



Graphene quantum dots as a novel sensing material for low-cost resistive and fast-response humidity sensors



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ABSTRACT

A room temperature graphene quantum dots (GQDs) based sensing material for relative humidity monitoring is presented. GQDs are synthesized by pyrolysis of citric acid and are deposited on a metallic interdigitated microelectrodes by drop-casting technology. GQDs are nanosheets around 20 nm in average lateral size and an average height of 2.7 ± 0.9 nm. The response time is around few seconds and the sensitivity shows an exponential relation between 15 and 80% of RH, in resistive configuration device working at room temperature. The electrical changes as a function of the RH are related to the capillary condensation produced on the surface of the GQDs. Due to this physical behavior, a resistive path is formed between the microelectrodes and the condensed water vapor, and the resistivity of the system diminishes as the RH increases. A comparison on real time between the sensor developed and a commercial device corroborates the potential application of the novel sensor presented in this work.

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1. Introduction

Graphene quantum dots (GQDs), which are graphene sheets smaller than 100 nm, have been recently attracting tremendous attention due to their unique electronic and optical properties arising from quantum confinement and edge effects [1–5]. In addition to these properties, their chemical inertness, biocompatibility, low toxicity and strong photoluminescence have triggered the use of GQDs in a number of applications such as bioimaging [6], OLEDs [7], fuel cells [8], photovoltaic devices [9], composites [10] and biosensors [11].

In the specific field of sensing, different types of GQD-based sensors have been proposed that benefit from their particular optical or electronic properties. Zhao et al. [12] developed an immunosensor for the detection of human immunoglobulin based on quenching of the GQD photoluminescence by luminescence resonance energy transfer (LRET) as sensing mechanism. Quenching of GQD fluorescence as sensing mechanism has also been applied to the detection of several analytes of environmental relevance such as phosphate [13] or free chlorine [14] in water. Li et al. [15] developed a Cd²⁺ sensor based on electrochemiluminescence observed in GQDs.

On the other hand, other authors have developed electrochemical biosensors for the detection of single-stranded DNA [16] or glucose [17] exploiting the excellent conductivity, large surface-to-volume ratio and electrochemical response of GQDs. A different type of sensing devices relying on the singular electronic properties of GQDs are single electron transistor (SET) based charge sensors, which are switching devices that use controlled electron tunneling to amplify a current [18]. Besides charge detection, electronic sensors for the detection of humidity and pressure have been demonstrated based in electron-tunneling modulation by humidity and pressure in a percolating network of GQD embedded in a polyelectrolyte microfiber [19]. Compared with traditional graphene-based sensors, the GQD-polyelectrolyte based electronic sensor exhibits one order of magnitude higher current modulation (43-fold) and operates under a lower RH (Relative Humidity) range: 0–40% RH.

In addition to GQDs, other nanomaterials have been applied as sensing elements for humidity control applications, due to its low cost and functionality. Other superior properties of nanostructures as sensing materials include a high surface/volume ratio, fast kinetics and sensor response, high sensitivity, reduced device size and room temperature operation, which allows diminishing the power consumption of the system [20,21]. In this context, sensors with several functional materials (ZnO [21–26], MgCr₂O₄–TiO₂ [27], TiO₂ [28], SnO₂ [29], In₂O₃ [30], poly(vinylalcohol)–KOH–H₂O [31], Cd-doped ZnO [20], ZnO–TiO₂ [32], p-ZnO/n-Si [33], graphene

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[34], graphene oxide [35] and reduced graphene oxide [36]) have been produced by different methods (chemical vapor deposition, pulse laser deposition and screen-printing technology, among others) [21,24–26,31–33], showing different performance for humidity sensing.

In this work, the analytical properties of room temperature GQD-based resistive sensors under different humidity concentrations are presented and discussed. We report the good performance for humidity sensing of plain GQD networks prepared by a simple and low-cost method consisting on drop casting few microliters of GQD aqueous solutions onto interdigitated electrodes. As the interaction between water molecules and GQD surface takes place at room temperature, the humidity sensing mechanism is based on physisorption phenomena.

2. Experimental

2.1. Materials

Citric acid was purchased from Panreac. All reagents were analytical grade and used without further purification. Solutions were prepared with ultrapure water of Synthesis A10 from Millipore (18 M Ω cm) (Massachusetts, USA).

2.2. Synthesis of GQDs

GQDs were synthesized by pyrolysis of citric acid according to a protocol recently reported elsewhere [37]. Briefly, 2 g of citric acid was placed in a beaker and heated to 220 °C until it turned from solid to colorless liquid in a first stage and gradually to pale orange. The orange liquid was added dropwise into 50 mL of 0.25 M NaOH solution under vigorous stirring. A neutral (pH 7) aqueous solution of GQDs was obtained, which was stored at 4 °C.

2.3. Device fabrication

The obtained aqueous solution of GQDs, without any further purification treatment, was deposited by drop-casting (50 μ L drop, 5 times) on a patterned metallic interdigitated microelectrode. The final conductometric device was subjected to 5 min air annealing at 100 °C to eliminate the solvent of the GQDs solution.

2.4. Instrumental methods

AFM images of GQDs on mica substrates were obtained by tapping mode at room temperature using a Molecular Imaging PicoScan scanning probe microscope equipped with a nanosensors tips/cantilever, at a resonance frequency of \sim 330 kHz, with a spring constant of about 42 N/m and a tip nominal radius lower than 10 nm. Fluorescence spectra were recorded using a Cary Eclipse Varian fluorescence spectrophotometer. Photographs of GQD solutions under UV light were taken in a UVP imaging system (BIO DOC-IT 220). FE-SEM images of GQDs on FTO substrates were analyzed using a Field Emission Scanning Electron Microscope (ULTRA plus ZEISS FESEM).

Electrical characterization was performed inside a sealed plastic chamber by a Keithley 2400 sourcemeter. Tests were carried out under different RH at room temperature (25 ± 1 °C). The target humidity atmosphere was obtained by means of a mixing system consisting of mass flow controllers (MFCs) from Bronkhorst Hi-Tech controlled by a PC. A Dynamic Data Exchange communication was established between the computer and the MFCs operated by Labview[®]. Inside the chamber, a commercial humidity sensor (LinPicco[™] A05 Basic, Capacitive Humidity Module) was used as a humidity indicator in order to control the different atmospheres.

3. Results and discussion

3.1. Characterization of GQDs

Solutions of GQDs emit blue light when excited with UV light, as shown in the photograph in Fig. 1. Interestingly, GQDs exhibit photoluminescence (PL) with a maximum emission wavelength that is nearly excitation-independent, as can be seen in the emission spectra at different excitation wavelengths shown in Fig. 1. The maximum excitation and emission wavelengths are 376 and 463 nm, respectively.

AFM (Fig. 2) indicates that GQDs are nanosheets of approximately 13 ± 3 nm in lateral size estimated from the flat part of the height profile and an average height of 2.7 ± 0.9 nm. The height distribution is shown in the histogram in Fig. 2. Additionally, FE-SEM (Fig. 2) analysis indicates that GQDs are nanosheets of 22 ± 4 nm in lateral size. It is pointed out that the estimated value of the lateral size by AFM depends considerably on how the height profile is measured so it could be concluded that the small variation between the two techniques corroborate the average size estimated around 20 nm.

3.2. Electrical characterization of GQD-based sensors under different RH atmospheres

In order to get a stable sensor signal, the operation voltage has been fixed at 1 V in a pulse mode, 1 s of period and 50% of duty cycle. Under continuous operation voltage the sensor baseline was not stable. The instability is related to the temperature gradient produced within the interface between the water vapor molecules and the GQD. The Joule effect associated to the electrical current density is responsible for this phenomenon, which can be minimized using pulse operation mode. A thermodynamical equilibrium is reached in this typical electrical technique very often implemented in sensors signal conditioning.

Fig. 3 shows the dynamic sensor response at different RH conditions for the GQD-based sensor and a commercial device, respectively. The time necessary to fill/evacuate the chamber was estimated to be around 1 min due to the step data acquisition (30 s) and the response time of the commercial device (lower than 5 s, datasheet parameters, DigiPicco[™] Capacitive Humidity Module). In this context, the GQD sensors show excellent response times (less than 5 s) according to the commercial sensor datasheet parameters. The fast system kinetics is in good agreement with the reduction of diffusion effects between the target gas and the bulk of the material occurring when going from classic coating systems to

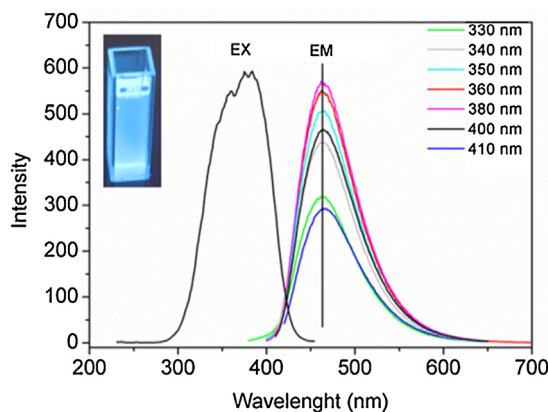


Fig. 1. Excitation spectra at 463 nm and emission spectra at different excitation wavelengths of the GQDs. Inset: photographs of GQD solutions under exposure to UV light.

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