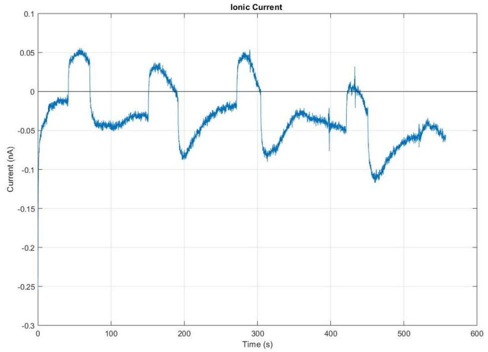

Figure 1: Ionic current with light, Pt wires

This experiment indicates that under a 10-fold concentration gradient, we can obtain active anti-gradient ion transport upon asymmetric light illumination in GOM.

Conclusions

Emerging hydrovoltaic technologies form an new research field and in many aspects a blank page. The study of hydrovoltaic technologies points to manifold fundamental questions in physics and chemistry, and at the same time it has the potential to bring important innovations for key societal challenges, such as in water remediation and energy harvesting.

In our experiment, we detected a photo-induced ionic current through GOM nanochannels. The recorded photo-induced ionic current is still low ($\sim 1\ nA$), and the route towards real application of hydrovoltaic technologies is quite long.

Hydrovoltaic technologies can allow to realize hybrid devices, combining carbon nanomaterials with other energy conversion structures, such as thin film solar cells, silicon solar cells and active ion pumps, with the aim to study a device which is able to generate electricity in all-weather conditions.

The low output power and poor conversion efficiency are the main problems of emerging hydrovoltaic technology, it is important to study how to optimize the device performances, and hopefully how to realize a high-performance device.

New hydrovoltaic devices represent an important opportunity for new renewable energy production, even if the study of hydrovoltaic technologies has just begun.

The physical/chemical properties of graphene change under interactions with water and thus generate many interesting phenomena including power generation. Through the optimization of materials and nanophotonic device design, we now have the technology to convert the motion of water and ions into electricity.

However, the current research on graphene-based hydrovoltaic materials and technologies is still in its infancy and there are several problems to resolve. The low power output is not enough to meet the needs of practical production. The mechanism of generating the electricity is not fully clear, which is not beneficial to improve the device performance. The study is currently carried out in the ideal environment under laboratory conditions, so it is difficult to guarantee the long-term stability in the real environment.

Despite all these obstacles, graphene-based hydrovoltaic materials have shown great potentials for self-powered devices and more research efforts should be directed to this fast growing field.

Using nanophotonic design strategies, studying the impact of graphene photocharging on its solid-fluid interactions and controlling ion-transport in a liquid electrolyte in contact with graphene, we want to achieve a breakthrough in emerging hydrovoltaic technologies, towards the generation of clean and sustainable energy.

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Finally, I dedicate this thesis to myself, to my sacrifices and my tenacity that have allowed me to get here.

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MSc PROGRAMME IN PHYSICS

ANGELO BONANNO

PHOTOTGATING OF CARBON-BASED MATERIALS FOR IONIC ENERGY DEVICES

FINAL PROJECT

RELATORI:
CHIAR.MO PROF. A. TERRASI
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Abstract

Harvesting energy in clean and sustainable way is one of the most important challenges of our society. Nature can help us in our effort, because sun and water can potentially provide the most abundant renewable supply of energy.

Nanostrusctured materials, and in particular Carbon-based materials, can generate electricity on interaction with water, this phenomenon was recently called hydrovoltaic effect. Some experimental advances show electricity generation in carbon nanomaterials on exposure to water flows, waves, rains, natural evaporation and moisture. The ion and water transport inside the nanometer channels of carbon nanomaterials can be controlled and then used for energy harvesting, in new ionic energy devices.

Ionic-based systems have recently emerged as an important alternative to electronic ones for energy generation and storage devices. Ion transport processes are strongly affected by the presence of surfaces charges at the solid/liquid interface, which are typically controlled via surface functionalization or electrostatic gating. Harnessing nanophotonic design strategies for extreme light-concentration, we study how photogating can be exploited to realize novel ionic-based devices, such as graphene-based energy generation systems.

In this work, we study new strategies for photogating graphene and graphene oxide, in order to develop more efficient ionic energy devices.

Background

The motion of electrolytes induced by a pressure gradient through a narrow channel (lower than the Debye length of ions in fluid) generates a voltage in the fluid, this phenomenon is called electrokinetic effect and it is known from many years. Recently other effects have been observed. A voltage can be induced by drawing a droplet of water on graphene sheet. An electric current is formed in graphene by two moving boundaries of the electrical double layer at the front and rear of the running droplet, respectively.

A voltage can be induced in graphene also by waving water, or from raindrops on graphene sheet. These process can allow new forms of energy harvesting from the whole water cycle.

Objectives

In this project we want to study fundamental properties of water–solid interactions and basic mechanisms of harvesting water energy with nanostructured materials, in particular water interactions with carbon based nanomaterials, such as graphene or graphene oxide (GO).

Photogating of graphene is considered as a way of conductance modulation of the graphene layer, through photo-induced gate voltage. Also in graphene oxide (GO) and carbon nanotubes (CNTs) light can create a photo-induced gate voltage.

In the first part of the work, we focus on assessing strategies for photogating graphene, for the study of ionic devices based on liquid flow on interaction with the graphene layer. We perform numerical simulations, in order to study how to control the charging state of graphene using light. In devices based on graphene/SiO_2/Si junction, the accumulation of photogenerated carriers at the Si/SiO_2 interface results in additional gate voltage under light illumination. This photogate voltage can shift the Fermi level of graphene, and results in a light-induced doping in graphene. In order to increase the photogating of graphene, we study the effects of devices based on graphene/SiO_2/p-n junction. The built-in electric field of a p-n junction can increase the carriers separation, and the consequent charge accumulation at the Si/SiO_2 interface. This results in higher photogating effect.

In the second part of the work, we focus on the fabrication and characterization of graphene oxide membranes (GOM) based ionic energy devices. Ion active transport is a promising way for solar energy conversion and storage. GOM show exceptional ionic and molecular transport properties, but very low light absorption. To overcome the otherwise poor light absorption in GOM, we study two nanophotonic strategies. The first strategy is the use of Salisbury screen, consisting of a three layer structure based on metallic-back-reflector/SiO_2/GO. We report the fabrication of two ionic energy devices, and we detect a photo-induced ionic current of $\sim 1\ nA$ under asymmetric light illumination.

The second strategy is the use of Plasmonic resonances from gold nano-cubes. In this case, plasmonic resonances can enhance absorption inside the GOM, and further enhance the electron hole pairs generation. Our simulations show that using gold nanocubes with silver mirror, we can increase the absorption in GOM and obtain an electric field enhancement. This is due to a plasmonic gap mode and two dipole modes.

Techniques

We fabricated two different nanofluidic devices. These devices are based on a three layers tructure: GOM, SiO_2, and Gold back reflector. This structure is emebedded in a transparent polydimethylsiloxane (PDMS) elastomer. The PDMS has two holes that we use as reservoirs for the electrolyte solutions. We can put two electrolyte solutions in the two reservoirs, and we measure the ionic current through the GOM nano-channels.

We used e-beam evaporation to deposit the Au layer, sputtering to growth the SiO_2 layer, and a spin coating process to fabricate the GOM from a graphene oxide solution.

We used optical microscopy to analyse the absorption spectra of our devices, and estimate the thickness of the SiO_2 layer and GOM layer.

For the characterization of our device, we send a laser light near one side of the GOM, and we record the ionic current.

Results

In our experiment, we use the sample with SiO_2 thickness of $\sim 380\ nm$, and GO thickness of $\sim 50\ nm$. In this case, we use electrolyte concentration $C_L/C_R = 10\ \mu M/1\ \mu M$, central laser wavelength $\lambda_c = 545\ nm$, bandwidth $\Delta\lambda = 100\ nm$, and light intensity $I \simeq 360\ mW/cm^2$. We don't apply any potential difference between the two electrodes. Fig. 1 shows the recorded ionic current as a function of time. The ionic current is initially negative, it means cations move from the high concentration solution to the low concentration solution. When we send light in the system, the current rapidly increases, crosses the zero line, and goes to positive values. This indicates that ions revers their direction of motion, flowing from the low concentration solution to the high concentration solution. When we turn off the light, the current rapidly decreases and it returns to negative values. This behaviour is repeated four times in Fig. 1.