Sensors and Actuators B 262 (2018) 902–912

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Enhanced photostability and sensing performance of graphene quantum dots encapsulated in electrospun polyacrylonitrile nanofibrous filtering membranes

Virginia Ruiz [a,*], Ana Pérez-Marquez [b], Jon Maudes [b], Hans-Jürgen Grande [a], Nieves Murillo [b,*]

[a] CIDETEC, Paseo Miramón 196, E-20014 Donostia-San Sebastián, Spain
[b] TECNALIA, Paseo Mikeletegi 2, E-20009 Donostia-San Sebastián, Spain

ARTICLE INFO

Article history:
Received 14 September 2017
Received in revised form 8 February 2018
Accepted 9 February 2018
Available online 12 February 2018

Keywords:
Graphene quantum dots
Nanofibers
Membranes
Electrospinning
Fluorescence sensor
Chlorine detection

ABSTRACT

We report a method to encapsulate graphene quantum dots (GQD) in polyacrylonitrile (PAN) nanofibrous membranes to manufacture robust filtering membranes by electrospinning. GQD-PAN membranes with different nanofiber diameter were prepared tuning the electrospinning parameters, all exhibiting the characteristic fluorescence fingerprint of the GQD probes. The photoluminescence (PL) stability of GQD embedded in the PAN fibers was significantly enhanced with respect to that of water dispersed GQD luminescent probes. The PL of GQD-PAN filtering membranes showed remarkable time stability, both stored dry and immersed in phosphate buffer solutions (PBS), as well as exposed to continuous light irradiation. However, the PL intensity of GQD-PAN membranes was irreversibly quenched by highly oxidant free chlorine solutions. Thus, electrospun GQD-PAN membranes exhibited excellent performance as turn-off fluorescence sensing platforms for free chlorine detection in PBS 0.1 M pH 7. The analytical performance of GQD-PAN membranes was comparable to that of GQD solutions with optimal concentrations, displaying a fast (no need of incubation time) and linear response to chlorine concentration in the 10–600 μM range, a low detection limit of 2 μM, high sensitivity, reproducibility and selectivity. Moreover, the sensing performance of the membranes was very stable after being immersed in PBS for months, outperforming the stability of GQD solutions.

1. Introduction

Graphene quantum dots (GQD) are graphene sheets smaller than 100 nm that are attracting enormous interest in view of their fascinating and easily tunable electronic and optical properties [1,2]. GQD are regarded as versatile fluorophores due to their size- and composition-dependent emission that can be tailored by the synthetic method [3]. Moreover, depending on the preparation method GQD may exhibit outstanding luminiscence properties such as high photostability against bleaching and blinking in addition to biocompatibility, excellent solubility and lower toxicity than semiconductor quantum dots [4]. All these attractive features have triggered investigation of GQD for applications in different fields such as lighting, bioimaging, photovoltaics, energy conversion and storage, catalysis or sensing [5–9]. Among them, GQD have attracted tremendous attraction in the analytical field as sensing probes for diverse environmental and biological applications [10,11]. Based on different GQD properties and sensing mechanisms, GQD have been applied in electronic, electrochemical, electrochemiluminescence and photoluminescence (PL) sensors [9]. In "turn-off" PL sensors, GQD fluorescence is selectively quenched by the analyte. Fluorescence quenching is based on photo-induced electron transfer from excited GQD to the analyte. By tailoring the bandgap and functional groups in GQD, selectivity towards detection of different target analytes has been achieved, such as Hg^{2+} [12], Fe^{3+} [13], Cu^{2+} [14], Ni^{2+} [15], ClO^- [16], glucose [17], fructose [18], melamine [19], among others. In most studies, GQD are used as soluble fluorescent probes for turn-off selective sensing co-dispersed with the target analyte.

On the contrary, the development of PL sensing platforms based on GQD confined to surfaces is comparatively scarce despite being more practical from the application's viewpoint. There are several studies reporting incorporation of GQD in filtration membranes by

* Corresponding authors.
E-mail addresses: vruiz@cidetec.es (V. Ruiz), nieves.murillo@tecnalia.com (N. Murillo).

https://doi.org/10.1016/j.snb.2018.02.081
0925-4005/

different methods (covalent bonding, interfacial polymerization, layer-by-layer assembly) to produce membranes with bactericidal properties [20], enhanced antifouling performance [21] and chlorine resistance [22]. In the field of sensors, there are just few examples of surface-confined GQD-based PL sensing platforms. Thus, GQD-chitosan-creatinine mixtures were deposited on silica slides and the resulting fluorescent films were applied to detect picric acid in water by measuring film PL quenching [23]. A solid fluorescent sensor for selective detection of Fe^{3+} was also developed by adsorbing GQD on a polystyrenic anion-exchange resin [24]. Similarly, a fluorescent polyacrylonitrile membrane for Fe^{3+} detection was reported where carbon dots were encapsulated in a mesoporous silica coating around the membrane fibers [25]. GQD were also chemically bonded to nylon membranes to yield fluorescent membranes with excellent sensing performance for Cr^{6+} detection [26].

All these studies highlight the preservation of GQD intrinsic fluorescence and sensing ability after immobilization onto different surfaces. However, the preparation methods involve post-deposition of GQD on the host matrix or complex encapsulation methods. Developing strategies for one-step integration of GQD during membrane preparation would contribute to large-scale and high-throughput manufacturing of the sensing membranes. In this regard, electrospinning represents an attractive and versatile strategy to embed GQD in filtering membranes as it enables control over membrane fiber diameter, thickness, good mechanical strength, high porosity and surface area per unit mass, areal weight control, GQD loading, etc [27,28]. Electrospinning represents a low-cost solid route to manufacture filtering membranes with sensing properties. As an example, Zhang et al. immobilized GQD into a nanofibrous membrane by electrospinning water-soluble GQD and polyvinyl alcohol, fabricating a fluorescence and electrochemical biosensing platform for H_2O_2 detection [29].

On the other hand, determination of free residual chlorine in water is very important as its concentration should be strictly controlled and maintained at appropriate level, because of its relevance as quality control index. Too high concentration may lead to production of harmful trihalomethanes by reaction with organic matter present in water [30]. On the other hand, too low concentration may not ensure the microbiological level of disinfection required to keep water clean [31]. The different chlorine-based oxidizing compounds (Cl_2, HClO, ClO^-) accounting for the total amount of free residual chlorine in water are extensively used as disinfectants in water treatment, hence the need of efficient analytical methods to monitor their concentration in water. Common analytical techniques for selective determination of free chlorine include different spectrophotometric, electrochemical and liquid chromatographic methods, each having different drawbacks [32,33,34]. The main concern related with analytical methods for free chlorine measurement is the time-delay due to water travel from chlorine dosage station to the distribution networks and measurement points. Under this complex scenario, low cost, selective and robust sensors to monitor free chlorine are needed.

In this paper, we report the successful incorporation of GQD into electrospun polyacrylonitrile (PAN) membranes, demonstrating the excellent and stable performance of GQD-PAN filtering membranes as turn-off fluorescent sensing platforms for selective and sensitive detection of free chlorine in water. The capacity of strongly oxidizing chlorine to quench the luminescence of dispersed GQD probes has been previously demonstrated [16], which is the fundamental sensing principle of the nanofibrous filtering membrane developed by the authors. Here we have produced PAN membranes containing GQD by one-step electrospinning solutions of both components with very homogeneous GQD distribution across the membrane volume. The resulting fluorescent GQD-PAN membranes have proven to be very sensitive fluorescence sensing platforms for selective determination of free chlorine in water. Moreover, we will demonstrate that GQD exhibit more stable luminescence emission protected by the PAN fibers than dispersed in water. As a result, the analytical performance of GQD-PAN membranes remained very stable after months immersed in aqueous buffer solution.

2. Materials and methods

2.1. Reagents and materials

NaCl, KCl, $NiCl_2{\cdot}6H_2O$, $ZnCl_2$, $CuCl_2{\cdot}2H_2O$, $MnSO_4$ and $CoCl_2{\cdot}6H_2O$ purchased from Scharlau. Stock NaClO (10%) solution, $Cd(ClO_4)_2$, $FeCl_2{\cdot}4H_2O$, $MgCl_2{\cdot}7H_2O$, $CaCl_2$, $AgNO_3$, $Pb(ClO_4)_2$, $Hg(ClO_4)_2$, KH_2PO_4, Na_2HPO_4, pyrene, ammonia, hydrazine hydrate, polyacrylonitrile (PAN) with molecular weight $M_w = 150.000\ gmol^{-1}$ and *N*,*N*-dimethylformamide (DMF) were purchased from Sigma Aldrich (Spain) and $FeCl_3{\cdot}6H_2O$ from Panreac. All chemicals were of analytical grade and used without further purification. All solutions were prepared with ultrapure water of Synthesis A10 from Millipore (18 Ω cm) (Massachusetts, USA). The concentration of free chlorine in the stock solution was determined by iodometric titration.

2.2. Instrumentation

GQD-PAN nanofibrous filtering membranes were prepared using a custom-made needle electrospinning apparatus. The NE-1000 dosage pump speed range available is 0.73 μL/h to 2100 mL/h. The applied voltage between needle and collector (30 kV) was generated using a high voltage power supply (model AU-30R1-L from Matsusada Precision Inc). The needle – collector configuration was vertically oriented (Supporting information, Fig. S1). The electrospinning setup is equipped with humidity control until 20% RH.

The morphology of nonwoven GQD-PAN nanofibrous membranes was studied by scanning electron microscopy (JSM 5910-LV JEOL) to determine electrospun nanofiber diameter, homogeneity and defect concentration. The average diameter of the GQD-PAN nanofibers in the filtering membrane was determined using the Image-J image processing program [35]. GQD-PAN membrane photoluminescence was characterized using a BX51 fluorescence microscope (OLYMPUS) equipped with a Color View III camera and an U-LH100HG mercury excitation source with λ = 450–495 nm. Absorption and fluorescence spectra were measured with a Jasco V-570 UV-VIS-NIR spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively. TEM images of GQD on carbon-coated copper grids were taken using a TECNAI G2 20 TWIN (FEI) transmission electron microscope, operating at an accelerating voltage of 200 KV in a bright-field image mode. AFM images of GQD on mica substrates were obtained in tapping mode at room temperature using a scanning probe microscope (Molecular Imagings PicoScan) equipped with a Nanosensors tips/cantilever, at a resonance frequency of 330 kHz and a spring constant of about 42 N/m, with a tip nominal radius lower than 7 nm. XPS measurements were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Magnesium Kα line of 1253.6 eV energy and a power applied of 250 W) and calibrated using the $3d_{5/2}$ line of Ag with a full width at half maximum (FWHM) of 1.1 eV. Measurements were made in an ultra-high vacuum chamber at a pressure around 8×10^{-8} mbar. Raman spectra of freeze-dried solutions were measured with a Confocal Raman Voyage spectrophotometer (BWTEK, USA) at an excitation wavelength of 532 nm.