ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Graphene-Based Nanomaterials: Synthesis, Properties, and Optical and Optoelectronic Applications

Haixin Chang and Hongkai Wu**

Graphene, a two-dimensional, single-atom-thick carbon crystal arranged in a honeycomb lattice, shows extraordinary electronic, mechanical, thermal, optical, and optoelectronic properties, and has great potential in next-generation electronics, optics, and optoelectronics. Graphene and graphene-based nanomaterials have witnessed a very fast development of both fundamental and practical aspects in optics and optoelectronics since 2008. In this Feature Article, the synthesis techniques and main electronic and optical properties of graphene-based nanomaterials are introduced with a comprehensive view. Recent progress of graphene-based nanomaterials in optical and optoelectronic applications is then reviewed, including transparent conductive electrodes, photodetectors and phototransistors, photovoltaics and light emitting devices, saturable absorbers for ultrafast lasers, and biological and photocatalytic applications. In the final section, perspectives are given and future challenges in optical and optoelectronic applications of graphene-based nanomaterials are addressed.

1. Introduction

Graphene, a two-dimensional, single-atom-thick carbon crystal arranged in honeycomb lattices, has attracted enormous attention since its first discovery by isolation from bulk graphite using adhesive tape.[1–6] Graphene has demonstrated extraordinary electronic, mechanical, thermal, optical and optoelectronic properties such as ultrahigh carrier mobility, thermal conductivity, and mechanical strength.[3–9] Inspired by another carbon allotrope, carbon nanotube (CNT), research on graphene has expanded explosively in electronic, mechanical, biology, and energy directions, and has shown great potential in high frequency transistors, mechanical resonator, transparent conductors, spintronics, sensors, and drug delivery.[10–23]

Both fundamental research and practical applications of graphene are pursued with great interest in almost all the above-mentioned areas.[3–6] Electrons in two-dimensional atomic crystals of graphene behave as massless, relativistic Dirac fermions with linear energy dispersion, and exhibit some unique electronic properties.[4] Graphene has shown various transport properties such as pseudospin, chirality and anomalous quantum Hall effect.[1–4] Although graphene is a zero gap semimetal, for a large graphene sheet, graphene-based nanomaterials can act as a semiconductor with a bandgap for a narrow nanoribbon, bilayer graphene in electrical field, and graphene under substrate interactions or with different defects.[24–29] Chemically derived colloidal graphene quantum dots (QDs) have also been developed.[30,31] Graphene-based nanomaterials now consist of many derivatives of various dimensions, from zero, one, two dimensions, and are explored with increasingly growing standing points. It is no surprise that graphene can be considered as the mother of several carbon materials including C_{60}, CNTs, and graphite (**Figure 1**).

One significant challenge that has limited the exploration of graphene in the long run is how to produce high quality graphene on a large scale. Mechanical exfoliation can draw high quality graphene from graphite, but the process is tedious and the quantity of obtained graphene is tiny.[1] Therefore,

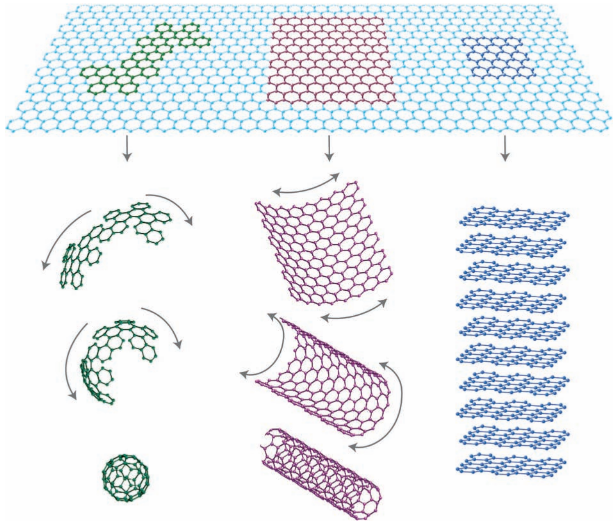

Figure 1. Schematic demonstration of graphene as mother of different kinds of carbon-based materials. Reproduced with permission.[4] Copyright 2007, Nature Publishing Group.

Prof. H. X. Chang, Prof. H. K. Wu
WPI-Advanced Institute for Materials Research
Tohoku University
Sendai 980-8578, Japan
E-mail: hxchang@wpi-aimr.tohoku.ac.jp; chhkwu@ust.hk

Prof. H. K. Wu
Department of Chemistry
The Hong Kong University of Science and Technology
Hong Kong SAR

DOI: 10.1002/adfm.201202460

this method is usually confined to fundamental studies in physics. Another method is epitaxial growth of graphene from the decomposition of a SiC surface.[32] This method produce a large area of supported graphene with acceptable quality, and is widely used both in fundamental and practical researches. Many alternative methods have been developed to produce graphene. For example, chemical vapor deposition (CVD) can produce large area single-layer or few-layer graphene with reasonable quality.[33,34] Chemically derived graphene, such as reduced graphene oxide, a graphene derivative with oxygen groups on the carbon bone scaffold of graphene, is also a rising star in the graphene family because such a kind of graphene can be produced on a mass scale up to tons.[35–39] The disadvantage of this method is the large amount of defects induced during the oxidization process in producing graphene oxide, and the resulting low mobility and conductivity in chemically reduced graphene oxide. However, such defects are advantageous in certain practical applications, such as sensors, functionalization, and for electronic property tuning.[36]

With the advance of graphene fabrication techniques and knowledge in electronics, there has been an increasing interest in applications of graphene in optical and optoelectronic fields since 2008.[40–48] For example, graphene is a promising transparent conductive electrode (TCE) to replace indium tin oxide (ITO), which is brittle, expensive, and is based on the rare element indium. Prototype 30-inch transparent graphene electrodes has been developed and used in touch screens.[13] Graphene also finds great potential in high frequency photodetectors, photovoltaics, and biosensors.[41,42] Although some achievements have been made in graphene optics and optoelectronics, there are still many challenges for graphene in high performance and large scale optical and optoelectronic applications.

Therefore, in this Feature Article, we will review recent progress in the development of graphene-based nanomaterials for optical and optoelectronic applications, including transparent conductive electrodes, photodetectors and phototransistors, photovoltaics and light emitting devices, saturable absorbers for ultrafast lasers, and biological and just emerging photocatalytic applications (**Figure 2**). The dynamic combination of unique structure and electronic/optical properties of graphene makes it a wonderful platform for optical and optoelectronic applications. Therefore, to maintain a holistic view, the electronic and optical properties of graphene, together with the synthesis techniques are introduced before the sections of optical and optoelectronic applications. Finally, the challenges and the prospects of using graphene in optical and optoelectronic applications are discussed.

2. Synthesis of Graphene-Based Nanomaterials

2.1. Mechanical Exfoliation from Graphite

Mechanical exfoliation is the method by which the first high quality graphene was exfoliated using scotch tape from bulk graphite (**Figure 3**A).[1] It is a primitive and low efficiency method but retains the completeness of original two-dimensional atomic lattices of graphene. This method involves repeatedly exfoliating graphite with scotch tape against SiO_2/Si substrates. With the unique color contrast,[1] though time consuming and low yielding, single- or few-layer graphene with very high quality can be identified with reasonable differentiation. The completeness of mechanically exfoliated graphene makes ultrahigh mobility and many interesting electronic properties easily observed.[1–4] The successful mechanical exfoliation of the first high quality graphene from graphite inspired huge interest in graphene-based nanomaterials and other two-dimensional atomic crystals.[49]

2.2. Epitaxial Growth from Thermal Deposition of SiC

Epitaxial growth from thermal deposition of SiC is another method frequently used to study the physics of graphene due to the relative high quality of graphene.[32,50] The epitaxial deposition growth of graphene from SiC happens on the Si terminated (0001) face of single-crystal 6H-SiC in high vacuum condition under controlled temperatures over 1000 °C (Figure 3B).[50] Monolayer and few layer graphene can be obtained on SiC substrate. The vacuum and temperature control are most important parameters in the growth. The advantage of this method is that the graphene is on insulating surfaces and therefore various kinds of devices

Haixin Chang is an Assistant Professor in WPI-Advanced Institute for Materials Research, Tohoku University, Japan. He received his Ph.D. in Materials Science in 2007 from Institute of Metal Research, Chinese Academy of Sciences. He then worked in the Department of Chemistry, Tsinghua University and Nanotechnology Centre, Hong Kong Polytechnic University before moving to Tohoku University in the beginning of 2011. He joined in the faculty of Tohoku University as an Assistant Professor in 2012.

Hongkai Wu is an Associate Professor in Department of Chemistry, Hong Kong University of Science and Technology, and a junior Principle Investigator in WPI-Advanced Institute for Materials Research, Tohoku University, Japan. He obtained his Ph.D. from Harvard University in 2002 followed by 3 years at Stanford University as postdoctoral fellow. He moved to Hong Kong in 2007 as an Assistant Professor.

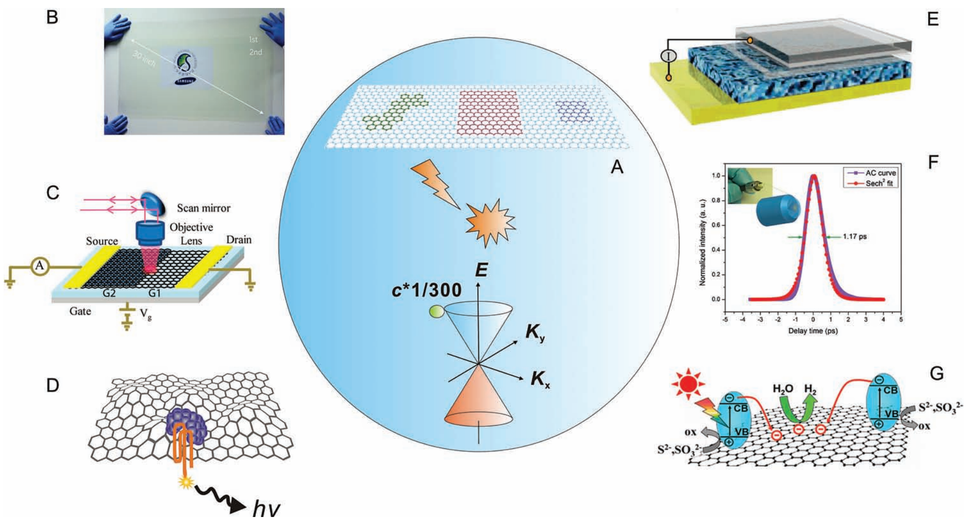

Figure 2. Graphene-based nanomaterials in optical and optoelectronic applications. The dynamic combination of unique structure and electronic/optical properties of graphene have encouraged many new optical and optoelectronic possibilities. Reproduced or adapted with permission.[4,13,21,47,97,107,133] Copyright 2007, Nature publishing group (A); copyright 2010, Nature Publishing Group (B); copyright 2010, American Chemical Society (C and D); copyright 2008, American Chemical Society (E); copyright 2012, American Chemical Society (G).

can be directly fabricated on SiC substrates. Large area, uniform graphene films can be epitaxial grown depending on the substrate size. However, the disadvantage is that graphene on SiC substrates is very difficult to transferred to other substrates, unlike CVD-grown graphene on metal. The carrier mobility of epitaxial graphene on SiC usually can reach around 2700 cm^2 v^{-1} s^{-1}.[32]

2.3. Chemical Vapor Deposition

Chemical vapor deposition is one of most important advances in large scale graphene growth technique. Metal (e.g., Ni, Cu) can catalyze the deposition of carbon sources (gas CH_4 or methanol, or solid poly(methyl methacrylate)) on the metal surfaces to form large area, uniform, high quality graphene (Figure 3C).[33,34,51] The process usually happens at high temperatures around 1000 °C followed by a transfer process for removal of metal by an etching agent. Nickel and copper are mostly used metal in CVD growth of graphene. Nickel-based CVD graphene growth is developed earlier, but copper can have larger grains than nickel after annealing and favors larger domain growth in graphene.[33] CVD growth of graphene on copper was even used to produce 30-inch graphene transparent electrodes for touch screens. Moreover, CVD-grown graphene on metal can be transferred to any substrate, in principle, which makes it very attractive for many applications. Some direct CVD growth methods on insulating surface without transfer have been also developed recently.[52]

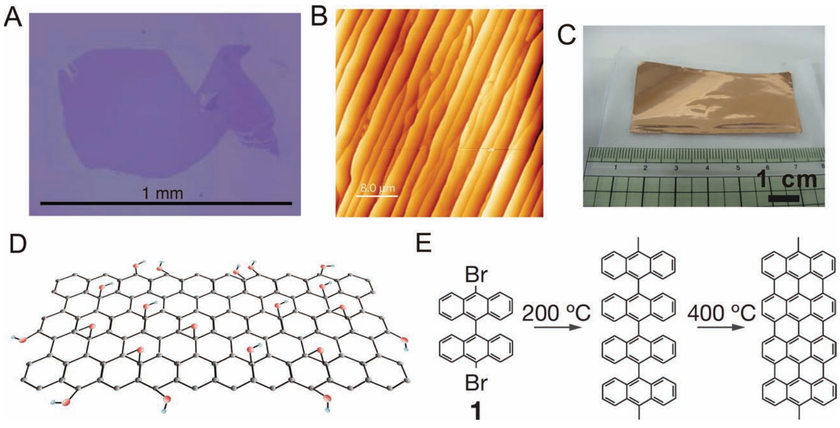

Figure 3. Synthesis methods for graphene-based nanomaterials. A) Mechanical exfoliation from graphite by tape against SiO_2/Si substrate. B) High vacuum decomposition from atomic terraces on SiC wafer. C) Chemical vapor decomposition of gas or solid carbon sources on copper. D) Reduced graphene oxide by exfoliating graphite oxide following by the chemical or thermal reduction. E) Bottom-up synthesis of graphene from organic molecules with benzene rings. Reproduced with permission.[3,50,57] Copyright 2009, American Association for the Advancement of Science (A); copyright 2009, Nature Publishing Group (B); copyright 2010, Nature Publishing Group (E).

2.4. Solution-Based Exfoliation from Graphite Oxide and Graphite

Another frequently used method to synthesize graphene is solution-based exfoliation of graphite oxide.[53] Graphite oxide is obtained from oxidization of graphite by chemicals (usually strong acids in Hummer's method) to expand the layer spacing and weaken the interactions between layers.[53] Graphite oxide can be easily exfoliated to be single layer graphene oxide-graphene scaffold with functional oxygenous groups-by ultrasonication or even mechanical stirring (Figure 3D). Graphene oxide, one of the most important graphene derivatives, is then chemically or thermally reduced to restore the conjugation structures of graphene and is called reduced graphene oxide or chemically reduced graphene.[14,15,28,53] Such chemically derived graphene is available by the ton, and easily functionalized because of the oxygenous groups on surfaces.[54] A similar method is applied to CNTs instead of graphite, resulting in graphene nanoribbons.[25] However, this solution-based exfoliation of graphite oxide is limited by the large scale residue defects and low quality of graphene after reduction. The conductivity and charge carrier mobility is relatively low compared with mechanically exfoliated graphene and CVD-grown graphene. Therefore, some other solution-based methods are developed to exfoliate graphite or intercalated graphite compounds without oxidization.[55,56] High quality graphene with few defects or even no defects can be obtained but with a much lower production efficiency than exfoliating graphite oxide.

2.5. Bottom-Up Organic Synthesis Methods

The bottom-up method is another way to synthesize graphene.[37,57–59] Graphene can be obtained from the conjugation of large benzene ring molecules by organic reactions (Figure 3E). Graphene nanoribbons with controlled edges with atomic precision has been reported by this kind of bottom-up organic synthesis.[57] The main shortcoming of this method is the tedious organic processing of reactions and lack of the capability to produce large-scale graphene materials for practical use. In another bottom-up method, graphene on a gram-scale can be synthesized from common agents such as ethanol and sodium through solvothermal reactions following by rapid pyrolysis and sonication.[58] Bottom-up synthesis can also obtain highly nitrogen doped graphene by careful design from the beginning of the synthesis.[59]

3. Electronic and Optical Properties of Graphene-Based Nanomaterials

3.1. Electronic Properties

Graphene has unique electronic properties which come from the two-dimensional, single-atom-thick, honeycomb lattices.[3,4,60–62] Graphene has a two-carbon-atom unit cell, resulting in an electronic structure with a point where the two bands touch, so-called Dirac point. More importantly, the energy dispersion shows a linear relation close to the Dirac point, where the electrons resemble massless Dirac fermions but with a speed of 1/300 light speed (*c*/300) (**Figure** 4A). Therefore, the charge carriers in graphene are relativistic particles rather than normal charge carriers in semiconductors or metals. Many peculiar properties can be derived from this unique electronic structure, for example, the high charge carrier mobility, ambipolar field effect, anomalous quantum hall effect, ballistic transport, chirality, Klein paradox, and weak antilocation.[60–62]

In principle, graphene has very a high charge mobility due to its electronic structure. However, over a long period, the mobility of graphene is largely limited to 2000–15000 cm^2 v^{-1} s^{-1} by microscopic ripples, scattering, and defects.[1–4] Recently, it was demonstrated that suspended graphene with a clean surface had a carrier mobility up to 200 000 cm^2 v^{-1} s^{-1}.[7] Suspending graphene can help to reduce the scattering by substrate and thus makes the observation of ultrahigh carrier mobility and ballistic transport possible. The ultrahigh carrier mobility of graphene will enable new arrangements for ultrafast electronics and optoelectronics. For example, wafer-scale 100 GHz transistors have been achieved by using epitaxial graphene on SiC on a large scale.[10] The high frequency performance of

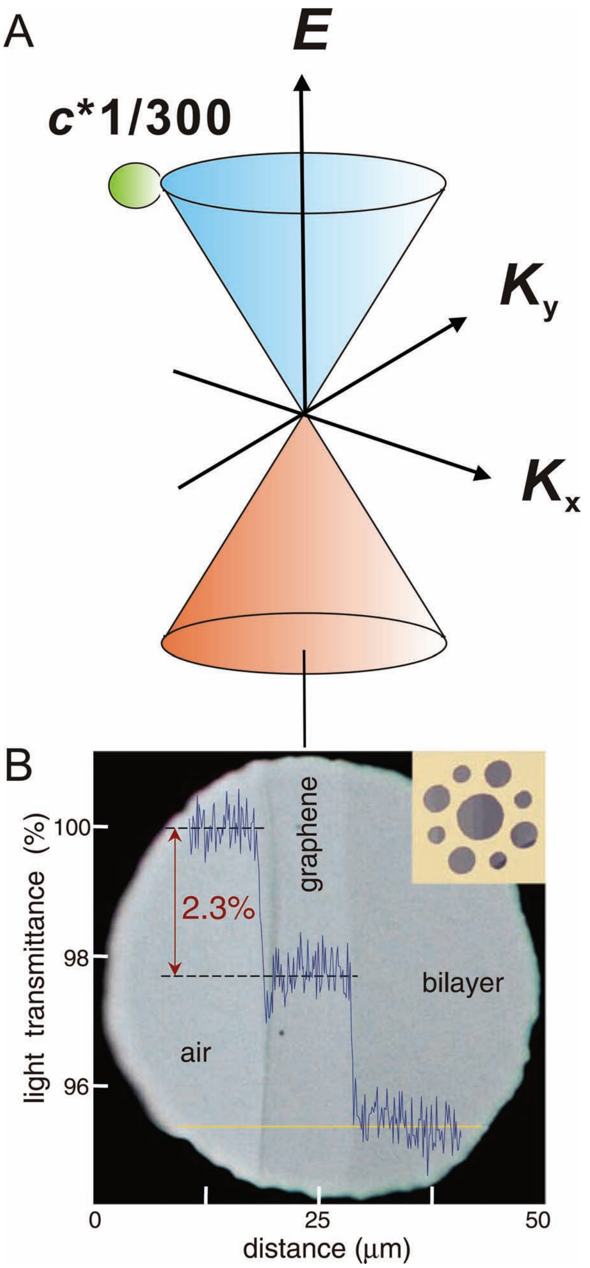

Figure 4. Electronic and optical properties of graphene. A) Linear energy dispersion of massless Dirac fermions in graphene. B) Constant optical absorption in broad range defined by the graphene's atomic structures. Reproduced with permission.[40] Copyright 2008, American Association for the Advancement of Science (B).

graphene transistors can be further improved to 200 GHz by using a self-aligned nanowire gate.[63]

Another electronic property of graphene is its ambipolar field effect transport.[3,4,61] The field effect in graphene which may be used in transistors has initiated the explosion of graphene applications in electronics.[1] Graphene can be well modulated to transport by either holes or electrons by field effect. Unfortunately, graphene is a zero gap semimetal, and the on-off ratios of graphene based field effect transistors are very low (less than 10 usually) comparing with other semiconductors. Therefore, many efforts have been done to open a bandgap in graphene by narrowing two-dimensional graphene to one dimensional nanoribbon, forming nanomesh, and hydrogen patterning.[24,25,64,65] The best performance of a graphene transistor has demonstrated an on-off ratio of over 10^4 in very narrow nanoribbons.[66]

Graphene also shows pseudo spin, chirality, and an anomalous quantum Hall effect, which are the direct result of the electronic structure and energy dispersion of graphene.[3,4,60–62] The chirality of graphene comes from the two carbon atoms per unit cell. The relative nature of Dirac fermions makes the charges in graphene penetrate barriers in a totally different way compared with the carriers in other materials, which is called the Klein paradox. Moreover, the quantum Hall effect can be observed even at room temperature due to the high charge mobility.[67] A weak antilocation is also found in graphene where constructive quantum interference of charge carriers is restored when an outer magnetic field is applied. Since this article focuses on the practical applications of graphene, readers can refer to several excellent reviews on its electronic properties with a more fundamental discussion of chirality, Klein paradox, anomalous quantum hall effect, and weak antilocation.[4,60–62]

3.2. Optical Properties

Similar to the electronic properties, the optical properties are also strongly related with the two-dimensional, single-atom-thick, honeycomb carbon lattice. The optical transparency of graphene is well defined by its fine structure constant, $\alpha = e^2\hbar c$ where e is the electron charge, $\hbar$ is the Dirac constant and c is the speed of light.[40] Graphene has an absorption of $\pi\alpha$ (2.3%) in principle for white light due to its unique electronic structure, and 2–3% light absorption over a very wide range (from ultraviolet to infrared) has been observed in experimental studies (Figure 4B).[40] This absorption value is intriguing considering the single-atom carbon layer in graphene. The reflectance is also very low with about 0.1% for a single layer and 2% for 10 layers.[62] Moreover, monolayer and bilayer graphene had demonstrated a strong, layer-dependent interband optical transition which was well tunable by an electrical gate.[72] Monolayer and bilayer graphene showed distinctly different infrared optical responses. The normalized change of IR reflectivity was featureless in the monolayer while there was a clear peak at around 350 meV in the bilayer.[72] These optical properties are more interesting when coupled with ballistic transport and high charge carrier mobility.[7]

In addition, graphene is also found to have unique luminescent and photoluminescence quenching properties, which are very useful for biological applications.[20–22,68–71] Graphene oxide sheets were found to be photoluminescent in both the visible and infrared regions.[22] Ultrafast photoluminescence was observed in graphene with a broad energy range of photons from 1.7–3.5 eV while excited with a 30-fs ultrashort laser pulse.[73] Graphene has also been demonstrated to have high fluorescence quenching capability for various dyes and quantum dots due to energy or electron transfer.[21,74] The unique quenching capability comes from the energy transfer from the dyes to graphene. Except photoluminescence, electrogenerated chemiluminescence (ECL) was also observed in graphene oxide aqueous suspension with $NaClO_4$ and tri-n-propylamine (TPrA).[75] With the presence of graphene oxide, the ECL is significantly enhanced while very little ECL was observed without graphene oxide.

Another interesting optical aspect of graphene is colloidal graphene QDs. Graphene QDs—irrespective of the synthesis method, whether it be the bottom-up synthesis from small molecules,[69] top-down cutting (chemically or electrochemically) from graphene oxide, reduced graphene, graphite or carbon fiber,[70,71,76]—have inherited the unique properties of inorganic colloidal semiconductor QDs.[30,69–71] Graphene QDs can be blue or green luminescent and act as a good charge carrier separator in bulk heterojunction photovoltaic cells.[69–71] The photoluminescence of graphene QDs can be tuned by atomic doping. For example, nitrogen-doped colloidal graphene QDs with a N/C atomic ratio of 4.3% from the electrochemical method was highly blue photoluminescent, quite different from nondoped ones.[77] Graphene QDs may provide a flexible and general platform for advanced optical and optoelectronic applications.

In comparison with the huge efforts made in exploring the electronics of graphene, the optical and optoelectronic applications initially received less attention. However, rapid advances in these fields are currently being made. Graphene has shown great potential in transparent conductive electrodes, photodetectors and phototransistors, photovoltaics and light-emitting devices, saturable absorbers for ultrafast laser, and biological, photocatalytic and other optical and optoelectronic applications. We will briefly review recent advances in this fast developing field in the next section. Due to the rapidly growing numbers of references, despite trying our best to include all the important works, we acknowledge that some may have been missed in the Feature Article.

4. Optical and Optoelectronic Applications of Graphene-Based Nanomaterials

4.1. Transparent Conductive Electrodes

The transparent conductive electrode (TCE) is one of the most important elements in modern optoelectronic devices, from various kinds of displays to solar cells. ITO is usually used as the TCE in these applications. However, the fragile nature of ITO limits its application in some conditions. ITO is also limited by the scarcity and thus increasing cost of indium. Therefore, there has been a strong quest for replacing ITO with other flexible and cost-effective materials. CNTs and graphene are both intensively pursued for TCE applications.[78] As a relative of CNTs, graphene has the advantages of low cost and easy processing for thin film electrode fabrication.

Large area reduced graphene oxide (RGO) was first explored as TCE because of its availability in large scale and solution processability.[14,15,79,80] For example, the reduced graphene oxide can be found to have a sheet resistance of ≈1000 Ω/square at the transparency of ≈80%.[78–80] RGO can be effective TCE for solar cells and light emitting diodes.[41,42] However, the conductivity of RGO is still two orders of magnitude lower than ITO due to large scale residue defects in RGO even after chemical or thermal reduction. Reduced graphene oxide sheets with larger size up to several hundreds of micrometers have a better conductivity than normal, smaller graphene oxide with a size distribution from several hundreds of nanometers to several micrometers.[80] This method applied slightly oxidized graphite oxide to prepare single layer graphene oxide. The lower content of oxidization reduced the oxygenous defects, and the size of graphene oxide can be controlled from ≈100–300 to ≈7000 μm^2. Large sheet-based conductive thin film obtained a conductivity of 840 Ω/square at 78% transmittance. Another way is to use a graphene composite with a conductive polymer such as poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS).[15] Solution processable, large size reduced graphene was first mixed with conductive polymer PEDOT:PSS to form a conductive thin film on polyethylene terephthalate (PET). The obtained GCE with a lowest sheet resistance of 80 Ω/square and only 5% increase after 1000 bending and stretching cycles with a strain of ≈2.4%. Exfoliated graphene from graphite without oxidation is also explored for TCE applications. For example, graphene from exfoliated intercalated graphite compounds can be used to make a single layer graphene sheet that is stable in organic solvents. The highly conductive graphene was obtained by Langmuir–Blodgett assembly and the layer-by-layer technique.[56]

CVD-grown graphene has better quality than RGO and can be fabricated in a large area, and is more promising as a TCE than RGO. Recently, a roll-to-roll method of CVD-grown graphene was developed to fabricate large-area, flexible, and highly conductive TCE with a size of up to 30 inches (**Figure 5**A).[13] After nitrogen doping by HNO_3, the sheet resistance can be as low as 20 Ω/square at 90% transmittance with only 4 layers of graphene. Large scale pattern growth of graphene was well developed for stretchable transparent electrodes (Figure 5B).[12] Patterned thin nickel layers on SiO_2/Si substrate was used to grow graphene using CVD method. The graphene had mobility over than 3700 cm^2 v^{-1} s^{-1}, and the thin film demonstrated low resistance of 280 Ω/square at 80% transparency. The graphene films were also proved to be excellent transparent electrodes in flexible, stretchable, foldable electronics.[12] Some further improvements to get higher quality graphene were also developed to enlarge the grain size of CVD-grown graphene.[81] To date, CVD is one of the most promising methods to produce graphene meeting the three requirements needed for TCE applications, i.e., large scale production, high quality, and relatively easy processing.

4.2. Photodetectors and Phototransistors

The photodetector is a crucial element in modern optical communications. Graphene has a high charge carrier mobility and short lifetime of carriers, and therefore is a potential candidate for high frequency, ultrafast photodetectors. Indeed, a 40 GHz photodetector has been reported based on mechanically exfoliated single- and few-layer graphene with a potential intrinsic bandwidth over 500 GHz (**Figure 6**A).[43] The generation and transport of photocarriers are very different from conventional semiconductors. The ultrafast photodetectors did not need bias, and were driven by the internal electric field between metal electrodes and graphene. The responsivity of the photodetector was ≈0.5 mA/W, and can be improved to 6.1 mA/W by using intercalating heterogeneous electrodes.[82]

Although pure graphene-based photodetectors have high performance in high frequency devices, their photoresponsivity is quite low due to the fast carrier dynamics and low light absorption by single layer graphene. Therefore, several methods are developed to improve the photoresponsivity. For example, semiconductor quantum dots and nanorods are introduced to graphene to enhance the light absorbance.[83–89] CdS QDs, PbS QDs, and ZnO nanorods were in situ grown on the graphene surfaces to enhance the visible and UV absorption. The responsivity can reach 22.7 A/W for ZnO nanorods/graphene heterostructures with high selectivity, and 10^7 A/W in PbS QD/graphene hybrids.[87] Other methods have also been developed by tuning defects in graphene by using reduced graphene oxide with controlled reduction.[28,90–92] Recently, solution-processable, bandgap tunable, large scale, few-layer reduced graphene oxide (FRGO) has been developed for both UV and visible sensitive photodetectors with high photoresponsivity of 0.8 A/W for 365 nm UV light (Figure 6B).[28] Large scale, few-layer graphene oxide film was fabricated by spinning coating and the following low-temperature, well controlled thermal reduction. The bandgap of few-layer reduced graphene oxide can be tuned with oxygenous groups from 0.5–2.2 eV, and the photoresponses changed with reduction states. The oxygenous defects were found to have strong influences on the field effect transport of photocarriers.[28] The enhanced photoresponsivity with a loss of high frequency responses results from the

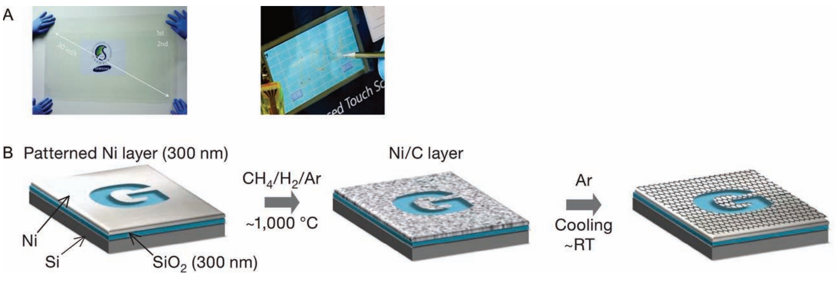

Figure 5. Graphene-based transparent electrodes for optoelectronic applications. A) 30-inch transparent electrodes for touch screens. B) Large scale patterned growth of graphene on nickel. Reproduced with permission.[13,12] Copyright 2010, Nature Publishing Group (A); copyright 2009, Nature Publishing Group (B).

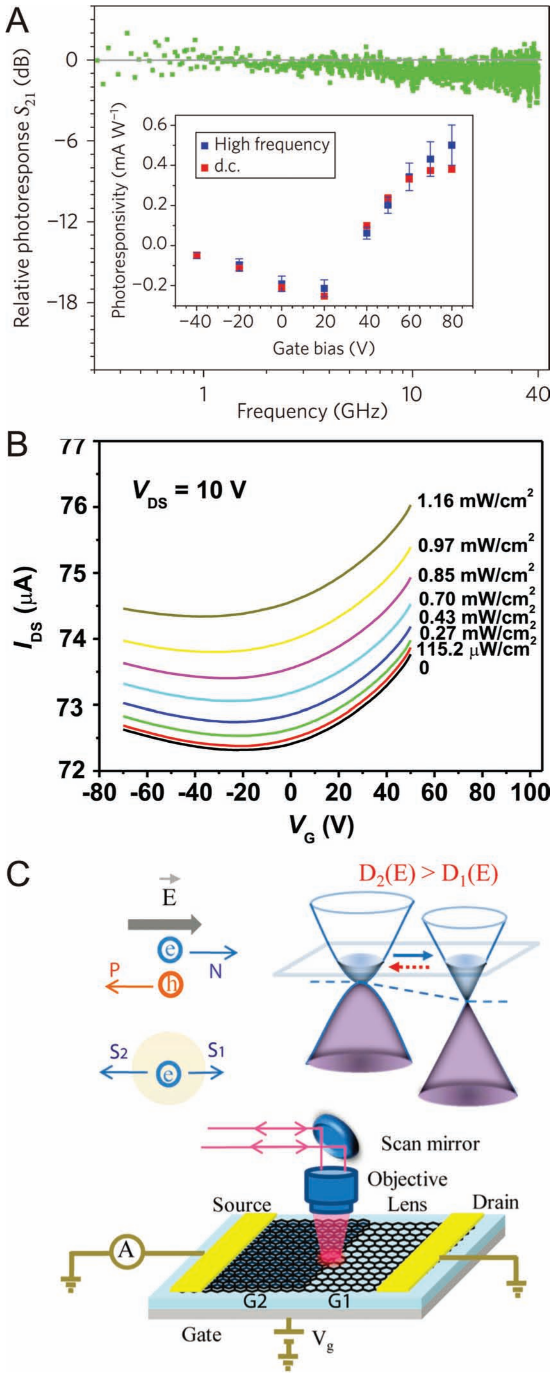

Figure 6. Phototransistors and photodetectors based on graphene. A) 40 GHz ultrafast photodetector based on mechanically exfoliated graphene. B) Phototransistor based on thermally reduced few-layer reduced graphene oxide (FRGO). C) Monitoring photo-thermoelectric effect in the junction of single-bilayer in phototransistors. Reproduced with permission.[43,28,47] Copyright 2009, Nature Publishing Group (A); copyright 2010 American Chemical Society (C).

changes in recombination dynamics of excited charge carriers by defects.[90–92] In another example, graphene nanoribbon obtained from carbon nanotubes splitting demonstrated two orders of magnitude higher photoresponse and efficiency than normal, large size reduced graphene oxide sheet in infrared photodetectors.[90] The responsivity of graphene nanoribbon photodetectors reached ≈1 A/W. The performance of graphene nanoribbon photodetectors can be further improved by using narrower nanoribbons.

Phototransistors are also extensively studied to explore the optoelectronic transport in graphene.[28,43,45,47,48,93–96] The contact edge induced internal field has been demonstrated to have a significant influence on the optoelectronic behavior, evidenced by photoimaging of the photocurrent distribution in the device.[96] Ballistic photocurrent generation and manipulation in graphene were also explored.[94] Furthermore, photothermal effect and hot carriers were found to have strong influence on the optoelectronic transport.[45,47,48] In a demonstration, the polarity and amplitude of the photocurrent in graphene single-bilayer interface junction was measured with a tunable Fermi level in phototransistors (Figure 6C).[47] The photocurrent increased 10-fold at cryogenic temperature when compared with room temperature. The photothermal effect induced the photocurrent generation in the single-bilayer graphene junctions, and might improve graphene-based optoelectronics such as photovoltaics and photothermocouples. In most of these studies, mechanically exfoliated graphene and thermal deposition graphene from SiC were used. Recently, few-layer reduced graphene oxide was also developed for phototransistors with high photoresponsivity (Figure 6B). The oxygenous groups were found to have a significant influence on the transfer characteristics of the phototransistors based on few-layer reduced graphene oxide as a result of their influences on the photocarrier transport.[28]

4.3. Photovoltaic and Light Emitting Devices

The increasing demand for clean energy makes photovoltaic conversion an intensively studied field. Graphene can play several different roles in photovoltaic devices, including the above-mentioned transparent electrodes, active materials in solar cells (charge separator and transporter in bulk junction polymer solar cells and dye-sensitized solar cells (DSSCs)), and counter electrodes replacing platinum in DSSCs.[83,84,97–105] In one example, a transparent, conductive and ultrathin graphene film was applied as top window electrodes for solid-state DSSCs (**Figure** 7A).[97] The graphene films had a conductivity of 550 S/cm and a transparency of over 70% in the range of 1000–3000 nm, with high chemical and thermal stabilities. The power conversion efficiency is 0.84% for the DSSCs. In another case, graphene composite with conductive polymer was found to be an excellent counter electrode to replace platinum counter electrodes for DSSCs.[105] Graphene derivative such as graphene oxide and quantum dots have been used as active acceptor materials in organic solar cells.[99,100] Graphene oxide was first functionalized with phenyl isocyanate to make it soluble in organic solvents and more suitable to be used as an electron-acceptor material in bulk heterojunction organic solar cells. The highest power conversion efficiency reached 1.4% for poly(3-octylthiophene) (P3OT)-based bulk heterojunction solar cells. Electrochemically derived graphene quantum dots were recently used in bulk heterojunction solar cells with

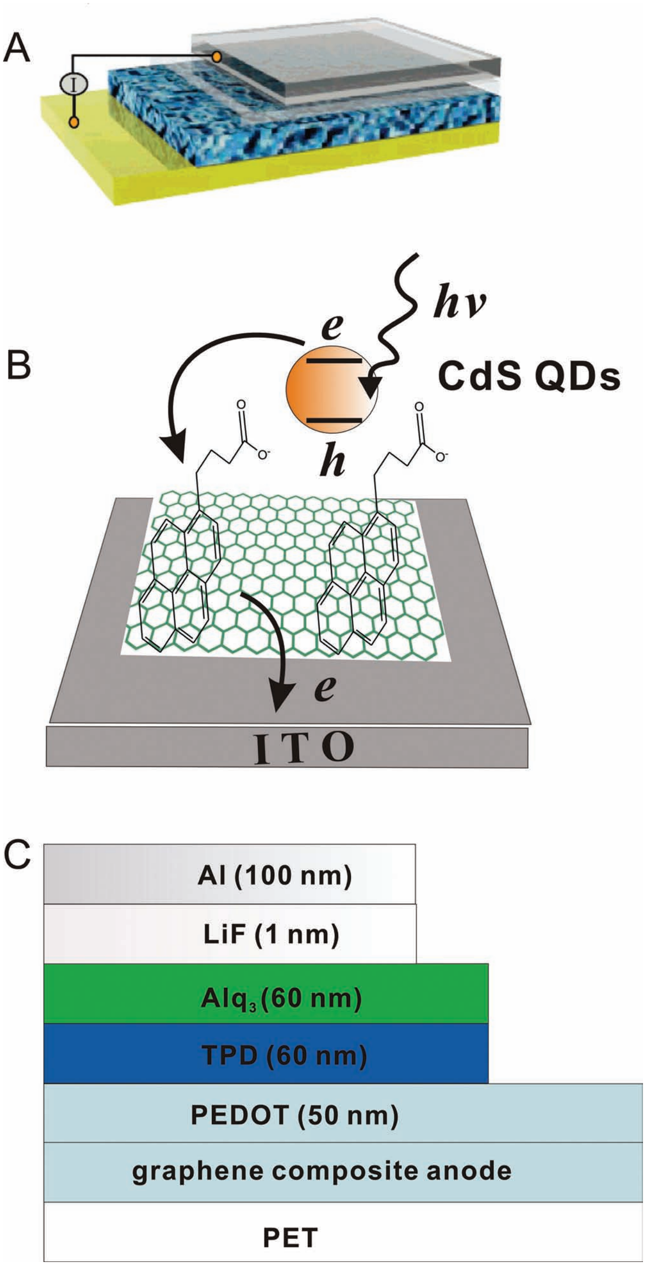

Figure 7. Photovoltaic and light-emitting devices based on graphene. A) Graphene as top window electrodes for photovoltaic cells. B) QDs sensitized graphene for photoelectrochemical cells. C) Transparent, flexible graphene composite electrodes for organic light emitting diodes. Reproduced or adapted with permission.[97,83,15] Copyright 2008, American Chemical Society (A); copyright 2010, Elsevier (B).

poly(3-hexylthiophene) (P3HT) as the donor and graphene quantum dots as the acceptor. The power conversion efficiency for a primitive device was 1.28%.[70]

Graphene was also applied as conductive scaffold and charge transporter and collectors in semiconductor quantum dots based photoelectrochemical cells, and DSSCs (Figure 7B).[83,84,103,104] In an example, CdS QDs are in situ grown on non-covalently modified, chemically reduced graphene to form CdS QD/graphene heterostructures and used in photoelectrochemical cells.[83] The photocurrent generation and internal photoelectron conversion efficiency (IPCE) of heterostructures was over 3 times higher than pure QDs with higher on-off ratio and faster photocurrent dynamics, and was 2.4-fold higher than that in the CNT/QD counterpart. Layered QD/graphene composites were also applied in photovoltaic devices with enhanced IPCE compared with the CNT/QD composite.[84] The graphene scaffold was reported to have a five-times larger power conversion efficiency in TiO_2 based DSSC.[104]

Similarly, light emitting devices such as light-emitting diodes are some of the most important devices frequently used in display technology.[13,15,106] The lower-energy-consuming advantage of light-emitting diodes (LEDs) is more intriguing in the age of energy shortage and increasing concern about environmental pollution. A roll-to-roll technique was developed to fabricate 30-inch few-layer graphene transparent electrodes for touch screens.[13] Graphene and graphene composite transparent electrodes are also used for organic LED (OLED) applications. A novel, low-temperature, solution-processed, flexible, transparent graphene composite electrode (GCE) was applied as a TCE for OLEDs with a comparable efficiency to ITO electrodes (Figure 7C).[15] Efficient OLED devices can also be achieved by using transparent electrodes based on graphene oxide.[106] However, this method requires high temperature (1100 °C) annealing to reduce the graphene oxide and to obtain high conductivity of transparent electrodes.

4.4. Saturable Absorber for Ultrafast Lasers

The ultrafast laser is one of the most important technologies in optoelectronic devices.[107,108] Saturable absorbers are extensively used in mode-locked ultrafast lasers, whereby saturable absorbers transform continuous light to ultrafast short optical pulses. Graphene has linear electronic dispersion with a zero bandgap, ultrafast carrier dynamics, and broad band absorption, which makes it an excellent nonlinear optical material for use as a saturable absorber. Both pure graphene and graphene composites have been investigated as saturable absorbers in ultrafast lasers.[107,108] In one demonstration, atomic graphene layers, single-layer graphene by chemical vapor deposition, or few-layer random stacks of single-layer graphene, had a saturable absorption at a much lower threshold than CNTs. Therefore, such atomic graphene layers were suitable to work as saturable absorber to generate ultrashort soliton pulse in mode-locked fiber lasers (**Figure** 8A).[107] The ultrashort pulse was as short as 756 fs with a bandwidth of 5 nm, and the modulation depth was well tuned in a range of 6.2% to 66.5% by controlling the graphene thickness. Similarly, graphene composites with polymer such as polyvinyl alcohol (PVA) are also a good alternative of pure few-layer graphene for saturable absorbers (Figure 8B). The graphene used in the composite was obtained from exfoliating graphite by inorganic salt and was highly solution processable. More importantly, this graphene/polymer composite allowed the wet-chemistry processing and easy integration of the composite with many photonic systems. 50-µm-thick graphene/PVA composites can work as an excellent absorbers for ultrafast mode-locked lasers with 5.24 nm spectral bandwidth and 460 fs duration.[108]

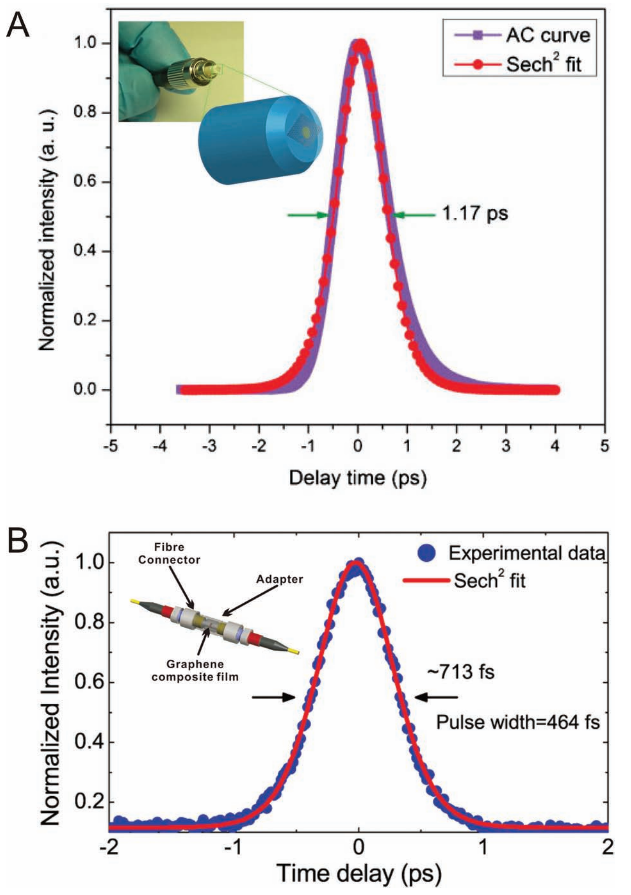

Figure 8. Ultrafast lasers based on graphene saturable absorbers. A) Single and few-layer graphene as saturable absorbers. B) Graphene/PVA composites as saturable absorbers. Reproduced with permission.[107,108] Copyright 2010, American Chemical Society (B).

4.5. Biological Applications

The unique structural, electronic and optical properties of graphene make it promising in many biological applications, such as biosensors, drug delivery, and bioimaging.[19–23,109–121] Graphene itself has only weak fluorescence, but it is an excellent electronic and energy acceptor, suitable as a general fluorescence quencher for many kinds of materials from dyes to quantum dots.[19,21,109,117] Many fluorescence resonance energy transfer (FRET) biosensors can be designed based on this strategy, using either graphene or graphene oxide.[19,21,115–117] It has been demonstrated that by combining the unique FRET properties of graphene with the selectivity of aptamers, a highly sensitive aptasensor for thrombin can be achieved (**Figure** 9A).[21] The aptamer was attached to graphene by self assembly between graphene and DNA base pairs. After self assembly, the fluorescence of dyes attached to aptamers was quenched due to FRET. Aptamers were transformed to quadruplexes upon binding to targets, resulting in the recovery of fluorescence. Therefore, the turn-on biosensors can be achieved for proteins, inorganic ions, and even cells with the various aptamers. The sensitivity of graphene FRET sensors is two magnitudes of order higher than the CNT-based sensors with a detection limit of 31 pM for thrombin.[21] Similar fluorescent sensors were developed to detect DNA and heavy metal ions.[115–117] For example, graphene nanoprobes for Hg^{2+} and Ag^+ were developed by forming graphene-based hybrids with Hg^{2+} sensitive aptamers or Ag^+-specific cytosine-rich oligonucleotides. The dye-labeled aptamers or oligonucleotides were attached to graphene oxide surfaces by self assembly, followed by the quenching of fluorescence of dyes. The fluorescence of dyes recovered in presence of Hg^{2+} and Ag^+. The detection limit was 30 nM for Hg^{2+} and 5 nM for Ag^+.[115,116] This strategy was also used to detect oligonucleotides, where hybridized DNA duplex had weaker binding forces compared with single stranded DNA. Note that duplex DNA can also react with graphene but with a lower affinity compared with single stranded DNA.[113]

Other promising fields for graphene-based nanomaterials are bioimaging, drug delivery, and photothermal therapy.[22,23,114] Nanographene oxide is visible and infrared luminescent and is an excellent bioimaging agent in cells.[22] Nanographene oxide is also easily modified by functional groups for drug loading and cell uptake.[22,23] Functionalized nanographene oxide has been used as a loading carrier of anticancer drugs and as photothermal agent to kill cancer cells.[22,23,114] For example, nanographene oxide or graphene with a lateral size less than 50 nm was modified by polyethylene glycol (PEG) to form PEGylated nanographene oxide and nanographene sheets, which makes them soluble in water for loading drugs or photothermal therapy.[23] PEGylated nanographene oxide can load aromatic, water-insoluble anticancer drugs SN38 via noncovalent van der Waals

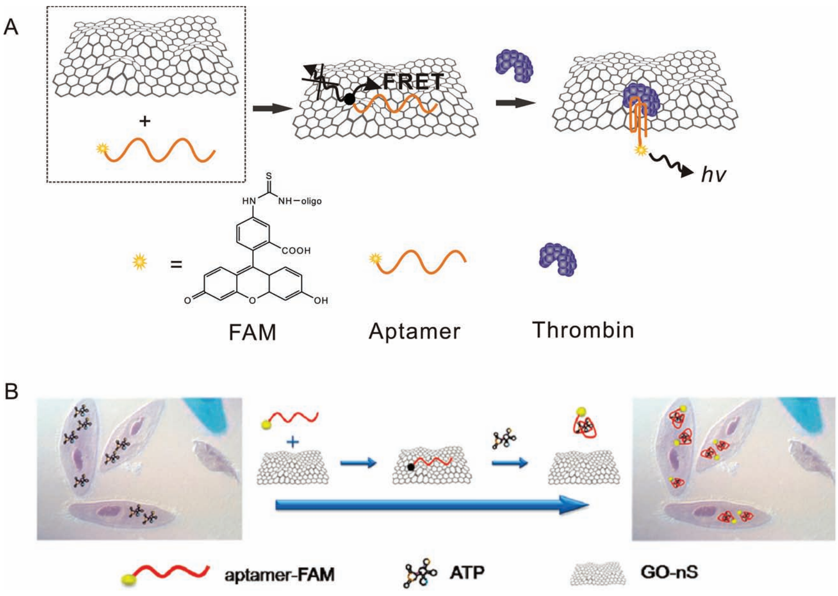

Figure 9. Biological applications of graphene-based nanomaterials. A) FRET aptamer sensors based on graphene. B) In situ molecular monitoring based on graphene oxide/aptamer nanoprobes. Reproduced with permission.[21,112] Copyright 2010, American Chemical Society.

interaction without damaging the potency of SN38. PEGylated nanographene sheets have shown ultrahigh tumor uptake efficiency in mice, and efficient photothermal therapy by strong near-infrared absorption of nanographene sheets.[114] Efficient tumor ablation under low-power, near-infrared laser irradiation was easily achieved after intravenous administration. No obvious side effect of PEGylated nanographene sheets in mice was observed in histology, blood chemistry, and complete blood panel analysis, although greater effort is needed to fully understand the in vivo behavior of nanographene sheets.

Graphene or its derivatives can also be a potential platform for monitoring cell behavior. For example, graphene oxide/aptamer nanocomplex was used to monitor the molecular behavior in cells (Figure 9B).[112] By forming adenosine triphosphate (ATP) aptamer/graphene oxide nanocomplex, the ATP activity in the cells can be monitored with the fluorescence recovery in the nanocomplex after the uptake of nanocomplex to cells. The uptake of nanocomplexes by mice epithelial cells was found to be very efficient after co-incubation of the ATP aptamer/graphene oxide nanocomplex with the cells. The ATP aptamers were released when met ATP in living cells, and the fluorescence of dyes labeled to aptamers was recovered. Very recently, the behavior of cells on transparent, few-layer reduced graphene oxide was demonstrated to be well controlled by tuning the oxygenous functional groups in the reduced graphene oxide.[118] Oxygen groups have a profound influence on the cell behavior on graphene oxide surfaces, with the best cell attachment and proliferation on moderately reduced graphene oxide, and the worst on the highly reduced graphene oxide. The weak forces, such as electrostatic, hydrogen bonding, and hydrophobic interactions, have strong influence on protein absorption at graphene oxide surfaces and the subsequent cell behavior at graphene oxide surfaces.[118] Graphene also showed great potential in neural cell studies due to its compatibility with cells, high conductivity, and transparency.[119,120]

4.6. Photocatalytic Applications

In addition to the applications mentioned above, there are emerging applications of graphene in the field of photocatalysis.[122–134] Graphene-based composites with semiconductors are found to have much better photocatalytic properties than pure semiconductors.[124–126] Graphene composite photocatalysts are increasingly used both in photodegradation of pollution and in solar water splitting for hydrogen generation. The degradation of dyes and the photocatalytic hydrogen evolution from water were found improved significantly by introducing graphene to semiconductors, where graphene works as a charge separator and cocatalyst.[124–126,128–134] Graphene based photocatalysis is an emerging new application of graphene, although the real advantage of graphene over other carbon nanomaterials is still not clear.

There are several methods to produce graphene-based photocatalysts, including in situ growth, solution mixing, and solvothermal reactions.[122–126,128–134] In situ growth starts from ion salts as precursors, e.g., Cd^{2+},[130] Zn^{2+},[126] followed by in situ chemical reactions of ions on graphene surfaces. Metal oxide, metal sulfide, and more complex semiconductor like $BiVO_4$ can be grown by this in situ growth method.[124–126,130–134] Solution mixing is another commonly applied method to prepare graphene based photocatalysts.[122] Hydrothermal and solvothermal methods can grow many kinds of inorganic semiconductors on graphene, and induce strong electronic connections between graphene and semiconductors.[122,124] Solvothermal process enhances the electronic transfer between two parts of graphene-based photocatalytic hybrids.

One of the most important applications of photocatalysts is pollutant photodegradation.[124–126] TiO_2 is the mostly used semiconductor in photocatalytic applications due to its stability and large bandgap. Therefore, TiO_2-graphene based composites are developed to construct highly efficient photocatalysts for dye degradation.[124] A highly efficient P25-graphene composite photocatalyst was fabricated by hydrothermal reaction of P25 and graphene oxide, and had a higher performance for methyl blue degradation than pure P25 or P25/CNT composite photocatalysts (**Figure 10**A).[124] The improved performance was ascribed to the higher efficiency in photoexcited electron transfer between dyes and graphene. Other semiconductors such as ZnO were also used to form composite photocatalysts with graphene.[125] ZnO nanoparticles were grown on graphene oxide followed by

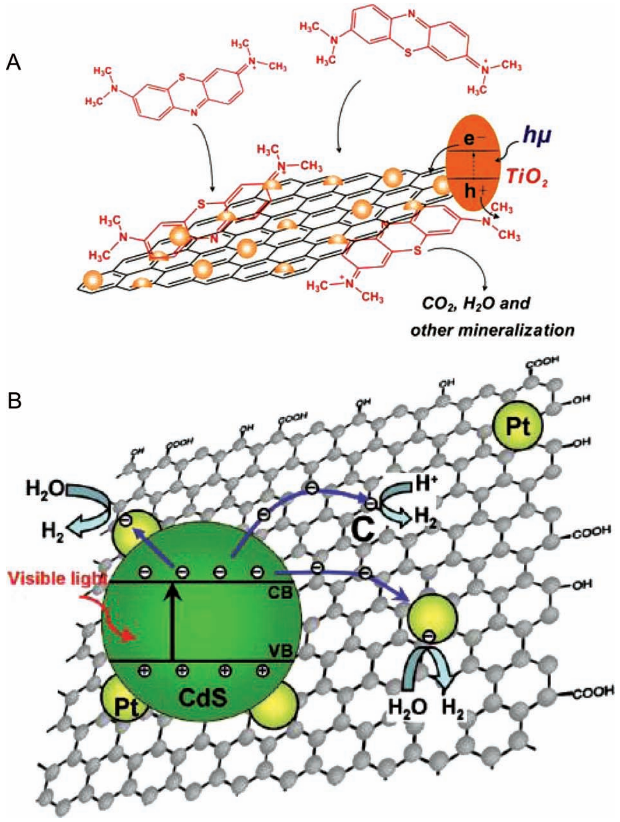

Figure 10. Photocatalytic applications of graphene-based photocatalysts. A) P25/graphene hybrids for photocatalytic degradation of pollutant dyes. B) CdS cluster decorated graphene for photocatalytic generation of hydrogen from water splitting. Reproduced with permission.[124,129] Copyright 2010, American Chemical Society (A); copyright 2011 American Chemical Society (B).

chemical reduction of graphene oxide to graphene. A four-times higher photocatalytic efficiency was observed than pure ZnO, and was attributed to the highly efficient transfer of electrons from ZnO to graphene and thus the inhibition of recombination between excited electron-hole pairs.

Another application of graphene-based photocatalysts is photocatalytic hydrogen generation from water splitting.[127–134] Although most photocatalysts are graphene/semiconductor hybrids, graphene oxide itself was found to have a good performance in the generation of hydrogen by splitting water and a water/methanol mixture.[127] In addition to the application of TiO_2/graphene in the photodegradation of pollutants, it is also found to have a high performance in solar water splitting to generate hydrogen.[128,130] Complex oxide materials such as $BiVO_4$ can also be used as high performance photocatalysts by forming graphene based hybrids.[134] For example, $BiVO_4$ was grown on a reduced graphene oxide surface using a one-step method and was highly efficient in water photoelectrochemical splitting.[134] The efficiency of visible light photoelectrochemical water splitting was improved by a factor of 10 by incorporating graphene in the $BiVO_4$ photoelectrodes. Other than oxide, metal sulfides such as CdS are also common semiconductors in photocatalytic hydrogen generation.[129,130] In one demonstration, CdS nanoparticles were grown on the graphene surfaces via an in situ growth hydrothermal method followed by deposition of a Pt nanoparticle cocatalyst (Figure 10B).[129] The hybrid photocatalysts had a 4.87-times higher H_2 production rate than pure CdS nanoparticles with Pt cocatalysts under visible light. The quantum efficiency of 22.5% was obtained at 420 nm. Note that CdS nanoparticles were also found to have comparable photocatalytic efficiency in hydrogen generation when forming hybrids with graphene or Cu cluster-graphene as cocatalysts without using noble metal cocatalysts like Pt.[130,131] Similar hydrogen generation performance was observed in the $Zn_{0.8}Cd_{0.2}S$/reduced graphene oxide hybrids with 450% improvement compared with pure $Zn_{0.8}Cd_{0.2}S$, and the energy conversion efficiency reached 0.36%.[133]

In addition to the above-mentioned examples of optical and optoelectronic applications of graphene, many other interesting and just emerging applications can be found in more detail in several excellent reviews.[41,42] Due to the rapidly growing number of references in this field, we cannot possibly cover all the important progress within this Feature Article. In the following section we will discuss some perspectives and future challenges that need to be addressed in order to realize large scale and practical optical and optoelectronic applications of graphene.

5. Conclusions and Perspectives

The interest in optical and optoelectronic aspects of graphene-based nanomaterials has evolved along with interest in their electronic properties. It is normal that the extraordinary electronic properties of graphene generate great interest in its optical and optoelectronic properties. The combination of the unique electronic and optical properties of graphene has encouraged numerous explorations of graphene-based nanomaterials in transparent conductive electrodes, photodetectors and phototransistors, photovoltaics and light emitting devices, saturable absorbers for ultrafast lasers, and biological and photocatalytic applications. Graphene-based nanomaterials have demonstrated their excellent performance in these fields and much progress has been made in the past few years. We should note that the excellent performance of graphene in optics and optoelectronics has lead to the increasing exploration of other two-dimensional atomic crystals such as MoS_2.[135–139] We believe there are still many two-dimensional atomic crystal mines that remain to be discovered.

The most important optical and optoelectronic progress in graphene-based nanomaterials has been made for graphene TCEs. The high transparency and flexibility together with high conductivity of graphene make it a good flexible element where conventional electrodes, e.g., ITO, cannot work because of brittleness. Graphene thus enables many new device arrangements, including flexible, wearable electronics and optoelectronics. The most exciting development of graphene in TCE practical applications is large-area CVD graphene TCEs for touch screens.[13] However, there are still many fundamental and technical challenges for the optical and optoelectronic applications of graphene before they becomes industrially viable.

Firstly, the mass production of high quality graphene with controlled functionalization and properties still remains challenging. High quality graphene on a large scale is the fundamental issue limiting the applications of graphene, although some advances have been made. Both reduced graphene oxide and CVD graphene could be more promising than other methods in mass production. CVD has a better quality in terms of conductivity and carrier mobility while reduced graphene oxide can be easily functionalized because of the residual oxygenous groups. However, there is still a lot of work to be done to improve the quality of CVD graphene, and to conduct the functionalization in a more controllable manner.

Secondly, it is still a big challenge for large scale, low temperature production of high quality TCE from graphene. CVD graphene has an excellent performance in terms of conductivity and transparency for TCE applications (20 Ω/square at 90% transparency). However, the CVD method needs high temperature deposition growth by carbon sources on metal (≈1000 °C) and tedious transfer process afterwards. Thereby it is very challenging to develop a method to produce TCE under low temperature processing (less than 200 °C) without the need of tedious transfer. It is also important to produce TCE as large as desired with convenient techniques like spin coating. Therefore, high quality, solution-processable graphene may be a promising alternative for CVD graphene in graphene TCE with the commercial ITO quality (8–100 Ω/square conductivity, over 85% transparency and high environmental stability).

Thirdly, graphene has shown advantages in high frequency optoelectronic devices such as ultrafast photodetectors. However, the responsivity of ultrafast photodetectors based on graphene is low due to the weak photon absorption and fast charge carrier kinetics. Very recently, the coupling of semiconductors with graphene has been successful in improving the responsivity of graphene-based photodetectors, although this is accompanied by a reduced high frequency performance. Therefore, it is highly expected to develop high frequency photodetector with high photoresponsivity.

Finally, biological and environmental toxicity of graphene-based nanomaterials are still poorly understood. Although graphene has great potential in bioimaging in cells or drug delivery, graphene's toxicity to cells, organisms and the environment has not yet been completely assessed. They are biocompatible in some cases, while very toxic in others. Therefore, the biocompatibility of graphene needs to be better understood and to be controlled in a more rational manner.

We expect to see fast development in these directions in future decades. As one of the most important discoveries in recent years in condensed physics and materials science, graphene, the thinnest material in universe, will improve our understanding of the fundamental questions in physics. At the same time, graphene, along with other two-dimensional atomic crystals will impact human society through brand new technologies in near future.

Acknowledgements

H.X.C. and H.K.W. acknowledge the support of World Premier International Research Center Initiative (WPI) and WPI-AIMR fusion research funding from MEXT, Japan. H.K.W. acknowledges the support from Hong Kong UGC (#RPC11SC19).

Received: August 28, 2012

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
[2] Y. B. Zhang, Y. W. Tan, H. L. Stormer, P. Kim, *Nature* **2005**, *438*, 201.
[3] A. K. Geim, *Science* **2009**, *324*, 1530.
[4] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
[5] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, A. Govindaraj, *Angew. Chem. Int. Ed.* **2009**, *48*, 7752.
[6] Y. W. Zhu, S. Murali, W. W. Cai, X. S. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* **2010**, *22*, 3906.
[7] X. Du, I. Skachko, A. Barker, E. Y. Andrei, *Nat. Nanotechnol.* **2008**, *3*, 491.
[8] A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, *Nano Lett.* **2008**, *8*, 902.
[9] R. Grantab, V. B. Shenoy, R. S. Ruoff, *Science* **2010**, *330*, 946.
[10] Y. M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H. Y. Chiu, A. Grill, P. Avouris, *Science* **2010**, *327*, 662.
[11] J. S. Bunch, A. M. van der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead, P. L. McEuen, *Science* **2007**, *315*, 490.
[12] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706.
[13] S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, *5*, 574.
[14] G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **2008**, *3*, 270.
[15] H. X. Chang, G. F. Wang, A. Yang, X. M. Tao, X. Q. Liu, Y. D. Shen, Z. J. Zheng, *Adv. Funct. Mater.* **2010**, *20*, 2893.
[16] C. L. Kane, E. J. Mele, *Phys. Rev. Lett.* **2005**, *95*, 226801.
[17] N. Tombros, C. Jozsa, M. Popinciuc, H. T. Jonkman, B. J. van Wees, *Nature* **2007**, *448*, 571.
[18] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 652.
[19] C. H. Lu, H. H. Yang, C. L. Zhu, X. Chen, G. N. Chen, *Angew. Chem. Int. Ed.* **2009**, *48*, 4785.
[20] C. S. Shan, H. F. Yang, J. F. Song, D. X. Han, A. Ivaska, L. Niu, *Anal. Chem.* **2009**, *81*, 2378.
[21] H. X. Chang, L. H. Tang, Y. Wang, J. H. Jiang, J. H. Li, *Anal. Chem.* **2010**, *82*, 2341.
[22] X. M. Sun, Z. Liu, K. Welsher, J. T. Robinson, A. Goodwin, S. Zaric, H. J. Dai, *Nano Res.* **2008**, *1*, 203.
[23] Z. Liu, J. T. Robinson, X. M. Sun, H. J. Dai, *J. Am. Chem. Soc.* **2008**, *130*, 10876.
[24] X. L. Li, X. R. Wang, L. Zhang, S. W. Lee, H. J. Dai, *Science* **2008**, *319*, 1229.
[25] D. V. Kosynkin , A. L. Higginbotham, A. Sinitskii, J. R. Lomeda, A. Dimiev, B. K. Price, J. M. Tour, *Nature* **2009**, *458*, 872.
[26] Y. B. Zhang, T. T. Tang, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen, F. Wang, *Nature* **2009**, *459*, 820.
[27] S. Y. Zhou, G. H. Gweon, A. V. Fedorov, P. N. First, W. A. De Heer, D. H. Lee, F. Guinea, A. H. C. Neto, A. Lanzara, *Nat. Mater.* **2007**, *6*, 770.
[28] H. X. Chang, Z. H. Sun, Q. H. Yuan, F. Ding, X. M. Tao, F. Yan, Z. J. Zheng, *Adv. Mater.* **2010**, *22*, 4872.
[29] H. X. Chang, J. S. Cheng, X. Q. Liu, J. F. Gao, M. J. Li, J. H. Li, X. M. Tao, F. Ding, Z. J. Zheng, *Chem. Eur. J.* **2011**, *17*, 8896.
[30] L. S. Li, X. Yan, *J. Phys. Chem. Lett.* **2010**, *1*, 2572.
[31] I. P. Hamilton, B. S. Li, X. Yan, L. S. Li, *Nano Lett.* **2011**, *11*, 1524.
[32] C. Berger, Z. M. Song, X. B. Li, X. S. Wu, N. Brown, C. Naud, D. Mayou, T. B. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, W. A. de Heer, *Science* **2006**, *312*, 1191.
[33] X. S. Li, W. W. Cai, J. H. An, S. Kim, J. Nah, D. X. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science* **2009**, *324*, 1312.
[34] A. Reina, X. T. Jia, J. Ho, D. Nezich, H. B. Son, V. Bulovic, M. S. Dresselhaus, J. Kong, *Nano Lett.* **2009**, *9*, 30.
[35] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* **2007**, *448*, 457.
[36] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228.
[37] S. Park, R. S. Ruoff, *Nat. Nanotechnol.* **2009**, *4*, 217.
[38] M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, *110*, 132.
[39] O. C. Compton, S. T. Nguyen, *Small* **2010**, *6*, 711.
[40] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, *Science* **2008**, *320*, 1308.
[41] F. Bonaccorso, Z. Sun, T. Hasan, A. C. Ferrari, *Nat. Photonics* **2010**, *4*, 611.
[42] K. P. Loh, Q. L. Bao, G. Eda, M. Chhowalla, *Nat. Chem.* **2010**, *2*, 1015.
[43] F. N. Xia, T. Mueller, Y. M. Lin, A. Valdes-Garcia, P. Avouris, *Nat. Nanotechnol.* **2009**, *4*, 839.
[44] A. Vakil, N. Engheta, *Science* **2011**, *332*, 1291.
[45] N. M. Gabor, J. C. W. Song, Q. Ma, N. L. Nair, T. Taychatanapat, K. Watanabe, T. Taniguchi, L. S. Levitov, P. Jarillo-Herrero, *Science* **2011**, *334*, 648.
[46] Q. L. Bao, H. Zhang, B. Wang, Z. H. Ni, C. H. Y. X. Lim, Y. Wang, D. Y. Tang, K. P. Loh, *Nat. Photonics* **2011**, *5*, 411.
[47] X. D. Xu, N. M. Gabor, J. S. Alden, A. M. van der Zande, P. L. McEuen, *Nano Lett.* **2010**, *10*, 562.
[48] J. C. W. Song, M. S. Rudner, C. M. Marcus, L. S. Levitov, *Nano Lett.* **2011**, *11*, 4688.
[49] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10451.
[50] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Röhrl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, T. Seyller, *Nat. Mater.* **2009**, *8*, 203.

[51] Z. Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu, J. M. Tour, *Nature* **2010**, *468*, 549.
[52] C. Y. Su, A. Y. Lu, C. Y. Wu, Y. T. Li, K. K. Liu, W. J. Zhang, S. Y. Lin, Z. Y. Juang, Y. L. Zhong, F. R. Chen, L. J. Li, *Nano Lett.* **2011**, *11*, 3612.
[53] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007**, *45*, 1558.
[54] M. Segal, *Nat. Nanotechnol.* **2009**, *4*, 611.
[55] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Y. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, *Nat. Nanotechnol.* **2008**, *3*, 563.
[56] X. L. Li, G. Y. Zhang, X. D. Bai, X. M. Sun, X. R. Wang, E. Wang, H. J. Dai, *Nat. Nanotechnol.* **2008**, *3*, 538.
[57] J. M. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. L. Feng, K. Müllen, R. Fasel, *Nature* **2010**, *466*, 470.
[58] M. Choucair, P. Thordarson, J. A. Stride, *Nat. Nanotechnol.* **2009**, *4*, 30.
[59] D. H. Deng, X. L. Pan, L. A. Yu, Y. Cui, Y. P. Jiang, J. Qi, W. X. Li, Q. A. Fu, X. C. Ma, Q. K. Xue, G. Q. Sun, X. H. Bao, *Chem. Mater.* **2011**, *23*, 1188.
[60] M. I. Katsnelson, *Mater. Today* **2007**, *10*, 20.
[61] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* **2009**, *81*, 109.
[62] D. R. Cooper, B. D'Anjou, N. Ghattamaneni, B. Harack, M. Hilke, A. Horth, N. Majlis, M. Massicotte, L. Vandsburger, E. Whiteway, V. Yu, arXiv:1110.6557v1.
[63] L. Liao, Y. C. Lin, M. Q. Bao, R. Cheng, J. W. Bai, Y. A. Liu, Y. Q. Qu, K. L. Wang, Y. Huang, X. F. Duan, *Nature* **2010**, *467*, 305.
[64] J. W. Bai, X. Zhong, S. Jiang, Y. Huang, X. F. Duan, *Nat. Nanotechnol.* **2010**, *5*, 190.
[65] R. Balog, B. Jorgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Laegsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann, L. Hornekaer, *Nat. Mater.* **2010**, *9*, 315.
[66] X. R. Wang, H. J. Dai, *Nat. Chem.* **2010**, *2*, 661.
[67] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, A. K. Geim, *Science* **2007**, *315*, 1379.
[68] C. Peng, W. B. Hu, Y. T. Zhou, C. H. Fan, Q. Huang, *Small* **2010**, *6*, 1686.
[69] X. Yan, X. Cui, B. S. Li, L. S. Li, *Nano Lett.* **2010**, *10*, 1869.
[70] Y. Li, Y. Hu, Y. Zhao, G. Q. Shi, L. E. Deng, Y. B. Hou, L. T. Qu, *Adv. Mater.* **2011**, *23*, 776.
[71] D. Y. Pan, J. C. Zhang, Z. Li, M. H. Wu, *Adv. Mater.* **2010**, *22*, 734.
[72] F. Wang, Y. B. Zhang, C. S. Tian, C. Girit, A. Zettl, M. Crommie, Y. R. Shen, *Science* **2008**, *320*, 206.
[73] C. H. Lui, K. F. Mak, J. Shan, T. F. Heinz, *Phys. Rev. Lett.* **2010**, *105*, 127404.
[74] R. S. Swathi, K. L. Sebastian, *J. Chem. Phys.* **2008**, *129*, 054703.
[75] F. R. F. Fan, S. Park, Y. W. Zhu, R. S. Ruoff, A. J. Bard, *J. Am. Chem. Soc.* **2009**, *131*, 937.
[76] J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. H. Ge, L. Song, L. B. Alemany, X. B. Zhan, G. H. Gao, S. A. Vithayathil, B. A. Kaipparettu, A. A. Marti, T. Hayashi, J. J. Zhu, P. M. Ajayan, *Nano Lett.* **2012**, *12*, 844.
[77] Y. Li, Y. Zhao, H. H. Cheng, Y. Hu, G. Q. Shi, L. M. Dai, L. T. Qu, *J. Am. Chem. Soc.* **2012**, *134*, 15.
[78] A. Kumar, C. W. Zhou, *ACS Nano* **2010**, *4*, 11.
[79] H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, Y. Chen, *ACS Nano* **2008**, *2*, 463.
[80] J. P. Zhao, S. F. Pei, W. C. Ren, L. B. Gao, H. M. Cheng, *ACS Nano* **2010**, *4*, 5245.
[81] X. S. Li, C. W. Magnuson, A. Venugopal, J. H. An, J. W. Suk, B. Y. Han, M. Borysiak, W. W. Cai, A. Velamakanni, Y. W. Zhu, L. F. Fu, E. M. Vogel, E. Voelkl, L. Colombo, R. S. Ruoff, *Nano Lett.* **2010**, *10*, 4328.
[82] T. Mueller, F. N. A. Xia, P. Avouris, *Nat. Photonics* **2010**, *4*, 297.
[83] H. X. Chang, X. J. Lv, H. Zhang, J. H. Li, *Electrochem. Commun.* **2010**, *12*, 483.
[84] C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song, C. M. Li, *Angew. Chem. Int. Ed.* **2010**, *49*, 3014.
[85] X. M. Geng, L. Niu, Z. Y. Xing, R. S. Song, G. T. Liu, M. T. Sun, G. S. Cheng, H. J. Zhong, Z. H. Liu, Z. J. Zhang, L. F. Sun, H. X. Xu, L. Lu, L. W. Liu, *Adv. Mater.* **2010**, *22*, 638.
[86] A. N. Cao, Z. Liu, S. S. Chu, M. H. Wu, Z. M. Ye, Z. W. Cai, Y. L. Chang, S. F. Wang, Q. H. Gong, Y. F. Liu, *Adv. Mater.* **2010**, *22*, 103.
[87] H. X. Chang, Z. H. Sun, K. Y. F. Ho, X. M. Tao, F. Yan, W. M. Kwok, Z. J. Zheng, *Nanoscale* **2011**, *3*, 258.
[88] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. de Arquer, F. Gatti, F. H. L. Koppens, *Nat. Nanotechnol.* **2012**, *7*, 363.
[89] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. de Arquer, F. Gatti, F. H. L. Koppens, *Nat. Nanotechnol.* **2012**, *7*, 363.
[90] X. Lv, Y. Huang, Z. B. Liu, J. G. Tian, Y. Wang, Y. F. Ma, J. J. Liang, S. P. Fu, X. J. Wan, Y. S. Chen, *Small* **2009**, *5*, 1682.
[91] S. Ghosh, B. K. Sarker, A. Chunder, L. Zhai, S. I. Khondaker, *Appl. Phys. Lett.* **2010**, *96*, 163109.
[92] B. Chitara, L. S. Panchakarla, S. B. Krupanidhi, C. N. R. Rao, *Adv. Mater.* **2011**, *23*, 5419.
[93] F. N. Xia, T. Mueller, R. Golizadeh-Mojarad, M. Freitag, Y. M. Lin, J. Tsang, V. Perebeinos, P. Avouris, *Nano Lett.* **2009**, *9*, 1039.
[94] D. Sun, C. Divin, J. Rioux, J. E. Sipe, C. Berger, W. A. de Heer, P. N. First, T. B. Norris, *Nano Lett.* **2010**, *10*, 1293.
[95] E. C. Peters, E. J. H. Lee, M. Burghard, K. Kern, *Appl. Phys. Lett.* **2010**, *97*, 193102.
[96] E. J. H. Lee, K. Balasubramanian, R. T. Weitz, M. Burghard, K. Kern, *Nat. Nanotechnol.* **2008**, *3*, 486.
[97] X. Wang, L. J. Zhi, K. Müllen, *Nano Lett.* **2008**, *8*, 323.
[98] P. V. Kamat, *J. Phys. Chem. Lett.* **2011**, *2*, 242.
[99] H. X. Chang, Y. Liu, H. Zhang, J. H. Li, *J. Electroanal. Chem.* **2011**, *656*, 269.
[100] Z. F. Liu, Q. Liu, Y. Huang, Y. F. Ma, S. G. Yin, X. Y. Zhang, W. Sun, Y. S. Chen, *Adv. Mater.* **2008**, *20*, 3924.
[101] L. G. De Arco, Y. Zhang, C. W. Schlenker, K. Ryu, M. E. Thompson, C. W. Zhou, *ACS Nano* **2010**, *4*, 2865.
[102] Z. Y. Yin, S. X. Wu, X. Z. Zhou, X. Huang, Q. C. Zhang, F. Boey, H. Zhang, *Small* **2010**, *6*, 307.
[103] N. L. Yang, J. Zhai, D. Wang, Y. S. Chen, L. Jiang, *ACS Nano* **2010**, *4*, 887.
[104] Y. B. Tang, C. S. Lee, J. Xu, Z. T. Liu, Z. H. Chen, Z. B. He, Y. L. Cao, G. D. Yuan, H. S. Song, L. M. Chen, L. B. Luo, H. M. Cheng, W. J. Zhang, I. Bello, S. T. Lee, *ACS Nano* **2010**, *4*, 3482.
[105] W. J. Hong, Y. X. Xu, G. W. Lu, C. Li, G. Q. Shi, *Electrochem. Commun.* **2008**, *10*, 1555.
[106] J. B. Wu, M. Agrawal, H. A. Becerril, Z. N. Bao, Z. F. Liu, Y. S. Chen, P. Peumans, *ACS Nano* **2010**, *4*, 43.
[107] Q. L. Bao, H. Zhang, Y. Wang, Z. H. Ni, Y. L. Yan, Z. X. Shen, K. P. Loh, D. Y. Tang, *Adv. Funct. Mater.* **2009**, *19*, 3077.
[108] Z. P. Sun, T. Hasan, F. Torrisi, D. Popa, G. Privitera, F. Q. Wang, F. Bonaccorso, D. M. Basko, A. C. Ferrari, *ACS Nano* **2010**, *4*, 803.
[109] Y. Wang, J. Lu, L. H. Tang, H. X. Chang, J. H. Li, *Anal. Chem.* **2009**, *81*, 9710.
[110] Y. Wang, Y. Y. Shao, D. W. Matson, J. H. Li, Y. H. Lin, *ACS Nano* **2010**, *4*, 1790.

[111] T. Cohen-Karni, Q. Qing, Q. Li, Y. Fang, C. M. Lieber, *Nano Lett.* **2010**, *10*, 1098.
[112] Y. Wang, Z. H. Li, D. H. Hu, C. T. Lin, J. H. Li, Y. H. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 9274.
[113] L. H. Tang, H. X. Chang, Y. Liu, J. H. Li, *Adv. Funct. Mater.* **2012**, *22*, 3083.
[114] K. Yang, S. A. Zhang, G. X. Zhang, X. M. Sun, S. T. Lee, Z. A. Liu, *Nano Lett.* **2010**, *10*, 3318.
[115] S. J. He, B. Song, D. Li, C. F. Zhu, W. P. Qi, Y. Q. Wen, L. H. Wang, S. P. Song, H. P. Fang, C. H. Fan, *Adv. Funct. Mater.* **2010**, *20*, 453.
[116] S. J. Xu, Y. Liu, T. H. Wang, J. H. Li, *Anal. Chem.* **2011**, *83*, 3817.
[117] H. F. Dong, W. C. Gao, F. Yan, H. X. Ji, H. X. Ju, *Anal. Chem.* **2010**, *82*, 5511.
[118] X. T. Shi, H. X. Chang, S. Chen, C. Lai, A. Khademhosseini, H. K. Wu, *Adv. Funct. Mater.* **2012**, *22*, 751.
[119] S. Y. Park, J. Park, S. H. Sim, M. G. Sung, K. S. Kim, B. H. Hong, S. Hong, *Adv. Mater.* **2011**, *23*, H263.
[120] C. Heo, J. Yoo, S. Lee, A. Jo, S. Jung, H. Yoo, Y. H. Lee, M. Suh, *Biomaterials* **2011**, *32*, 19.
[121] X. C. Dong, Y. M. Shi, W. Huang, P. Chen, L. J. Li, *Adv. Mater.* **2010**, *22*, 1649.
[122] Q. J. Xiang, J. G. Yu, M. Jaroniec, *Chem. Soc. Rev.* **2012**, *41*, 782.
[123] X. Q. An, J. C. Yu, *RSC Adv.* **2011**, *1*, 1426.
[124] H. Zhang, X. J. Lv, Y. M. Li, Y. Wang, J. H. Li, *ACS Nano* **2010**, *4*, 380.
[125] Y. H. Zhang, Z. R. Tang, X. Z. Fu, Y. J. Xu, *ACS Nano* **2010**, *4*, 7303.
[126] T. G. Xu, L. W. Zhang, H. Y. Cheng, Y. F. Zhu, *Appl. Catal., B* **2011**, *101*, 382.
[127] T. F. Yeh, J. M. Syu, C. Cheng, T. H. Chang, H. S. Teng, *Adv. Funct. Mater.* **2010**, *20*, 2255.
[128] X. Y. Zhang, H. P. Li, X. L. Cui, Y. H. Lin, *J. Mater. Chem.* **2010**, *20*, 2801.
[129] Q. Li, B. D. Guo, J. G. Yu, J. R. Ran, B. H. Zhang, H. J. Yan, J. R. Gong, *J. Am. Chem. Soc.* **2011**, *133*, 10878.
[130] X. J. Lv, W. F. Fu, H. X. Chang, H. Zhang, J. S. Cheng, G. J. Zhang, Y. Song, C. Y. Hu, J. H. Li, *J. Mater. Chem.* **2012**, *22*, 1539.
[131] X. J. Lv, S. X. Zhou, C. Zhang, H. X. Chang, Y. Chen, W. F. Fu, *J. Mater. Chem.* **2012**, *22*, 18542.
[132] H. X. Chang, X. J. Lv, Z. J. Zheng, H. K. Wu, *Proc. SPIE* **2011**, *8333*, 83330G.
[133] J. Zhang, J. G. Yu, M. Jaroniec, J. R. Gong, *Nano Lett.* **2012**, *12*, 4584.
[134] Y. H. Ng, A. Iwase, A. Kudo, R. Amal, *J. Phys. Chem. Lett.* **2010**, *1*, 2607.
[135] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* **2011**, *6*, 147.
[136] A. Splendiani, L. Sun, Y. B. Zhang, T. S. Li, J. Kim, C. Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, *10*, 1271.
[137] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. W. Chen, M. Chhowalla, *Nano Lett.* **2012**, *12*, 526.
[138] Z. Y. Yin, H. Li, H. Li, L. Jiang, Y. M. Shi, Y. H. Sun, G. Lu, Q. Zhang, X. D. Chen, H. Zhang, *ACS Nano* **2012**, *6*, 74.
[139] H. S. Lee, S. W. Min, Y. G. Chang, M. K. Park, T. Nam, H. Kim, J. H. Kim, S. Ryu, S. Im, *Nano Lett.* **2012**, *12*, 3695.