Research Proposal

Development Of A Highly-sensitive Electrochemical Sensor From Carbon Quantum Dots For Polyethylene And Polystyrene Microplastics Detection In Water Bodies

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Abstract

Microplastics (MPs) in water bodies pose a significant threat to the environment, marine life and even human health. Therefore, development of a rapid and affordable way of detecting MPs has caught scientists' attention. While there are many ways of doing so, there are many examples of them being inefficient, insensitive, and still on the proof-of-concept stage. In this paper, a way to develop a sensitive electrochemical sensor to detect microplastics in water bodies made from an electrode and Carbon Quantum Dots (CQDs) was proposed. Glassy carbon electrode coated with nitrogen-doped CQDs was employed as a platform for detection of MPs in water, while differential Pulse Voltammetry (DPV) was used as the main tool for doing so. GCE coated with CQDs possess exceptional electrochemical properties. Therefore, a high sensitivity for multiple types of MPs and multiple environments, including seawater, tap water, etc. is expected from this electrochemical sensor. This sensor is trying to propose a solution for a current research gap in this field and to contribute to the sustainable future of the world.

1 Introduction

Plastics are polymers that have revolutionized our life because of their useful and unique properties: they can be used at a wide range of temperatures, they are lightweight and flexible, they have exceptional light and chemical resistance, and they are extremely cheap to produce, making them perfect materials for packaging production, consumer goods, building and construction, fibers and textiles, automotive parts and medical products [1, 2]. Therefore, plastic production is a major part of global industry which will only grow in the future: in 2023, 413.8 million tons of plastic was produced worldwide, which is 3.3% higher than in 2022 [3, 4].

However, the increasing plastic waste is a major sustainability concern in a modern world. In 2019, the plastic waste was estimated to be 353 million tons and it is expected to increase up to 1014 million tons by 2060. The waste itself does not pose any danger to the environment, but its mismanagement leads to contamination of land and water bodies. In 2019, 23% of plastic waste was mismanaged, with 7.7 million tons of plastic ending up in the water bodies or at the coast [5].

When in the environment, plastics undergo degradation into smaller particles (with diameters ¡5 mm) called microplastics (MPs) [6]. Studies have confirmed the presence of microplastics in the water bodies [7]. In turn, marine organisms may accidentally mistake microplastics for food, which may have a variety of effects on them. Primarily, microplastics can cause mechanical or chemical harm to the organisms that were ingested with microplastics. In some cases, the microplastics may be eliminated out of the body by excretion or other means, as well as be transferred to another trophic level in case an organism feeds on those that were ingested with microplastics. More-

over, human health can also be negatively affected by the ingestion of microplastics through food, drinking water, or air [8, 9].

According to the data regarding the prevalence of specific polymers in the ocean, polypropylene (PP), polystyrene (PS), polyethylene (PE), and polyphthalamide (PPA) are dominant in the oceans in terms of their concentrations in water [10]. Additionally, microplastics contamination of water is not an easily remediated situation, as they often persist in the environment for up to 100 years and more, causing long-term damage to the environment and human health [9].

Recently, supranational organisations and governments have been proposing and implementing resolutions to combat marine litter, especially microplastics [11]. Therefore, being able to quickly, cheaply, accurately and environmentally friendly test water for the presence of microplastics in it is an important tool that would stimulate international initiatives regarding marine pollution and be useful in everyday life to evaluate the quality of water.

Many approaches for microplastics detection in water bodies are proposed, ranging from visual inspection methods and thermal analysis methods to spectral and other analysis techniques. However, there are common disadvantages shared by most of them. Poor selectivity is a major concern, as such methods can not assess the presence of microplastics in sea water, multiple types of microplastics at once, and they often have issues with the sizes of microplastics, not being able to detect particles that are ¡5 mm in diameter. Other concerns include high cost, time consumption, medium and sample treatment, and the fact that accuracy is highly susceptible to external factors [12, 13].

On the other hand, electrochemical methods are perfect for detection of MPs in water, as they are affordable, quick, and sensitive relative to other methods. Electrochemical sensors are one of the promising ways to detect microplastics in water due to their high sensitivity, low cost, and safety. However, this technology is not as developed yet to implement it in in situ microplastics detection for multiple reasons. Many sensors are on the proof-of-concept stage right now, and a lot of research needs to be done in order to apply them in real life. They primarily focus on detecting only 1 type of polymer in tap water, not in sea water, where there is high-ionic-strength that can reduce sensitivity. Extensive research is being done in this direction, making it one of the most relevant topics in electrochemistry today [13–15].

Carbon quantum dots, or CQDs, are nanoparticles that have been praised for their broad applicability in biomedical, electrochemical, and analytical purposes. They provide eco-friendly, affordable, safe and efficient solutions for sensing, bioimaging, drug delivery, etc [16–18]. Their high specific surface area and a large amount of functional sites make them good current conductors through electron transfer [18, 19]. Their potential in application as electrochemical sensors is proved to be high by many studies [19–23]. While CQD's fluorescence is the main property for sensing, carbon quantum dots may also be applied to improve upon glassy carbon electrodes

(GCEs), being sensitive to the differences in current [24]. While this approach is many times better than standard GCEs, it is not perfect and still can be further improved by nitrogen-doping of the CQDs. As a result, a more sensitive version of the electrochemical sensor is acquired [24–26]. Nitrogen-doped CQDs may be synthesized in a myriad of ways [27]. In this paper, synthesis of carbon quantum dots was conducted using citric acid and urea as precursors [27].

1.1 Research Aim

This research aims to develop an electrochemical sensor that would detect 2 major types of MPs in marine environments, namely PE and PS. This development will further assist in the measures taken to address the global trend on reducing microplastics waste in water bodies by providing tools for accurate monitoring of MPs' presence in water. The primary research objective is to suggest a solution for an exisiting research gap present in this field by proposing an electrosensor with high selectivity in high-ionic-strength environments capable of detecting multiple types of MPs at once. By using carbon quantum dots, spectrophotometry and electrodes, a model of such an electrochemical sensor is possible to develop.

2 Methodology

2.1 Chemicals and Materials

2.1 Chemicals and materials Citric acid, urea, deionized water, household microwave with a frequency of 2.45 GHz and a total microwave output of 900 W, phosphate-buffered saline (PBS, pH 7.4) as a medium for all measurements; glassy carbon electrode as a working electrode, platinum wire as a control electrode, Ag/AgCl (3 M KCl) solution as a reference electrode, respectively; 5 mM equimolar K3[Fe(CN)6]/K4[Fe(CN)6] mixture for electrochemical measures; potentiostat; PS microparticles were purchased from Sigma-Aldrich; PE microparticles were purchased from Cospheric [15, 27].

2.2 Synthesis of Nitrogen-doped Carbon Quantum Dots

Nitrogen-doped CQDs were synthesized through an exposure of a citric acid and urea (1:1 weight ratio) with 10 mL of water mixture to the microwaves exerted from the household microwave. The mixture was heated in a household microwave for 4 minutes using 154 W, 594 W, and 900 W of power. After 10 mg of the resulting powder was mixed with 100 mL of deionized water, it was sonicated for 10 min. The result, a yellow solution, was put in a centrifuge at 10000 rpm for

15 min, and, subsequently, filtered using a 0.22 micrometers membrane. The resulting N-CQDs solution was used for subsequent applications [27].

2.3 Characterization techniques

In order to evaluate properties of the acquired CQDs, transmission electron microscopy (TEM) is applied. To determine the specific surface area of the CQDs, Brunauer–Emmett– Teller (BET) analysis is employed [15, 24].

2.4 Electrode modification

First, glassy carbon electrodes were mechanically polished using a 0.05 micrometers alumina slurry on a polishing pad to ensure a clean and smooth surface. After rinsing the electrodes with DI water, they were ultrasonicated in ethanol and water for 5 minutes each to remove residual particles from the surface. The resulting two glassy carbon electrodes were ready for further application. To coat the GCE with the N-CQDs, 10 microliters of a well-dispersed N-CQDs solution (1 mg/ml in absolute ethanol) was drop-cast onto the polished GCE and dried at room temperature for 1 hour. 3 microliters of 0.05 wt% Nafion solution in ethanol were applied to the surface as an outer layer of the electrode to enhance electron transfer, film adhesion, and prevent mechanical delamination. This way, an unmodified control GCE and N-CQDs coated GCE were prepared. The resulting GCEs were stored in a dessicator to preserve their operating properties [15].

2.5 Electrochemical measures

A three-electrode setup was employed to conduct all electrochemical measures. GCEs were working electrodes, Ag/AgCl (3M KCl) was a reference electrode, and a platinum wire was a counter electrode. All experiments were conducted at room temperature in a 0.1M PBS with 5mM equimolar K3[Fe(CN)6]/K4[Fe(CN)6] as the redox probe. Cyclic Voltammetry was conducted in the range from -0.4V to + 0.6V relative to the Ag/AgCl at a fixed scan rate of 50mV/s to evaluate the electrochemical capabilities of N-CQDs coated GCE. Differential Pulse Voltammetry was conducted at pulse amplitude of 50 mV, pulse width 50 ms, and step potential 5 mV in order to sensitively detect microplastic binding events. Electrochemical Impedance Spectroscopy was performed to analyse the charge transferring in the electrodes at open-circuit potential from 0.1 Hz to 100 kHz of frequency with a sinusoidal perturbation of 5mV. Acquired data from EIS was analyzed using equivalent circuit modeling [15].

2.6 Microplastics detection in water

To evaluate the sensor's ability to detect microplastics in water, stock suspensions of PE and PS (1-5 micrometers in diameter) were homogenized by vigorous vortexing and sonication for 15 minutes to ensure a homogenous medium. Several solutions in PBS with concentrations of MPs ranging from 10^4 to 10^{10} particles/mL were prepared. Electrodes were submerged with 100 microliters of each MP solution for 10 minutes to let the sensing surface adsorb the particles. Then, the electrodes were rinsed with PBS to remove excess unbound particles and transferred to the electrochemical cell for further electrochemical measures.

To evaluate the sensor's selectivity in different environments, several experiments were conducted in tap water, seawater, laboratory wastewater, and rainwater. Water samples were filtered through 0.22 micrometers syringe filters to remove suspended solids. Suspensions of PS and PE were added at concentrations of $10^4, 10^7$, and 10^{10} particles/mL and mixed thoroughly to ensure a homogenous medium. DPV was used to evaluate the impact of the environment on sensor performance relative to the measurements made in PBS [15].

3 Expected results

3.1 Characterization of acquired CQDs

BET and TEM analysis of acquired N-CQDs will exhibit high electron transferring abilities backed up by high sensitive surface area, making them a perfect material for coating a sensor that detects MPs in water bodies [15].

3.2 Electrochemical performance of N-CQDs coated GCE

In PBS, Cyclic Voltammetry and Differential Pulse Voltammetry showed that a modified electrode exhibits high electron transfer rates and its overall electrochemical performance is many times better than that of an unmodified GCE, even in the presence of microplastic particles. However, when the microplastic particles are present, the conductivity decreases, serving as the main indicator of their presence in water bodies. Electrochemical Impedance Spectroscopy acquired Nyquist plots and Rct showed an increase in the electron transfer kinetics of the modified GCE in comparison with an unmodified GCE, implying that the modified electrode has more electroactive binding sites. As the microplastic concentration increased, Rct and Nyquist plots showed a decrease in the electron transfer kinetics [15].

3.3 Microplastics detection in water samples

Differential Pusle Voltammetry of the modified electrode in seawater, wastewater, tap water and rainwater was employed to extract normalized current response of the solutions with different concentrations of microplastics. These responses were significantly varying throughout different microplastics concentrations, serving as an evidence of N-CQDs' applicability as microplastics sensing materials [15].

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