.
4. The use of a portable microfluospectrometer allows on-site analysis.