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Electrochemical sensor for phosphate ions based on laser scriber reduced graphene oxide

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Abstract—This preliminary work shows a new and innovative way to produce laser scribed reduced graphene oxide (LSGO) electrodes using different porous substrates (ranging from paper to plastic and fabric). The obtained electrodes were also tested as electrochemical sensors towards the detection of phosphate ions in water. To obtain the electrodes, a water suspension of GO was filtered on top of substrate (such as Whatman® filter paper) and a complete sensor was obtained from its reduction using a CO2 laser. The electrode is composed of working and counter electrodes made of LSGO and a reference electrode of a Ag/AgCl obtained by using a commercial AgCl conductive paste. Phosphate ions were detected by exploiting the reaction between molybdate and phosphate ions in acidic media (known in literature as molybdenum blue method). This chemical reaction produces the Keggin-type complex (PMo12O40)3−, that can be reduced under applied potential. The obtained results show that phosphate ions can be detected in a wide linear range, from 0.001 mM to 1mM, in presence of 1mM molybdate with a very satisfying selectivity. We also tried to pre-treatment the paper substrate with acidic molybdate ions in order to obtain a ready-made sensor directly usable for the detection of phosphate ions in situ avoiding any kind of real sample manipulation For this aim, the paper substrate was soaked with sulphuric acid and molybdate solution and dried in order to desorb these chemicals directly into the water sample to be analyzed. Preliminary results, shows that the process of absorption and desorption can be carried out by optimizing the volume and concentration of the absorbed solution and thus can be used to obtain a portable, easy to use and fast phosphate sensor for in situ and real time monitoring of water quality.

Keywords—Phosphate ions, electrochemical sensor, voltammetry, reduced graphene oxide, paper based elecxtrodes.

I. INTRODUCTION

Nowadays, the concepts of smart cities, smart houses and Homo Deus (potential next stage in human evolution) are taking more and more attention [1,2]. Sensors play a key role in this context recording different parameters, such as pollution, traffic jam, blood pressure, blood composition, brain activities and the functioning of organs. Current way of detecting these parameters or molecules are often laborious and expensive and cannot be used as in situ and real time. In this scenario, the development of new kind of sensors, able to fit to these new necessities is of great importance. Electrochemical sensors are perfect candidates to address these challenges. Indeed, these sensors do not require special instrumentations to work, are cheap and suitable for in situ and real time action due to the electrical read-out [3–5]. Graphene is one of the most used active material for electrochemical sensors due to its excellent properties such as high surface area, high aspect ratio, high mechanical stability, high flexibility and excellent electrical and thermal properties. For these reasons, researchers all over the world are working with graphene for several applications such as energy storage [6], sensors and biosensors [7–9], transistors [10], as absorbent material [11]. In the sensor field, graphene-based electrodes have been used to detect proteins [12], DNA [13], neurotransmitters [14], and bacteria [15]. In fact, the high electron transfer rates, the high peak current response, the porosity and the flexibility are key features for electrochemical detection of biomolecules. There are different methods to produce graphene electrodes such as exfoliation of highly ordered pyrolytic graphite [16], epitaxial growth [17] and chemical vapor deposition [18,19]. These techniques produce uniform, homogeneous and reproducible graphene, but they have different disadvantages such as cost, use of highly toxic and/or dangerous chemicals, and are incompatible with a mass production. For these reasons, the most common way to obtain graphene electrodes starts from graphene oxide (GO), subsequently reduced to graphene by annealing it at high temperature [20], or through a chemical reduction [21,22] or electrochemically [23]. In this context, a new and innovative way to obtain reduced graphene is the use of laser light, obtaining the so-called Laser Scribed Graphene Oxide (LSGO). This technique is based on heating up the GO substrate in a very precise and localized area which breaks the C=O bond producing graphene [24,25]. At the best of our knowledge, this technology has been studied and developed in the last years basically using plastics or ITO as substrates to build sensors and capacitors [26–29]. There are no works employing paper as a substrate to grow LSGO electrodes. In this work, we have developed a new, fast and cheap protocol to fabricate paper based LSGO electrodes by using a commercial laser cutter and used as phosphate ions (PO43-) sensor. Due to human activities, natural waters are going to be more and more polluted by different chemicals, such as heavy metals, nitrate and nitrite ions, phosphate ions [30–33]. PO43- is mainly used as fertilizer and its overuse leads to water contamination causing the modification of biological lifecycle [32]. Indeed, the excess of phosphate ions (along with other inorganic anions) lead to eutrophication. The result of this phenomena is the overgrow of algal blooms and a consequent decrease of total dissolved oxygen that can kill aquatic life. Thus, it is very important to quantify the phosphate ions concentration in water samples. By the way, PO43- is an inorganic anion hard to quantify because its charged state (H2PO4-, HPO42-, PO43-) depends on different parameters such as water pH [34]. Main electrochemical and spectrophotochemical techniques to quantify this anion start from the reaction between molybdate and PO_4^{3-} at very low pH (ranging from

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0 to 2) producing the Keggin-type complex (PMo12O40)3− (phosphomolybdenum blue, PMB) [35–39]. This Keggin ion can be electrochemically oxidized and reduced by applying a low voltage to the electrode and thus the electrochemical signal of its oxidation/reduction can be used as readout of the sensor to quantify phosphate ions. This electrochemical method has been used in literature using different electrodes [35,37,40–43]. Main drawback of this protocol is the need to alter the sample using strong acids and the molybdenum salt. In this paper, we show the possibility to obtain a fully integrated electrochemical sensor (working, counter and reference electrodes all in the same substrate) made LSGO. A water suspension of GO was filtered on Whatman® filter paper and reduced by laser scabbing directly on the paper substrate. Besides the novel way to reduce GO, the main advantage of the proposed work is the presence of the paper substrate that is able to absorb the needed chemical (strong acid and molybdate ions) and release it directly in the sample without the needs to human alteration before analysis. The results of this work show a LOD of 0.0004 mM with a high sensitivity and the possibility to work directly without the needs of alter the water sample.

II. Results and Discussion

In order to obtain the full integrated sensor, a surface of a Whatman® filter paper was sputtered with a very thin gold layer for 2 minutes (Fig1A). This step was found to be crucial in order to make the electrode substrate conductive and avoid to lose of the electrical contact due to small cracks on reduced graphene oxide. Gold was sputtered on 75% of the paper substrate in order to avoid to shortcut of the three electrodes (Fig 1A). After sputtering, 20 ml of GO aqueous solution was filtered on top of the gold sputtered Whatman® filter (Fig 1B). After the filtration process, the GO layer was reduced using a laser cutter machine.

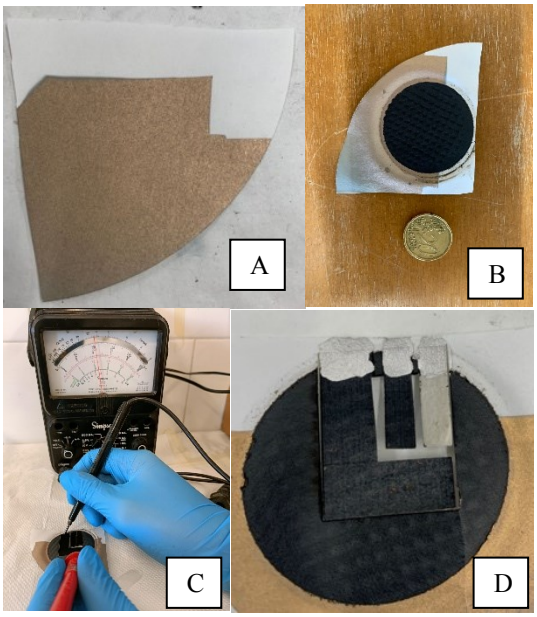


Figure 1 A) Gold sputtered Whatman filter, B) GO filtered on top of gold sputtered filter, C) Reduced graphene oxide process D) final LSGO based sensor

The laser parameters (speed and power) and the volume of GO solution used for filtration process, were optimezed in order to obtain a reduced graphene oxide layer as more conductive as possible. In particular, after the laser reduction, the GO layer became highly conductive with a resistance lower than 70 Ω cm-1 (Fig 1C). In order to avoid the electrical shortcut between the three electrodes, after the GO reduction, the three electrodes were cut with the laser cutter. The electrical contacts were made using a silver conductive paste while the reference electrode was obtained using a Ag/AgCl conductive paste (Fig 1D). In order to have a good electric contact, a sintering process was carried out at 50°C for 1h. The final dimensions of the thee electrodes of the sensor are summarized in table I, while in table II the parameters of the whole fabrication process were reported.

TABLE I. Dimension of the as prepared sensor

	Wire (mm)	*Long (mm)*	*Exposed area (mm^2)*
Working electrode	4.5	10	32.4
Counter Electrode	4.2	20	180
Reference electrode	4.5	10	32.4

TABLE II. Electrode Fabrication parameters

GO Concentration	*Laser Speed*	*Laser Power*
20 mL of 0.5 mg/mL	50 mm/s	1.87 W

The described preparation procedure has been optimized using paper as substrate, but it can be optimized for many kinds of substrates, such as plastic, fabric, band-aid. This could allow to use these sensors in a wide range of applications and for each one to be able to use the most suitable substrate. Morphology of the as prepared sensors was investigated using a scanning electron microscope (FEG-ESEM, FEI-Quanta 200) equipped with an X-ray energy dispersive spectrometer (EDS).

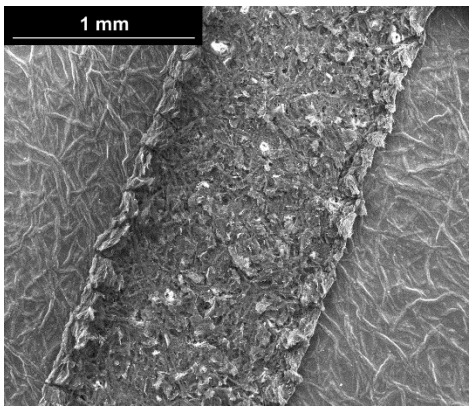


Figure 2 A) Scanning electron microscope image of LSGO electrode showing the reduced and unreduced GO. X-ray energy dispersive spectrum of GO (B) and (C) rGO

Fig 2 shows the morphology analysis of the paper based LSGO electrode. In details, Fig 2 shows a scanning electron microscope image of the electrode. In this image the reduced and the unreduced GO areas are clearly visible. In particular, it can be observed that the reduced area of GO is very rough and thus is characterized by a high surface area. The unreduced area appears almost smooth and the fibers that make up the paper substrate can be seen. The EDS spectra of the same electrode in the unreduced and reduced

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area, shows, apart from the C signal, arising from both GO/rGO and from the paper substrate, the O signal that decrease drastically in the reduced form of GO, confirming the reduction of the GO. Further characterization analysis (XRD and RAMAN spectroscopy) will be carried out in order to fully characterize the LSGO. The as prepared sensor was used to detect phosphate ion in water using the PMB method above discussed. As detection technique the linear scan voltammetry (LSV) was used. In particular, the potential was varied in the range from -0.3 to +0.4 V vs AgCl at a fixed scan rate of 50 mV s-1. The detection was carried out using 1 ml of 0.05M H2SO4 as blank and in this solution ammonium molybdate and different concentration of phosphoric acid were inserted in order to build the calibration line. The LSV curve in the blank solution (Fig. 3, black curve) is flat without any observable peak current. After the addition of 1 mM of molybdate ion (ammonium molybdate) in the resulting LSV, (Fig. 3, red curve), a small reduction peak current (≈ 3µA cm-2) at about +50 mV is observed. This peak is attributable to molybdate reduction. When phosphate ions were added to the solution (using phosphoric acid solution), three different reduction peaks appear located at +61, -55 and -155 mV vs AgCl. The two peaks at about -55 and -155 mV are related to the successive reduction of Keggin-type complex. In fact, this is a two step reduction process where the paek at -55 mV is due to the reduction of the Kegging type ion and the other one at -155 mV is attributed to a second reduction of this compound. As the phosphate concentration increase, these two peaks increases linearly with phosphate concentration from 1 µM to 1 mM. The average sensitivity is equal to 0.06 mA mM-1 cm-2.

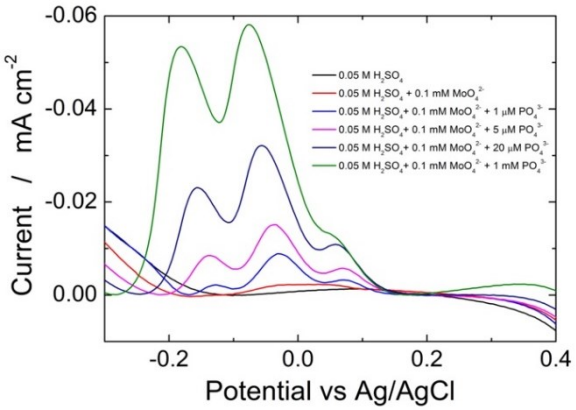


Figure 3 LSV (50 mV/s, from 0.4 to -0.3 V vs AgCl) of the LSGO electrode in absence of molybdate and phosphate ions (black curve), in presence of 1 mM molybdate (red curve) and in presence of 1mM molybdate and different phosphate concentration (1 µM to 1 mM)

The electrode selectivity was tested against different chemicals that could be found in natural waters such as heavy metals, silicate, nitrate, nitrite, carbonate, sodium and potassium. The results showed that all these chemicals have a negligible effect on the reduction peak of 0.1 mM of phosphate even if added at much higher concentration.

To obtain a ready-made sensor directly usable for the detection of phosphate ions in situ, we have pretreated the paper substrate with sulfuric acid and molybdate ions. The presence of these reagents in the sensor substrate avoids any kind of the real sample manipulation. The pretreatment was performed in the as prepared electrode soaking it into a solution of 0.1 M H2SO4. Particularly, 10 µL of this solution per square cm of electrode was used. After the complete drying of the electrode, it was soaked again into 1 ml of deionized water (DI). To quantify the amount of absorbed sulphuric acid, the pH of the DI used in the last step was measured using a standard laboratory pHmeter. We found that the pH of DI depends on the time of immersion in 0.1 M H2SO4 shifting towards acidic value for long immersion time. Particularly, a pH plateau was reached at about 1.3 after 20 seconds of immersion. Further tests are in progress to optimize the absorbed volume and sulphuric acid concentration in order to reach the optimal pH value of 1. A similar work of optimization was carried out by soaking the electrode with a solution of 5 mM of ammonium molybdate. The desorption of molybdate ions into the DI solution will be analyzed using a spectrophotometer. Here again, the molybdate concentration and the volume of the absorbed solution will be optimized in order to release a total concentration of 1mM.

III. Conclusions

In this work, we have shown a new and innovative protocol to obtain LSGO electrode. Here the process was demonstrated using a simple filter paper but different substrates such as porous plastic, fabric and band-aid will be used. The whole process is scalable, fast, cheap, and easy to carry out and therefore easily applicable in different fields. All the parameters of the electrode fabrication (GO concentration, laser speed, laser power) were optimized and sensors complete with working electrode, counter electrode and refence were obtained. Here the sensors were used to quantify phosphate ions in water samples, but many other applications can be tried in particular the many for which the reduced graphene oxide is electrically active. The phosphate detection was performed using the molybdenum blu method. The result shows that it is possible to quantify phosphate ions from 1 µM to 1 mM with a quiet high sensitivity and good selectivity. The final goal of the proposed research is to obtain a ready-made sensor directly usable for the detection of phosphate ions in situ avoiding the water sample manipulation. Thus, for this aim, the sensors were soaked in sulphuric acid and molybdate solution. In this way, the paper substrate will release these chemicals directly into the water sample to be analyzed avoiding its manipulation before the test. Preliminary results have shown that this process can be carried out by optimizing the absorbed solution volume and concentration of both reagents.

IV. Acknowledgment

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