Enhanced optical nonlinearities of hybrid graphene oxide films functionalized with gold nanoparticles

Scott Fraser, Xiaorui Zheng, Ling Qiu, Dan Li, and Baohua Jia

---

Articles you may be interested in

Increasing the effective work function of multilayer graphene films using silver nanoparticles
J. Vac. Sci. Technol. B **32**, 011214 (2014); 10.1116/1.4861372

Optical and carrier transport properties of graphene oxide based crystalline-Si/organic Schottky junction solar cells
J. Appl. Phys. **114**, 234506 (2013); 10.1063/1.4847515

Resonantly enhanced optical nonlinearity in hybrid semiconductor quantum dot−metal nanoparticle structures
Appl. Phys. Lett. **100**, 063117 (2012); 10.1063/1.3683548
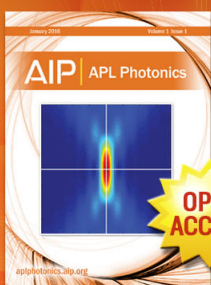
Huge enhancement of optical nonlinearities in coupled Au and Ag nanoparticles induced by conjugated polymers
Appl. Phys. Lett. **100**, 023106 (2012); 10.1063/1.3675911

Linear and nonlinear optical properties of gold nanoparticle-Eu oxide composite thin films
J. Appl. Phys. **104**, 033110 (2008); 10.1063/1.2967711

Enhanced optical nonlinearities of hybrid graphene oxide films functionalized with gold nanoparticles

Scott Fraser,[1,a)] Xiaorui Zheng,[1,a)] Ling Qiu,[2] Dan Li,[2] and Baohua Jia[1,b)]

[1]Centre for Micro-Photonics, Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn Victoria 3122, Australia
[2]Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia

We report a flexible method to functionalize highly transparent graphene oxide (GO) film with gold nanoparticles (AuNPs). Nonlinear absorption and refraction of the hybrid films are measured, which are strongly enhanced and tunable by different AuNP concentrations compared to both GO and AuNP-only samples. The enhanced nonlinearity is due to the effective functionalization of the hybrid films, which is verified by the ultraviolet-visible and Fourier-transform infrared spectra. Our low-loss hybrid GO-AuNP films provide a solid-state material platform for diverse nonlinear applications. The functionalizing method can serve as a universal strategy to manipulate the physical properties of hybrid GO. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4927387]

The discovery of the two-dimensional material graphene and its derivative, graphene oxide (GO), has attracted tremendous interest due to their unique physical and chemical properties, which promise new solutions to address outstanding challenges.[1,2] In particular, the nonlinear optical properties of GO have been extensively investigated and the giant third-order nonlinear responses have been demonstrated, including saturable absorption, optical limiting, and nonlinear refraction.[3,4] With a larger nonlinear coefficient, the required interaction length of light with the nonlinear media is significantly reduced, enabling a high level of miniaturization.[5] In particular, for nonlinear materials with a significant linear loss, such as GO, it becomes critically important to ensure sufficient signal transmission through the devices. Therefore, there is an on-going demand to increase its optical nonlinearity.

Chemical functionalization of GO has been proposed and enabled by the oxygen-containing groups in GO, which takes advantage of the excellent properties of both GO and the functionalizing materials. Various multifunctional materials have been attached to GO, including organic materials, dye ionic molecules, and dielectric and metallic nanoparticles.[6–12] Enhanced optical nonlinearities of such functionalized GO hybrid materials have been discovered and are attributed to strong interactions between GO and the functionalizing materials. However, the current results of hybrid GO materials are mostly limited to the hybrid GO solutions,[6–11] which create the main barrier for solid-state integrated photonic applications. Studies on the nonlinear refraction (Kerr effect) of GO hybrid materials, especially the GO hybrid films, which is essential for on-chip signal regeneration, all-optical switching, and fast optical communications,[13] have remained largely unexplored.[9] Moreover, though different strategies have been used to effectively functionalize GO, including chemical,[6–9] laser-induced photochemical,[10] and laser ablation methods,[11] they require either environmentally hazardous chemicals or complex experimental setups, which largely restrict both the versatilities and flexibilities of the hybrid GO materials.

In this paper, we propose and demonstrate a flexible method to functionalize highly transparent GO film with gold nanoparticles (AuNPs). The solid-state hybrid GO-AuNP films at different AuNP concentrations have been synthesized through a vacuum filtration process.[14] Significantly enhanced nonlinear absorption and nonlinear refraction behaviors of the hybrid GO-AuNP films are characterized by the Z-scan measurement, which are tunable by changing the AuNP concentration. Both the nonlinear absorption and refractive coefficients have also been retrieved by fitting the open-aperture and close-aperture Z-scan curves.

In order to achieve highly uniform distribution of AuNPs inside the GO films, homogeneous GO and AuNP water solutions are mixed together. The concentration of GO in GO solution is 1.4 mg/ml, and the concentration of AuNP in AuNP solution is 0.1% by weight. The hybrid GO-AuNP films can be obtained through the vacuum filtration method.[14] Then, the hybrid GO-AuNP films are carefully peeled off as free-standing films, so that they can be easily attached on any desired substrates. In our experiment, three hybrid GO-AuNP films with increased AuNP concentrations have been prepared and labelled as GO-AuNPs1, GO-AuNPs2, and GO-AuNPs3, respectively. The film thicknesses are kept the same at ~1 μm. The ratio of AuNP concentration in the three hybrid films is specifically fixed as 1:2:4 (as listed in Table I) to ensure a comparable linear absorption at the measured wavelength of 800 nm. A pure GO film with the same GO quantity is prepared and used as a reference sample throughout the experimental characterization. The AuNP-only sample with the highest AuNP concentration as that used in the GO-AuNPs3 sample has also been measured as a reference.

To confirm the effective functionalization of GO with AuNPs through the vacuum filtration method, we measure the ultraviolet-visible (UV-Vis) absorption spectra of the

a)S. Fraser and X. Zheng contributed equally to this work.
b)bjia@swin.edu.au

107, 031112-1

TABLE I. The mixing of GO solution and AuNP solution in GO, GO-AuNPs1, GO-AuNPs2, and GO-AuNPs3 films, respectively.

GO film	GO-AuNPs1	GO-AuNPs2	GO-AuNPs3
2 ml GO solution	2 ml GO solution and 0.5 ml AuNP solution	2 ml GO solution and 1 ml AuNP solution	2 ml GO solution and 2 ml AuNP solution

three hybrid GO-AuNP films and compare them with the spectrum of the reference GO sample, as shown in Figure 1(a). For the absorption spectrum of the GO film, significant absorption below 400 nm can be observed. The characteristic shoulder at 305 nm is attributed to the n $\rightarrow \pi*$ transitions of the C=O bonds.[15] Clearly, the measured smooth UV-Vis spectrum and the characteristic absorptions of the GO film suggest both the purity of our GO solutions and high quality of the GO film made by the vacuum filtration method.

In comparison, the absorption spectra of the hybrid GO-AuNP films show similar behaviors as that of the reference GO film except for the strong absorption peaks at around 535 nm (dashed grey line in Figure 1(a)), which can be attributed to the localized surface plasmon resonance of AuNPs ($\sim$60 nm in diameter). The strong absorption peaks also imply the high density of loaded AuNPs and a significant interaction between AuNPs and GO. Moreover, the absorption peaks are strongly dependent on the AuNP concentration, in particular, monotonically increasing with the concentration of AuNPs. The microscopic images of the four films are shown in the inset of Figure 1(a). It can be seen clearly that the color varies from brown to red as the AuNP concentration increases, which is consistent with the absorption spectra. It should be emphasized that the linear absorptions of the four samples at 800 nm are reasonably low (less than 20%), and they are kept nearly the same by carefully adjusting the ratio of AuNP concentration in the three hybrid films (1:2:4), so that the optical nonlinearities of the four samples can be compared directly.

To examine the morphology of the hybrid GO-AuNPs films, scanning electron microscopic (SEM) images are obtained for the pure GO film in comparison with the GO-AuNPs3 film (the highest AuNP loading case), as

presented in Figures 1(b) and 1(c). It can be clearly seen from both the SEM image and the Energy-dispersive X-ray spectroscopic (EDX) image (Figures 1(d) and 1(e)) that the AuNPs are presenting in the GO-AuNPs3 film and they distribute evenly over the entire GO film. No aggregation has been observed, indicating the high quality of the hybrid GO-AuNP films.

The optical nonlinearities of the GO and hybrid GO-AuNP films are studied by the Z-scan measurement, and the result of AuNP-only sample is also provided as a reference. The open-aperture Z-scan curves at the same input fluence are shown in Figure 2(a). All of the four films present the optical limiting property, whereas no optical limiting effect can be observed in the AuNP-only sample. The optical limiting of GO is due to both excited state absorption of the sp^3 matrix and the multiphoton absorption when electrons transit from the ground state to the excited state in the sp^3 matrix.[4] The optical limiting ability, evidenced by the achievable minimal transmittance, has been greatly enhanced as the increase of AuNP concentration.

Theoretical fittings of the open-aperture results are shown as the solid lines in Figure 2(a). To further understand the entire nonlinear absorption behaviors, the excitation-fluence dependent open-aperture Z-scan measurement is conducted. The output fluence (F_{out}) versus input fluence (F_{in}) for the four films is plotted in Figure 2(b). High linear transmittance T ($\sim$80%) of the four films at 800 nm has been achieved and is plotted as a reference. The four films present similar nonlinear absorption behaviors. First, at the small input fluences, the F_{out}/F_{in} ratio is the same as T, indicating that the samples show only the linear absorption. As the input fluence increases, F_{out}/F_{in} starts to reduce and becomes smaller than T, representing the onset of the optical limiting behavior. Finally, the saturation of the optical limiting is
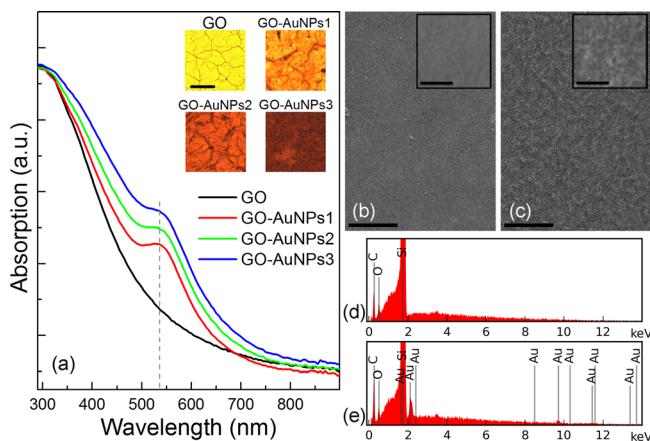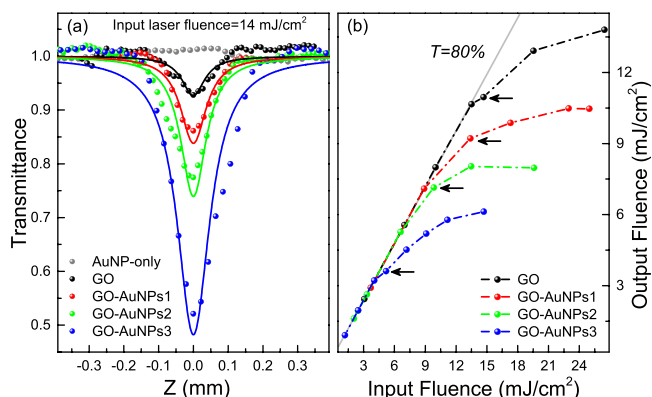

FIG. 1. (a) UV-Vis absorption spectra of the GO, GO-AuNPs1, GO-AuNPs2, and GO-AuNPs3 films. Inset: the microscopic images of the four films. Scale bar: 20 μm. ((b) and (c)) SEM images of the pure GO film in comparison with the GO-AuNPs3 film. Scale bars: 20 μm. Inset: enlarged views. Scale bars: 500 nm. ((d) and (e)) EDX images of the pure GO film in comparison with the GO-AuNPs3 film, which clearly show the presence of AuNPs in the GO-AuNPs3 film.

FIG. 2. (a) Open aperture Z-scan results (scatters) of the AuNP-only, GO, GO-AuNPs1, GO-AuNPs2, and GO-AuNPs3 samples at the same input fluence (14 mJ/cm^2). The theoretical fittings are indicated as the solid lines. (b) Plot of output fluence versus input fluence for the four films. T represents the linear transmittance (grey solid line). The arrows show the optical limiting onsets of the four films, respectively.

reached at the large input fluence, and no further reduction of F_{out}/F_{in} can be achieved. Therefore, all the four samples exhibit the characteristic optical limiting behaviors under various input fluences. However, there are differences among the four curves. First of all, the optical limiting onsets (defined as the input fluence at which the transmittance starts to depart from T) are monotonically reduced as the concentration of AuNP increases (see arrows in Figure 2(b)). The input fluences, at which the optical limiting saturates, are also found to be monotonically dependent on the concentration of AuNP. As a result, it is evidently proved that the enhanced nonlinear absorption of the hybrid GO-AuNP films is attributed to the hybridization of AuNPs.

The nonlinear refraction of the hybrid GO-AuNP films are also investigated by the close-aperture Z-scan measurement at the same input laser fluence and fitted theoretically, as shown in Figure 3. The pronounced valley-peak patterns can be observed in all the hybrid GO-AuNP films, corresponding to the positive nonlinear refractive index n_2 (self-focusing). However, no obvious nonlinear refraction of AuNP-only sample can be observed. The nonlinear refraction of GO is mainly attributed to the population redistribution of the π electrons and the free carriers of the sp^2 domain as well as the bound electrons and the free carriers of the sp^3 matrix.[4] Compared to the reference GO film, the hybrid GO-AuNP films demonstrate stronger nonlinear refraction as the concentration of AuNP increases, which is proved by the increase of the difference between the peak and valley transmittance ΔT_{p-v}.

To further evaluate the magnitude of the nonlinearities of the hybrid GO-AuNP films, both the nonlinear absorption coefficient β and the nonlinear refractive index n_2 have been deduced by fitting the open-aperture and close-aperture curves, respectively, as shown in Figure 4. β of the reference GO film is found to be as large as 17 cm/GW, which is the same order of the magnitude for the GO thin films reported recently.[3] However, β of the hybrid GO-AuNP films are found to increase as the concentration of AuNP increases, reaching 6 times of that of the reference GO film. On the other hand, the nonlinear refractive index of the reference GO film is fitted to be 4×10^{-13} cm^2/W. The hybridization

of AuNPs boosts the nonlinear refraction as large as 6 times of that of the reference GO film. As a result, both the nonlinear absorption and the nonlinear refraction can be effectively enhanced by the hybridization of AuNPs.

The Fourier-transform infrared (FTIR) spectra have been widely used to study the vibrations of the oxygen-containing groups in GO.[16–19] To further study the functionalization of the hybrid GO-AuNP films and understand the possible mechanism of the enhanced nonlinearity, the FTIR transmission spectra of the four films are measured and shown in Figure 5. It is worth mentioning that the FTIR spectra of free-standing films (both GO and GO-AuNP), enabled by the vacuum filtration method, have been measured to eliminate any influence of the substrate. The FTIR spectrum of the reference GO film shows characteristic oxygen configurations in the structure,[18] including the sp^2-hybridized C=C, carboxyl (COOH), ketonic species (C=O), hydroxyl (C-OH), and epoxide (C-O), as labelled in Figure 5. It can be observed with increased AuNP loading concentration, the hybrid GO-AuNP films show nearly similar FTIR spectra compared to the reference GO film, except for the increase of the absorption bands at 1651 cm^{-1} and

FIG. 4. Nonlinear absorption coefficient β and nonlinear refractive index n_2 of GO, GO-AuNPs1, GO-AuNPs2, and GO-AuNPs3, deduced by fitting the close aperture and open aperture Z-scan curves.

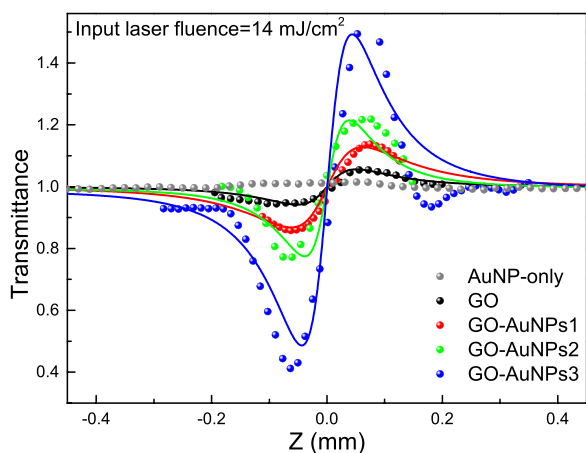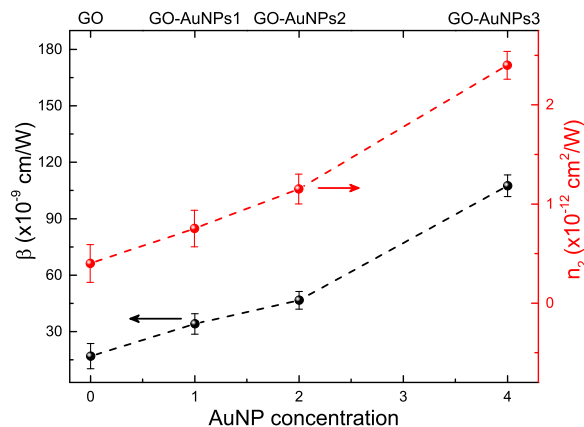FIG. 3. Close aperture Z-scan results (scatters) of the AuNP-only, GO, GO-AuNPs1, GO-AuNPs2, and GO-AuNPs3 samples at the same input laser fluence (14 mJ/cm^2). The theoretical fittings are indicated as solid lines.
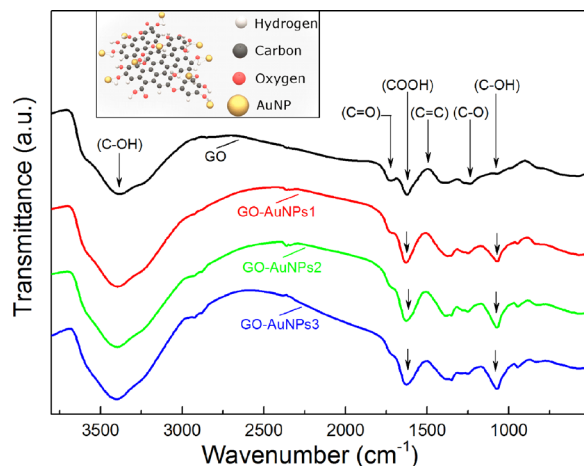

FIG. 5. FTIR transmission spectra of the GO, GO-AuNPs1, GO-AuNPs2, and GO-AuNPs3 films. Various absorption bands corresponding to the functional groups in the GO films have been labelled. Inset: schematic illustration of the hybrid GO-AuNP films.

$1074\,cm^{-1}$, corresponding to the COOH and C-OH groups. These results indicate that the AuNPs have been covalently bonded to the COOH and C-OH groups of the GO sheet, consistent with the previous report.[11] It is known that the C-OH group is located in the basal plane and the COOH group is at the edge site of the GO sheet.[20] Therefore, AuNPs are believed to be decorated on the surface at the edge and between the GO sheets (see the inset of Figure 5). This chemical functionalization of the GO film provides the potential enhancement mechanism for the observed high nonlinearity.

The enhanced optical nonlinearities of the hybrid GO-AuNP films are believed to be a result from the efficient energy and/or charge (electron) transfer upon photoexcitation and the synergistic coupling effects between the constituents. Upon focused laser illumination, AuNPs undergo a multiphoton absorption process,[5] which generates free electrons, making them function as electron donors in the GO-AuNP nanocomposite. The charge transfer from the electron donor, AuNPs, to the electron acceptor, GO, may result in the intramolecular donor-acceptor interaction between GO and AuNPs in our hybrid system. And GO could efficiently transfer the electrons, suppress the charge recombination, and produce a charge-separated excited state.[6,7,21–23] Therefore, it is believed that the photo-induced energy and/or charge (electron) transfer from AuNPs to GO in the hybrid GO-AuNP films lead to the enhanced nonlinear optical properties. On the other hand, the rich organic anionic groups in GO make it chemically possible for AuNPs to interact with GO and the formation of interfacial bonds between AuNPs and GO, as suggested in the FTIR spectra in Figure 5, which may lead to strong synergistic coupling effects and hence the enhancement of nonlinear optical properties.[24]

Recently, the photoreduction of GO has been reported under various laser illuminations due to the continuous removal of the oxygen-containing groups on the GO sheets.[25] A threshold laser fluence can be found at which GO starts to be reduced. In our nonlinear experiment, the photoreduction of the hybrid GO-AuNP film has also been observed at high input laser fluence above $30\,mJ/cm^2$. To ensure the nonlinear effects reported in this work are from the intrinsic GO-AuNP films before any photoreduction happens, low input laser fluences ($<25\,mJ/cm^2$) have been used. The linear absorption spectra of the hybrid films before and after the nonlinear measurements have been compared to confirm that no obvious change to the film has occurred during the measurement. As a result, the presented nonlinear effects of the hybrid GO-AuNP films are reversible and good stability of the GO-AuNP films can be observed under such laser illumination.

In summary, we present a universal and simple way to synthesize hybrid GO-AuNP films by the vacuum filtration method. The effective functionalization of GO with AuNPs has been revealed by both the UV-Vis and FTIR spectra. Both the nonlinear absorption and refraction of the low-loss hybrid GO-AuNP films are found to be enhanced monotonically with the increase of AuNP concentration by the Z-scan measurement. The enhanced nonlinear light-matter interactions of the hybrid GO-AuNP films can be attributed to the efficient energy and/or charge (electron) transfer upon photoexcitation and the synergistic coupling effects between AuNPs and GO. Our hybrid GO-AuNP films would provide a solid-state material platform for diverse nonlinear optical applications, such as ultra-sensitive optical limiter, optical modulator, and photodetector. Moreover, the vacuum filtration method can serve as a universal strategy to functionalize GO by easily doping various nanoparticles with tunable concentrations to manipulate the physical properties of hybrid GO materials.

[1] F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, Nat. Photonics **4**, 611 (2010).

[2] A. K. Geim and K. S. Novoselov, Nat. Mater. **6**, 183 (2007).

[3] X. F. Jiang, L. Polavarapu, S. T. Neo, T. Venkatesan, and Q. H. Xu, J. Phys. Chem. Lett. **3**, 785 (2012).

[4] X. L. Zhang, Z. B. Liu, X. C. Li, Q. Ma, X. D. Chen, J. G. Tian, Y. F. Xu, and Y. S. Chen, Opt. Express **21**, 7511 (2013).

[5] R. L. Sutherland, *Handbook of Nonlinear Optics* (Marcel Dekker, New York, 1996).

[6] Y. F. Xu, Z. B. Liu, X. L. Zhang, Y. Wang, J. G. Tian, Y. Huang, Y. F. Ma, X. Y. Zhang, and Y. S. Chen, Adv. Mater. **21**, 1275 (2009).

[7] J. Balapanuru, J. X. Yang, S. Xiao, Q. Bao, M. Jahan, L. Polavarapu, J. Wei, Q. H. Xu, and K. P. Loh, Angew. Chem., Int. Ed. Engl. **49**, 6549 (2010).

[8] B. Anand, A. Kaniyoor, S. S. S. Sai, R. Philip, and S. Ramaprabhu, J. Mater. Chem. C **1**, 2733 (2013).

[9] X. L. Zhang, X. Zhao, Z. B. Liu, S. Shi, W. Y. Zhou, J. G. Tian, Y. F. Xu, and Y. S. Chen, J. Opt. **13**, 075202 (2011).

[10] D. Tan, X. Liu, Y. Dai, G. Ma, M. Meunier, and J. Qiu, Adv. Opt. Mater. **3**, 836 (2015).

[11] A. R. Sadrolhosseini, A. S. M. Noor, N. Faraji, A. Kharazmi, and M. A. Mahdi, J. Nanomater. **2014**, 962917.

[12] F. Bei, X. Hou, S. L. Y. Chang, G. P. Simon, and D. Li, Chem.—Eur. J. **17**, 5958 (2011).

[13] M. X. Ren, B. H. Jia, J. Y. Ou, E. Plum, J. F. Zhang, K. F. Macdonald, A. E. Nikolaenko, J. J. Xu, M. Gu, and N. I. Zheludev, Adv. Mater. **23**, 5540 (2011).

[14] D. Li, M. B. Mueller, S. Gilje, R. B. Kaner, and G. G. Wallace, Nat. Nanotechnol. **3**, 101 (2008).

[15] J. I. Paredes, S. Villar-Rodil, A. Martınez-Alonso, and J. M. D. Tascon, Langmuir **24**, 10560 (2008).

[16] C. Zhu, S. Guo, Y. Fang, and S. Dong, ACS Nano **4**, 2429 (2010).

[17] V. Abdelsayed, S. Moussa, H. M. Hassan, H. S. Aluri, M. M. Collinson, and M. S. El-Shall, J. Phys. Chem. Lett. **1**, 2804 (2010).

[18] M. Acik, G. Lee, C. Mattevi, M. Chhowalla, K. Cho, and Y. J. Chabal, Nat. Mater. **9**, 840 (2010).

[19] L. Huang, Y. Liu, L. C. Ji, Y. Q. Xie, T. Wang, and W. Z. Shi, Carbon **49**, 2431 (2011).

[20] W. Gao, L. B. Alemany, L. J. Ci, and P. M. Ajayan, Nat. Chem. **1**, 403 (2009).

[21] M. Liu, R. Zhang, and W. Chen, Chem. Rev. **114**, 5117 (2014).

[22] A. Cao, Z. Liu, S. Chu, M. Wu, Z. Ye, Z. Cai, Y. Chang, S. Wang, Q. Gong, and Y. Liu, Adv. Mater. **22**, 103 (2010).

[23] T. Chen, I. Chang, M. Yang, H. Chiu, and C. Lee, Appl. Catal. B **142**, 442 (2013).

[24] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, and H. Dai, Nat. Mater. **10**, 780 (2011).

[25] X. Zheng, B. Jia, X. Chen, and M. Gu, Adv. Mater **26**, 2699 (2014).