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Abstract

Laser-Induced Graphitization of Polyimide Tape as Modifiable Sensor in Anodic Stripping Voltammetry †

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Abstract: The monitoring of toxic contaminant traces in the environment needs a simple and sensitive method, such as stripping analysis that applies a pre-concentration step to the analyte on the working electrode. The present work focuses on the realization of a two-electrode sensor made by means of laser-induced graphitization of a polyimide (PI) tape. Moreover, taking advantage of the strong affinity of Bi for metal ions for detection by Anodic Stripping Voltammetry (ASV), the proposed sensor implementation involved the use of Bi_2O_3 nanopowder as the precursor of Bi film as eco-friendly Hg substitute. Physicochemical analyses were conducted to investigate elemental and structural differences in relation to the shifts recorded in the voltametric behavior.

Keywords: laser-induced graphitization; carbon-based sensor; anodic stripping voltammetry; cadmium; lead; nano-adsorbent; polyimide; bismuth; chitosan; water quality

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1. Introduction

Heavy metals (HM) are high-density elements which progressively accumulate in the food chain with toxicological and carcinogenic effects on human health [1]. In an ecological framework, carbon-based materials are non-toxic and with an easy-to-functionalize surface promoting the specific recognition of analyte traces [2]. The laser writing technique allows laser-induced pattern graphitization (LIG) on polymeric substrates [3]; the process is simple, inexpensive, scalable and environmentally friendly. Also, nanomaterials are suitable elements for modifying electrode surfaces in electrochemical devices for metal ions detection [4]. Likewise, the stability of metal oxide NPs can be improved by combining them with chitosan, which can act as nano-adsorbent component for HM removal [5]. The combination of (i) direct laser patterning of a carbon-based material for sensing devices in stripping voltammetry, (ii) modification with a -HM-affinity bismuth film and (iii) the implementation of HM ion adsorption by chitosan hydrogel is the route followed in this study to achieve cheap and sensitive cadmium/lead contaminant monitoring in water.

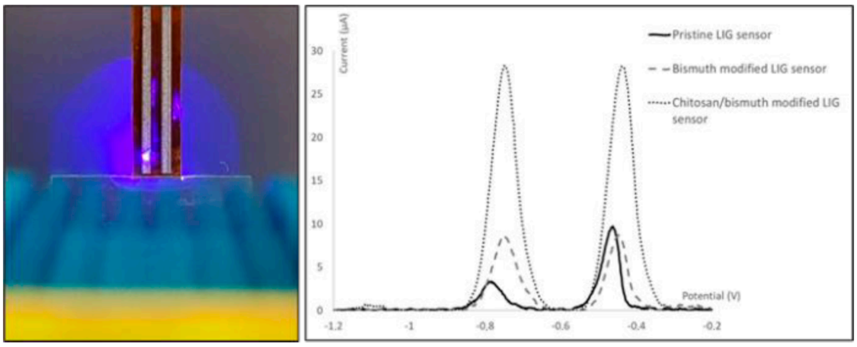
2. Materials and Methods

Single-sided Kapton polyimide tape (Ted Pella, Inc. Redding, CA, USA), bismuth (III) oxide nanopowder (80–200 nm, Alfa Aesar–Thermo Scientific Chemicals, Waltham, MA, USA) and lead (Pb) and cadmium (Cd) standard solutions (VWR International Srl, Milan, IT) were exploited for sensor fabrication, 3D surface functionalization and voltametric measurements.

The direct laser writing technique was carried out by the EleksMaker A3 pro, equipped with a diode laser (445 nm, 2.5 W). The two-step graphitization process was performed on a heating plate set at 20 °C, in a home-made writing chamber with a conditioned atmosphere. For each electrode (CE, WE), pulsed laser processing was repeated two times: the first one in ambient atmosphere and the second one in the presence of a nitrogen flow. Electrochemical measurements were carried out by the PalmSens4 analyzer with PSTrace 5 software and Ag/AgCl aqueous reference electrode (ItalSens, PalmSens, Houten, Netherlands) in 10 mL of 0.075 M KCL acidified solution. Known amounts of Cd and Pb standards were spiked in the measurement solution. The disposable sensors were used for a single cycle of ASV. Then, to improve the sensitivity and the selectivity towards Cd(II) and Pb(II) ions, an aqueous suspension of Bi_2O_3 nanopowder (with and without chitosan coating) was deposited on the electrode surface through an immersion-coating procedure; an electrochemical reduction of bismuth oxide to bismuth was conducted preceding ASV.

3. Discussion

We describe a quick and simple fabrication method of carbon-based electrodes on a polymeric tape using a laser patterning process (Figure 1a), confirmed by Raman spectra with typical vibrational modes of carbon-based material (around 1580 cm^{-1} and 1350 cm^{-1}). Interestingly, it was observed that the decoration of the electrode's 3D porous structure with Bi_2O_3 NPs (confirmed by Micro XRF) positively affects the response of the sensor in simultaneous detection of the same amounts of Cd and Pb ions, in terms of current peak amplitude. Moreover, exploiting chitosan (a natural polysaccharide, non-toxic and biodegradable as a metal-chelating agent) with the Bi_2O_3 NPs (confirmed by FT-IR spectra) effectively improves the sensitivity of the device (Figure 1b). In less than 200 s, the implemented flexible sensor is able to detect a 5 µg/L mixture of Cd(II) and Pb(II) ions, recording (5.2 ± 0.7) µA and (4.5 ± 0.2) µA, respectively (based on three independent experiments).



(a) **(b)**

Figure 1. (**a**) Focus on direct patterning of a Kapton tape applied on a PVC substrate: the PI film is converted into a conductive material through the carbonization process operated by a 445 nm laser, in N_2 conditioned atmosphere. (**b**) Representative responses of pristine, bismuth- and chitosan/bismuth-modified LIG sensors in the simultaneous detection of 25 µg/L of Cd(II) and Pb(II) in KCl solution, pH 2.

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