Review

Recent advances in experimental basic research on graphene and graphene-based nanostructures

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Abstract
The present work is a review of the results achieved in the experimental basic research on following rapidly developing modern topics of nanoscience and nanotechnology related to graphene and graphene-based nanosystems: reduction of graphene oxide and investigation of physical properties of reduced graphene oxide; fabrication and investigation of graphene quantum dots; study of light emission from excited graphene; fabrication and investigation of graphene nanopores; preparation and investigation of graphene oxide-liquid crystals as well as aqueous graphene oxide dispersions. Besides presenting the scientific content of the above-mentioned five topics in detail, we briefly mention promising and interesting works, demonstrating that the area of basic research on graphene and graphene-based nanostructures is still being enlarged.

Keywords: quantum field, Dirac fermion, electromagnetic field, Green’s function, perturbation theory
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1. Introduction

Soon after the discovery of the two-dimensional gas of massless Dirac fermions in graphene by Novoselov, Geim et al [1] and the subsequent experimental observation of the quantum Hall effect and Berry phase in graphene by Kim et al [2] as well as the demonstration of chiral tunneling and the Klein paradox in graphene by Katsnelson, Novoselov and Geim [3], the research activities on graphene have emerged like ‘a rapidly rising star on the horizon of materials science and condensed-matter physics’, and graphene has revealed ‘a cornucopia of new physics and potential applications’, as was stated by Geim and Novoselov [4]. An evident demonstration of the above-mentioned statement was the efficient application of graphene for detecting individual gas molecules adsorbed on the surface of the graphene-based sensor [5]. The operational principle of this graphene device was based on the change in its electrical conductivity due to adsorbed gas molecules acting as donors or acceptors.

During a short time, the research on applications of graphene was increased from being a domain of condensed-matter physics and materials science to also being explored in electronic engineering. In particular, Schwierz has published a comprehensive review on graphene transistors [6]. A review on graphene-based optoelectronics, plasmonics and photonics was recently presented in [7]. Graphene can also be efficiently
applied in photocatalysis. In [8] Jaroniec et al presented a review on graphene-based semiconductor photocatalysts. Recent advances in the research on graphene-based photocatalysis, which were achieved after the submission of the review [8], were presented in [9].

Beside the active study on the applications of graphene, during recent years, the basic research on graphene has achieved promising results. The purpose of the present work is to review recent advances in basic experimental research on graphene as well as on graphene-based nanostructures and nanomaterials.

In section 2 we present the results of the experiments on the reduction of graphene. Section 3 is devoted to the review on the fabrication, characterizations and luminescence study of graphene quantum dots. The subject of section 4 is the light emission from excited graphene. In section 5 we present the results of the research on graphene nanomolecules, and section 6 is devoted to the study of graphene oxide-liquid crystals and aqueous graphene oxide dispersions. The conclusion and discussions are presented in section 7.

2. Reduction of graphene oxide and investigation of some physical properties of reduced graphene oxide

The reduction of graphene oxide (GO) was efficiently performed by two different methods: the thermal reduction [10] and the Birch reduction [11]. In [10] Banerjee et al conjectured that on annealing, the random epoxy groups in the native GO migrate over the GO surface by acquiring thermal energy and self-assemble to form several long chains of epoxy groups. Subsequently, upon thermal reduction the GO sheet is unzipped along these long chains giving rise to moving zigzag edges, resulting in the enhancement of the magnetization. The authors also found that the density of the epoxy groups plays an important role in the unzipping process. If the density of the epoxy groups is low, then unzipping of GO is not possible. The chemical reduction of GO also does not favor unzipping.

In the interesting article [12] Sofer, Pumera et al systematically evaluated the suitability of GOs prepared by various standard methods such as the Staudenmaier [13], Hoffman [14] and Hummers [15] methods to undergo Birch reduction [11] using Na as the electron donor and methanol as the proton donor. The authors investigated the nature of Birch-reduced GOs by using various material characterization methods such as scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), combustible elemental analysis, energy-dispersive x-ray fluorescence spectroscopy (ED-XRF), inductively-coupled plasma optical emission spectroscopy (ICP-OES), Raman spectroscopy, photoluminescence (PL) measurements and electrical resistivity measurements. The magnetic properties of the hydrogenated graphenes (graphanes) prepared via the Birch reduction of graphite oxides were investigated by using superconducting quantum interference device (SQUID) magnetometry. For the first time, the authors demonstrated that the Birch reduction of graphite oxides can lead to highly hydrogenated graphenes. The investigation on the magnetic properties showed that this material has an intrinsically complex structure, consisting of both ferromagnetic and antiferromagnetic components.

Recently, Tamiguchi, Yokoi et al [16] applied the photoreduction method to reduce GO without using additional chemicals and investigated the ultraviolet-visible (UV–vis) absorption, the steady-state and time-resolved PL in the visible-near infrared (NIR) range, and the magnetic properties of reduced graphene oxide (rGO).

The black-colored rGO dispersion obtained after photoreduction for 6 h maintained high colloidal stability, while photoreduction for 40 h resulted in the precipitation of hydrophobic rGO sheets. The absorption intensity in the visible range increased with the increase of the photo-irradiation duration, where the optical energy gap shifted towards the low-energy side from 2.9 to 1.5 eV. Raman spectroscopic analysis showed that the integrated intensity ratio of the D band at ∼1350 cm⁻¹ to the G band at ∼1600 cm⁻¹ (√D/√G) slightly increased after photoreduction for 6 h.

PL measurements were performed to further investigate the effect of photoreduction on GO electronic states. Unreduced GO induced a broad PL band at ∼650 nm due to the π—π* transition. As the photoreduction progressed, PL was red-shifted and weakened. The NIR PL properties of GO and photoreduced GO were investigated by steady-state and time-resolved measurements.

The optical investigations suggested that photoreduction of GO introduced localized levels. If these levels come from local structures with unpaired electrons, then they would afford localized spin moments and thus the magnetic properties of GO. The authors investigated the influence of photoreduction on the magnetic properties of GO using a superconducting quantum interference device. It was found that GO displayed diamagnetic behavior at room temperature, while a paramagnetic signal was predominantly observed for the rGO sample.

The local structure of rGO was investigated using C₁s XPS, transmission electron microscopy (TEM), ¹³C solid-state nuclear magnetic resonance (SSNMR) and FTIR spectroscopy in order to seek the origins of the photoreduction-included change in the optical and magnetic properties. Ab initio calculations were also carried out to investigate how the formation of C-H bonding and carbon vacancies affect the optical and magnetic properties of an sp² nanodomain. Integrating all the calculated and experimental results, it is possible to explain the photoreduction-induced modifications of both the optical and magnetic properties in terms of the hydrogenation of the sp² nanodomain surface and vacancies without contradiction.

In [17] Rea et al investigated the enhancement and wavelength modulation of the PL spectrum of GO sheets infiltrated by a spin-coating technique into silanized mesoporous silicon (PSi). The chemical nature of GO was confirmed by Raman spectroscopy: the broad G and D peaks and
the low-intensity 2D and D+G bands characteristic of GO were clearly visible.

The chemical composition of the hybrid structure was investigated by FTIR spectroscopy. The PL signal emitted from the GO nanosheets infiltrated in PSi was investigated at the excitation wavelength of 442 nm. Results were reported together with PL emission of bare silanized PSi and of GO spin-coated on silanized crystalline silicon, for comparison. It was observed that after infiltration in PSi, the PL signal emitted from GO was enhanced by a factor of almost 2.5. This strong enhancement was attributed to the high GO concentration inside the sponge-like PSi structure. Moreover, the modulation of the photoluminescence signal was also observed. This wavelength modulation of GO PL opened a new perspective for GO exploitation in innovative optoelectronic devices and highly sensitive fluorescence sensors.

3. Fabrication, characterizations and luminescence study of graphene quantum dots

Graphene quantum dots (GQDs) were known to have fascinating optical and electronic properties. In several recent experimental works GQDs having various sizes, shapes and chemical compositions and therefore displaying a high heterogeneity were fabricated, and their material characterizations as well as their luminescence properties were investigated. In [18] Ajayan et al demonstrated that during the acid treatment and chemical exfoliation of traditional pitch-based carbon fibers, the stacked graphitic Submicrometer domains of the fibers were easily broken down, leading to the creation of GQDs with different size distribution in scalable amounts. The as-produced GQDs with the size range of 1–4 nm showed two-dimensional morphology, most of which exhibited zigzag edge structure and had a 1–3 atomic layer thickness. The PL of GQDs was tailored through varying their size by changing the process parameters. Due to the PL stability, nanosecond lifetime, and biocompatibility, GQDs were demonstrated to be excellent probes for high-contrast bioimaging and biosensing applications.

A facile synthetic method for pristine GQDs and graphene oxide quantum dots (GOQDs) was elaborated by Cho et al [19]. The structures were synthesized by chemical exfoliation from the graphitic nanoparticles with high uniformity in terms of shape (circle), size (less than 4 nm) and thickness (monolayer). The physical origin of the blue and green PL of GQDs and GOQDs was attributed to intrinsic and extrinsic energy states, respectively.

Greenish-yellow luminescent GQDs with a quantum yield (QY) up to 11.7% were successfully fabricated via cleaving GO under acidic conditions by Zhu et al [20]. The cleaving and reduction processes were accomplished simultaneously using microwave treatment without additional reducing agent. When the GQDs were further reduced with NaBH₄ bright blue luminescent GQDs were obtained with a QY as high as 22.9%. Both GQDs showed well-known excitation-dependent behavior, which could be ascribed to the transition from the lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO). Electrochemiluminescence (ECL) was observed from the GQDs for the first time, suggesting promising applications in ECL biosensing and imaging. The ECL mechanism was investigated in detail. Furthermore, a novel sensor for Cd²⁺ was proposed based on Cd²⁺ induced ECL quenching with cystein (Cys) as the masking agent.

A hydrothermal route for cutting graphene sheets into blue luminescent GQDs was demonstrated by Wu et al [21]. The authors prepared water soluble GQDs with a diameter of ca. 10 nm that exhibited blue PL by the hydrothermal (chemical) cutting of oxidized graphene sheets. The mechanisms of the cutting and luminescence were discussed. This discovery of PL of GQDs might extend the range of application of graphene-based nanomaterials to optoelectronic and biological labeling.

In [22] Sun et al discussed the common origin of green PL in carbon nanodots and GQDs. Carbon nanodots (C-dots) synthesized by electrochemical ablation and small-molecule carbonization together with GQDs fabricated by solvothermally cutting graphene oxide are two kinds of typical green fluorescence carbon nanomaterials. Insight into the PL origin of these fluorescent carbon nanomaterials is one of the important topics of nanophotonics. In this article, a common origin of green luminescence in these C-dots and GQDs was investigated by ultrafast spectroscopy. According to the change of surface functional groups during surface chemical reduction experiments, which were also accompanied by obvious emission-type transform, these common green luminescence emission centers that emerged in these C-dots and GQDs synthesized by bottom-up and top-down methods were unambiguously assigned to special edge states consisting of several carbon atoms on the edge of carbon backbone and functional groups with C=O (carbonyl and carboxyl groups). The obtained findings suggested that the competition among various emission centers (bright edge states) and traps dominated the optical properties of these fluorescent carbon nanomaterials.

The physical origin of the green fluorescence of GQDs is an interesting problem of graphene photonics. In [23] Wang et al studied this problem by a combined usage of femtosecond transient absorption spectroscopy and femtosecond time-resolved fluorescence dynamics measured by a fluorescence upconversion technique as well as a nanosecond time-correlated single-photon counting technique. The authors have found a fluorescence emission-associated dark intrinsic state due to the quantum confinement of in-plane functional groups and two characteristic fluorescence peaks that appeared in all samples and were attributed to independent molecule-like states. This finding established the correlation between the quantum confinement effect and the molecule-like emission in the green fluorescent GQDs, and might lead to innovative technologies of GQD fluorescence enhancement as well as its industrial application.

The upconversion fluorescence in C-dots and GQDs was discussed in a recent interesting work of Wen et al [24]. The authors mentioned that in many previous works the upconversion fluorescence was frequently considered as an
important feature in C-dots and GQDs, and some mechanisms as well as potential applications were proposed. In contrast to such a general belief, the authors demonstrated that no upconversion fluorescence based on five different synthesized C-dots and GQDs was observed. The authors confirmed that the so-called upconversion fluorescence actually originates from the normal fluorescence excited by the leaking component from the second diffraction in the monochromator of the fluorescence spectrometer. Upconversion fluorescence can be identified by measuring the excitation intensity dependence of the fluorescence.

In [25] Röding et al performed the fluorescence lifetime study of GQDs. The heights of the GQDs with the largest value, about 1 nm, were determined by means of atomic force microscopy (AFM), while their sizes with the diameter distribution in the interval $d = 8.3 \pm 2.9$ nm were measured by using the TEM images.

Steady-state emission spectra of GQDs in the range 350–700 nm were recorded by a time-resolved PL spectrometer. At the emission intensity maximum $\lambda = 430$ nm the fluorescence lifetime was measured by using time-correlated single-photon counting (TCSPC). For each of the GQDs and fluorescein lifetime data sets, the following four models were fitted: the monoexponential, the stretched exponential, the log-normal distribution and the inverse gamma distribution models, and the estimated values of the mean and standard deviations were studied.

For comparison, a simulation study was also carried out. The authors compared the computational speeds and studied asymptotic bias in estimated parameters when the model was misspecified. It was found that the difference in the estimated values of the mean and standard deviations for different models could vary considerably and more so for strongly non-exponential decay.

A fully transparent quantum dot-light emitting diode (QD-LED) integrated with a graphene anode and cathode was fabricated by Ju et al for the first time [26]. The authors used the graphene films with controlled work function and sheet resistance for both the anode and cathode. The fabrication process was performed as follows: 1) formation of the graphene anode by the dry-transfer method; 2) fabrication of active layers by the spin-coating method; 3) formation of the graphene cathode by the dry-transfer method and dry etching, through which the emissive areas are defined as the overlapped ones between the cathode and the anode.

Either gold nanoparticles or silver nanowires were inserted between layers of graphene to control the work functions, whereas the sheet resistance was determined by the number of graphene layers. The inserted gold nanoparticles or silver nanowires in the graphene films caused a charge transfer and changed the work function to 4.9 or 4.3 eV, respectively, from the original work function of 4.5 eV in the case of pristine graphene. Moreover, the sheet resistances of the anode and the cathode were also improved significantly when the number of graphene layers increased. The variations of the optical characteristics such as Raman spectra, transmittance at the wavelength of 535 nm corresponding to the peak of the electroluminescence (EL) and the voltage dependence of EL spectra were carefully investigated by the authors.

The alleviation of immune-mediated liver damage using large GQDs was proposed by Volarevic et al [27]. For the first time, these authors demonstrated the immunomodulatory and cytoprotective effects of GQDs in a mouse model of immune-mediated liver damage: GQDs alleviate immune-mediated fulminant hepatitis by reducing hepatic inflammation, oxidative stress, apoptosis and autophagy. The observed effects apparently involved both immunomodulatory action exerted via the interference with T cell and macrophage activation as well as direct hepatoprotective action due to liver accumulation.

4. Light emission from excited graphene

In recent years, the research on the emission of radiation in different wavelength ranges was performed in several experimental works. The spatially resolved thermal radiation emitted from electrically biased graphene was investigated by Freitag et al [28]. These authors have demonstrated how to extract the information on temperature distribution, carrier densities and spatial location of the Dirac point in the graphene channel from the experimental data. It was shown that the graphene exhibits a temperature maximum with a location that can be controlled by the gate voltage. Stationary hot spots were also observed. Thus, the infrared emission can be used as a convenient and non-invasive tool for the characterization of graphene devices.

In [29] Berciaud et al examined the intrinsic energy dissipation steps in electrically biased graphene channels. By combining in situ measurements of the spontaneous optical emission with the Raman spectroscopy study of the graphene sample under conditions of current flow, the authors obtained independent information on the energy distribution of the electrons and phonons. The electrons and holes contributing to the light emission are found to obey a thermal distribution, with temperatures in excess of 1500 K in the regime of current saturation. The zone-center optical phonons are also highly excited and are found to be in equilibrium with the electrons. For a given optical phonon temperature, the anharmonic downshift of the Raman G mode is smaller than expected under equilibrium conditions, suggesting that the electrons and high-energy optical phonons are not fully equilibrated with all of the phonon modes.

Although graphene has no band gap and therefore PL is not expected from relaxed charge carriers, graphene excited by ultrashort laser pulses can emit PL light. In [30] Lui et al have observed significant light emission from graphene under excitation by 30 fs ultrashort laser pulses. Light emission was found to occur across the visible spectral range of 1.7–3.5 eV with emitted photon energies exceeding that of the excitation laser (1.5 eV). The emission exhibited a nonlinear dependence on the laser intensity. In two-pulse correlation measurements a dominant relaxation time of tens of femtoseconds was observed. The experimental data can be explained by a
two-temperature model describing the electrons and their interaction with strongly coupled optical phonons.

In [31] Pop et al performed imaging, simulation and electrostatic control of power dissipation in graphene devices. The authors directly image hot spot formation in functioning mono- and bilayer graphene field effect transistors (GFETs) using infrared thermal microscopy. Correlating with an electrical-thermal transport model provided insight into carrier distribution, fields and GFET power dissipation. The hot spot corresponded to the location of minimum charge density along the GFET. By changing the applied bias, this could be shifted between electrodes or held in the middle of the channel in ambipolar transport. The authors noted that the hot spot shape bore the imprint of the density of states in bilayer graphene. They also found that thermal imaging combined with self-consistent simulation provided a non-invasive approach for more deeply examining transport and energy dissipation in nanoscale devices.

In a recent interesting work [32] Bae et al observed the bright visible light emission from electrically biased suspended graphene devices. It was known that in these devices the heat transport was greatly reduced [33]. Therefore, hot electrons (~2800 K) became spatially localized at the center of the graphene layer, resulting in a 1000-fold enhancement of the radiation efficiency compared to that of the thermal radiation [1, 2].

Freely suspended graphene is largely immune to undesirable vertical heat dissipation [33] and extrinsic scattering effects [34], and therefore promises much more efficient and brighter radiation in the infrared-to-visible region. Due to the strong umklapp phonon–phonon scattering [35] the thermal conductivity of graphene at high temperature 1800 ± 300 K is greatly reduced (∼15 W m⁻¹ K⁻¹), which also suppresses lateral heat dissipation, so hot electrons (∼2800 K) become spatially localized at the center of the suspended graphene under modest electric field (∼0.4 μm⁻¹), greatly increasing the efficiency and brightness of the light emission. The bright visible thermally emitted light interacts with the reflected light from the separate substrate surface, giving interference effects that can be used to tune the wavelength of the emitted light.

The authors observed bright and stable visible light emission from hundreds of electrically biased suspended graphene devices. The emitted visible light was so intense that it was visible even to the naked eye, without additional magnification. An array of electrically biased multiple parallel-suspended chemical vapor deposition (CVD) few-layer graphene devices exhibited multiple bright visible light emission under ambient conditions. The observation of stable, bright visible light emission from large-scale suspended CVD graphene arrays demonstrated the great potential for the realization of the complementary metal-oxide-semiconductor (CMOS)-compatible, large-scale graphene light emitters in display modules and hybrid silicon photonic platforms with industry vacuum encapsulation technology.

A microscopic view on the ultrafast PL from photoexcited graphene was presented in a recent work of Malic et al [36]. The authors performed a joint theory-experiment study on this topic and revealed two distinct mechanisms behind the occurring PL. Besides the well-known incoherent contribution driven by nonequilibrium carrier occupation, the authors also found a coherent part that spectrally shifted with the excitation energy. For the first time, the authors demonstrated the predicted appearance and spectral shifts of the coherence PL.

5. Graphene nanopores

For localizing and detecting single DNA or protein molecules it was expected that the solid-state nanopore devices might be efficient tools [37]. In [38] Kril et al proposed the design of functionalized nanopores in graphene monolayers and showed by molecular dynamics simulations that they provide highly selective passage of hydrated ions. Only ions that can be partly stripped of their hydration shells can pass through these ultrasmall pores with diameters of ~5 Å. For example, a fluorine-nitrogen-terminated pore allows the passage of Li⁺, Na⁺ and K⁺ cations with the ratio 9:14:33, but it blocks the passage of anions. The hydrogen-terminated pore allows the passage of F⁻, Cl⁻ and Br⁻ anions with the ratio 0:17:33, but it blocks the passage of cations. The authors predicted that these nanopores could have potential applications in molecular separation, desalination and energy storage systems. The use of graphene with nanopores as a subnanometer trans-electrode membrane was discussed by Garaj et al [39]. Subsequently, Bashir et al [40] proposed to use nanopore sensors for nucleic acid analysis.

For creating extremely small pores in graphene with atomic precision Golovchenko et al [41] developed an efficient method: the atom-by-atom nucleation and growth of graphene nanopores. It consists of creating defect nucleation centers by using energetic ions, followed by edge-selective electron recoil sputtering. As a result, the authors successfully created graphene nanopores with radii around 3 Å corresponding to 10 atoms removed. The authors observed carbon atom removal from the nanopore edge in situ using an aberration-corrected electron microscope. This approach did not require focused beam and allowed scalable production of single nanopores as well as arrays of monodisperse nanopores for atomic-scale selectively permeable membranes.

The sharply peaked pore-size distribution indicated that the authors successfully developed an efficient method for generating monodisperse nanopores in semipermeable graphene membranes tuned to select molecules with a specific size and structure.

The graphene sheets with nanopores can be used as the ion exchange membranes in desalination technology. By applying the molecular dynamics simulations in [42] Xue et al investigated the selective ion transport behavior of electric-field-driven KCl solution through charge-modified graphene nanopores. They demonstrated that the presence of negative charges at the edge of the graphene nanopore can remarkably impede the passage of Cl⁻ while it can enhance the transport of K⁺. This is an indication of the ion selectivity of the graphene nanopores. The authors investigated the dependence of this selectivity on the pore size and the total
charge number assigned at the nanopore edge. By adjusting the nanopore diameter and the electric charge on the nanopore, a nearly complete rejection of Cl\textsuperscript{−} can be realized. The electrical resistance of nanoporous graphene, which is a key parameter to evaluate the performance of ion exchange membranes, is found two orders of magnitude lower than commercially used membranes. Thus, graphene nanopores are promising candidates to be used in electrodialysis technology for water desalination with a high permselectivity.

The experimental research on selective ionic transport through controlled, high-density, subnanometer diameter pores in macroscopic single-layer graphene membranes was performed by Karnik et al \cite{43}. Isolated reactive defects were first introduced into the graphene lattice through ion bombardment and subsequently enlarged by oxidative etching into permeable pores with diameters of 0.40 ± 0.24 nm and densities exceeding 10\textsuperscript{12} cm\textsuperscript{−2}, while retaining structural integrity of the graphene. Transport measurements across ion-irradiated graphene membranes subjected to \textit{in situ} etching revealed that the created pores were cation-selective at short oxidation times, consistent with the electrostatic repulsion from negatively charged functional groups terminating the pore edges. At longer oxidation times, the pores allowed the transport of salt, but prevented the transport of large organic molecules, indicative of steric size exclusion.

The heterogeneous sub-continuum ionic transport in statistically isolated graphene nanopores was also investigated in a recent work of Karnik et al \cite{44}. The authors demonstrated that isolated sub-2 nm pores in graphene exhibited, in contrast to larger pores, diverse transport behaviors consistent with ion transport over a free-energy barrier arising from ion dehydration and electrostatic interactions. Current–voltage measurements revealed that the conductance of graphene nanopores spanned three order of magnitude and that they displayed distinct linear, voltage-activated or rectified current–voltage characteristics and different cation-selectivity profiles.

The obtained results demonstrated that sub-2 nm graphene nanopores exhibited diverse transport behaviors that can be explained by electrostatic and hydration interactions of ions with the pores and that are reminiscent of biological channel. The pores are dynamic and can change their transport characteristics at different timescales. The above-presented results suggested the potential of sub-continuum nanopores in graphene to act as a new class of synthetic ion channels and provided a platform for probing sub-continuum transport for the engineering of the desired selectivity and transport characteristic at the single-pore level.

However, there was less understanding as to whether nanoporous graphene is strong enough to maintain its mechanical integrity under the high hydraulic pressure inherent to the reverse osmosis desalination process. The mechanical strength of nanoporous graphene as a desalination membrane was studied by Grossman et al \cite{45}. The authors showed that a nanoporous graphene membrane can maintain its integrity in reverse osmosis but the choice of substrate for graphene is critical to this performance. Using molecular dynamics simulations and continuum fracture mechanics, the authors showed that an appropriate substrate with openings smaller than 1 μm would allow nanoporous graphene to withstand pressures exceeding 57 MPa or ten times more than typical pressures for seawater reverse osmosis, and greater porosity may help the membrane withstand even higher pressure.

A graphene nanopore with a self-integrated optical antenna was fabricated by Lee et al \cite{46}. The authors demonstrated that a nanometer-sized heated spot created by photon-to-heat conversion of a gold nanorod resting on a graphene membrane forms a nanoscale pore with self-integrated optical antenna in a single step. The distinct plasmonic traits of metal nanoparticles, which have a unique capability to concentrate light into nanoscale regions, yield the significant advantage of parallel nanopore fabrication compared to the conventional sequential process using an electron beam. Tunability of both the nanopore dimensions and the optical characteristics of plasmonic nanoantenna were further achieved. Finally, the key optical function of the prepared self-integrated optical antenna on the vicinity of the graphene nanopore was manifested by multifold fluorescent signal enhancement during DNA translocation.

The molecular valves for controlling gas phase transport were fabricated from discrete angstrom-sized pores in graphene by Bunch et al \cite{47}. These authors showed that gas flux through discrete angstrom-sized pores in monolayer graphene can be detected and then controlled using nanometer-sized gold clusters, which are formed on the surface of graphene and can migrate as well as partially block a pore. In samples without gold clusters the authors observed stochastic switching of the magnitude of the gas permeance, which was attributed to molecular rearrangement of the pore. The fabricated molecular valves could be used, for example, to develop unique approaches to molecular synthesis based on the controllable switching of a molecular gas flux, reminiscent of ion channels in biological cell membranes and solid-state nanopores.

6. **Graphene oxide-liquid crystals and aqueous graphene oxide dispersions**

As an attempt to find a superior display for the application to the electro-optical switching, Song et al \cite{48} investigated the optical sensitivity to external electric field of graphene oxide (GO) liquid crystals (LCs) with controllable alignment. The sensitive response of the nematic GO phase to external stimuli makes this phase attractive for the above-mentioned purpose. Onsager’s theory predicted the transition from an isotropic to a nematic phase passing through a biphase as the concentration of plate-like GO in colloidal dispersions increases. The location of this transition depends sensitively on the aspect ratio (AR) diameter/thickness of the plates. Since the AR of GO-LCs with monoatomic thickness can be up to the order of 10 000 \cite{49}, the biphase was predicted to appear at the concentration around 0.01–0.1 vol%. In an experiment the authors used the GO flakes which were mostly single-layered and had the average AR of about 3200. The authors predicted
the concentrations for phase transitions from the isotropic phase to the biaxial phase to be 0.04 vol%, and from the biaxial phase to the nematic phase to be 0.17 vol%. On the other hand, by observing the macroscopic birefringence pattern the authors determined the experimental values of the above-mentioned concentrations of approximately 0.08 vol% and 0.2 vol%.

For determining the Kerr coefficient, the authors used a cuvette with parallel electrodes on two opposite walls and a beam-path length of 5 mm. The maximum Kerr coefficient was found to be approximately $1.8 \times 10^{-5}$ mV$^{-2}$, a value extremely large compared to the values of the orders of $10^{-2}$ and $10^{-9}$ mV$^{-2}$ for nitrobenzene and aqueous two-dimensional gibbsite platelet suspension [50] as well as of $10^{-5}$–$10^{-8}$ mV$^{-2}$ for blue phase LCs [51–53]. To demonstrate the significance of the obtained large Kerr coefficient the authors prepared an electro-optic device using two simple wire electrodes separated by 5 mm. This model optical device worked very well under an applied voltage of 20 V, although its performance was not comparable to those of commercial LC displays. The development of a real GO device requires an intensive study to synthesize a high-concentration isotropic GO dispersion for highly saturated birefringence, to control the ionic influence and precipitation for long-term stability, and to develop a new driving scheme suitable for electrolyte materials.

In the short note [54] the authors remarked that while the conventional LC displays take the advantage of the orientation from surface-induced to electric-field-induced alignment, the electric-field switching of GO-LCs occurs through a direct transition from an isotropic to a highly aligned liquid-crystalline phase. A high Kerr coefficient stems from the synergistic effect of the large GO polarizability anisotropy and the Onsager excluded-volume effect for LC ordering (LC alignment increases translational entropy at the expense of rotational entropy).

Because of the high shape anisotropy of GO and the electrical double layer formed at its surface, the GO polarizability parallel to the plane of the flake is greatly enhanced when the external electric field is switched on. The collective alignment of GO flakes occurring at low concentrations also contributes to the large Kerr coefficient. Another advantage of GO-LC displays is their low power consumption. However, for the development of GO-LC displays there exist several challenges which should be overcome.

In the subsequent work [55] Song et al investigated the material properties and electro-optic response of aqueous GO dispersions with varying ion types and ion concentrations. The material properties included the zeta potential, pH, and conductivity. The authors observed a clear contrast between the NaOH-GO dispersion and GO dispersions with other added ions. Other ions drastically desensitized the electro-optic response of GO dispersions, but the addition of NaOH slightly enhanced the electrical sensitivity of GO dispersions. The authors investigated the underlying mechanisms of the obtained results and clarified the ionic effect on both the characteristic contrast between the dispersed particles and solvent and the surface conductivity of GO. The authors demonstrated that solvent conductivity is important for the electrical sensitivity of GO dispersions, which influences the characteristic contrast between the dispersed particles and solvent. In addition, the authors investigated the surface electrical characteristic of GO depending on the ions of the solvent.

The authors experimentally and theoretically elucidated the underlying mechanism of the phenomena. The mechanism is closely related to the acidic nature of GO dispersion, which is neutralized by the addition of NaOH. The electro-optic response of GO dispersion was influenced more by the electrical properties of the solvent rather than by those of the GO particle itself. These results will help us to understand the electrochemical and liquid-crystalline characteristics of GO dispersions and to develop new electro-optic devices using these materials.

7. Conclusion and discussions

In this article, we have presented a review of recent interesting and promising basic experimental works on graphene as well as on graphene-based nanomaterials and nanostructures. These works were classified into the following five groups:

- Reduction of graphene oxide and physical properties of reduced graphene oxide.
- Fabrication and investigation of graphene quantum dots.
- Light emission from excited graphene.
- Fabrication and investigation of graphene nanopores.
- Graphene oxide-liquid crystals and aqueous graphene oxide dispersions.

Basic research on graphene has a wide diversity. Besides the five above-presented topics with impressive scientific content, there exist also other promising ones such as electron–phonon couplings in graphene [56–67], graphene nanoribbons [68–78], photothermoelectric effect [79–87], photo-induced doping effect on graphene heterostructures [88–90], superconducting phase in graphene-based hybrids [91–94], cobalt intercalation at the interface between graphene and iridium [95], surface-enhanced Raman signals for single-molecule magnets grafted on graphene [96], local deformations and incommensurability of high-quality epitaxial graphene on a weakly interacting transition metal [97], confined states in rotated bilayers of graphene [98], epitaxial graphene/ferromagnet hybrids [99], strains induced by point defects in graphene on metal [100], modulating charge density and inelastic optical response in graphene [101], H$_2$ plasma-graphene interaction [102], suppression of graphene multilayer patches [103], convergent fabrication of nanoporous two-dimensional carbon network from an aldol condensation on metal surface [104], thermodynamic and kinetic aspects of epitaxial growth of graphene [105] etc. Thus, the basic research on graphene is still continuing to enlarge the scientific content.
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