Effective Reduction of Oxygen Debris in Graphene Oxide

Orit Seri-Livni, Cecile Saguy, Faris Horani, Efrat Lifshitz,* and Dima Cheskis*

Graphene oxide (GO) raised substantial interest in the past two decades due to its unique properties beyond those of pristine graphene, including electronic energy bandgap, hydrophilic behavior, and numerous anchoring sites required for functionalization. In addition, GO is found to be a cheap mass-production source for the formation of the pristine graphene. However, the presence of numerous clusters containing oxygen functional groups (called debris) on the GO surface hinders the GO integration in electronic devices. Herein, a simple method aimed to reduce the density of oxygen debris weakly bonded to the surface is presented. The method consists of minimal treatments, like sonication and/or water rinsing processes. Whereas this simple method removed epoxy and hydroxyl oxygen groups weakly attached to the graphene matrix, the double C=O bonds are almost not affected by the applied treatment, as demonstrated by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Scanning tunneling microscopy and high-resolution transmission electron microscopy measure the designated nonuniform distribution of the oxidation sites, appearing as clusters concentrated preferentially on GO-defected regions, albeit separated by pristine graphene areas. The results should have an impact in the implementation of GO in electronic devices deposited on different substrates.

1. Introduction

The unique properties of graphene, a single layer of graphite, were first described theoretically by Wallace in 1947,[1] More than 50 years later, in 2004, Geim and Novoselov achieved mechanically exfoliated graphene.[2] Since then, additional methods to grow graphene were developed, such as chemical vapor deposition,[3] epitaxial growth,[4] electrochemical growth,[5] electrochemical[6] and chemical[7] exfoliations. Brodie was the first to oxidize graphite, as early as 1859.[8] More than a century later, in 1962, Boehm et al. achieved graphene oxide (GO).[9] Their material included both single-layers and multilayer flakes. Since 1962, the processes of synthesis and sonication have constantly improved. Today most of the GO are produced by the modified Hummers method where graphite is first oxidized, then sonicated and finally the amount of oxygen is decreased. During the exfoliation process, atoms of oxygen intercalate between the graphene layers, weakening the interlayer van der Waals forces. Then, a sonication process separates the exfoliated oxidized graphite into single oxidized graphene layers, called GO. These layers consist of a graphene sheets bonded with oxygen functional groups.[10] As the percentage of oxygen groups on the surface changes, the electronic behavior of a GO film can change from insulator via semiconductor toward graphene with zero energy bandgap. The semiconductor electronic behavior is characterized by the parabolic dependence of the electron energy on its momentum, whereas the graphene electronic behavior displays a linear dependence, producing a “V-shaped” electronic energy spectrum.[2]

When most oxygen groups are removed from the surface, the resulting material is called reduced graphene oxide (RGO).[11] This RGO material, also named chemical exfoliated graphene, is the last step of the exfoliation process. RGO structurally resembles a pristine graphene, however, differs from it by the residual number of oxygen atoms. Its electronic bandgap is determined by the oxygen concentration. In addition, the GO and RGO are accessible to functionality. The cheapest form for producing GO is as flakes inside water or an organic solution. It is hydrophilic, and can be deposited on various substrates. GO is used in several biomedical applications,[12–14] as catalysts,[15,16] water filters,[17] solar cell components,[18] part of lithium-ion battery devices (as RGO),[19] and in supercapacitors.[20]

However, alongside all these advantages, the major disadvantage in the production of GO and RGO films is that it is difficult to control the distribution of functional groups over the surface. Many efforts have been made to understand and control the structure of deposited GO.[21] The distribution of functional groups has been quantified by the Lerf–Klinowski (LK) theoretical model,[22] which is based on thermodynamic calculations. This model shows that the functional group distribution can affect many parameters, such as conductivity, energy band gap, mechanical strength, and thermal effects. In this model, epoxy and hydroxyl groups are distributed randomly over the GO flake, whereas carboxyl ones sit on the corners of the flake.

There have been many experimental attempts to image the microscopic structure and extract the microscopic parameters of GO using atomic force microscopy (AFM),[23–25] high-resolution
transmission electron microscopy (HR-TEM),\textsuperscript{[26–29]} scanning transmission electron microscopy (STEM),\textsuperscript{[30,31]} and scanning tunneling microscopy (STM).\textsuperscript{[32–37]} Scanning tunneling spectroscopy (STS) measurements were also used to study the local electronic density of states. Katano et al. demonstrated that STS spectra taken on unreduced GO deposited on Au exhibit gap energy related to the inhomogeneous size of the sp$^2$ domains and the charge transfer between the sp$^2$ domains and the oxygen functional groups attached to the basal plane of the GO. Thus, depending on the STM tip location on GO surface, different gap energies were measured.\textsuperscript{[14]} Wang et al. showed similarity between the electronic spectrum of RGO and that of pure graphene, as deduced from STS dI/dV curves,\textsuperscript{[37]} thus, suggesting that the residual oxygen groups have limited influence on the final spectrum. In contrast, Harthcock et al. showed that in locally oxidized CVD graphene samples, it is possible to detect different electronic behavior between pure graphene (dI/dV has a “V-shaped”) and the proximity of oxygen atoms (dI/dV has a parabolic shape) by local STS probing.\textsuperscript{[31]}

Due to the fact that oxygen groups are not arranged in any defined order, and that their distribution depends on synthesis and deposition procedures, the results of these experiments vary widely. For example, Pandey et al., showed using STM that in RGO samples,\textsuperscript{[35]} oxygen groups were aligned in rows. Katano et al. demonstrated that it is possible to carry out STM measurements of GO,\textsuperscript{[14]} but did not image the sample at atomic resolution due to the high density of oxygen groups. Moreover, during the synthesis and sonication processes required for producing GO, oxygen groups organized in clusters called oxygen debris (OD). The nature of the clusters and how they are bonded to the GO are still under debate. Thomas et al. developed a model showing that these OD actually changes the GO material into a system with two components: some regions of the film are pure graphene, whereas other regions are covered by functional oxygen groups.\textsuperscript{[38]} The OD can be washed away by a strong base such as NaOH. Controversially, Dimiev and Polson said that these clusters were actually created during the strong base wash.\textsuperscript{[19]} The discussion over OD has continued ever since, sustained by many authors using different techniques.\textsuperscript{[40–44]} Thomas et al.\textsuperscript{[40]} and Naumov et al.\textsuperscript{[41]} both conducted GO photoluminescence experiments, supporting and opposing the two-component model, respectively. Bonanni et al.\textsuperscript{[42]} demonstrated the influence of OD on inherent electroactivity. These researchers claimed that OD’s consist of highly oxidized polyaromatic fragments adsorbed to the graphene matrix by noncovalent bonds such as π–π stacking, hydrogen bonding, and van der Waals interactions. They also showed that OD can be removed by extensive sonication. Chen and Chen\textsuperscript{[43]} also showed that aromatic compounds have tendency to be organized by π–π interaction on defect sites of a graphene matrix.

In addition, the type of bonding between GO films and a substrate can drastically change the electronic behavior of the deposited GO films, and possibly their morphology as well. A chemical bonding to the substrate would generate a strong local distortion of the hexagonal matrix.\textsuperscript{[46,47]} According to recent experiments, covalent bonds are expected to cause local changes in topography and also in the STS curves.\textsuperscript{[48,49]} Strong interaction can be also seen in a Moiré pattern. For example, in an experiment where gold islands are covered by graphene, Pálinkás et al.\textsuperscript{[50]} observed Moiré superlattices and STS curves with different periodicities.

In this work, we investigate the structural, chemical, and electronic properties of the GO surface thin films and their bonding to oxygen functional groups as a function of minimal preparation treatments, like sonication and/or water rinsing processes. We show, by atomically resolved STM and HR-TEM, that OD concentrate preferentially on GO-defected regions. Sonication of the GO flakes dispersed in ethanol followed by simple water rinsing lead to removal of the noncovalently adsorbed OD and to the recovery of part of the C–C bonds, as shown by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. Moreover, comparison between the STM and HR-TEM images bestows that the morphology of GO after the described treatments, resembles that of suspended GO without any influence of the substrate. This is possible by assuming that part of the oxygen functional group clusters lay below the graphene film and that OD attached to the lower surface. The lack of a Moiré pattern supports this hypothesis.

2. Results

2.1. Sample Preparation

Industrial GO flakes dispersed in an ethanol solution and prepared by a standard modified Hummers method were purchased. The flakes were deposited on a precleaned Au/mica substrate using a drop-cast method (see Experimental Section). The investigation followed the GO nature through three different stages: 1) the as-purchased GO, 2) after 15 min of sonication, and 3) after 15 min sonication followed by water rinsing.

2.2. Characterization

2.2.1. As-Purchased GO Flakes

Drop-casted GO flakes from the purchased solution without dilution, sonication, or water rinsing were deposited onto an Au/mica substrate. AFM topography exhibited in Figure 1a shows flakes up to 10 μm width with a thickness between 5 and 14 nm, as shown in Figure 1b. The observed thicknesses demonstrate the agglomeration of a few layers, when a thickness of single layer is ≈1 nm.

Raman spectroscopy measurements of the as-purchased GO material are given in Figure S1, Supporting Information, exposing the expected resonance transitions that reflect GO composition.\textsuperscript{[51]}

The STM image (Figure 2a) shows bright patterns superimposed onto the graphene atomically resolved structure. The randomly dispersed bright spots are most probably related to agglomeration of oxygen functional groups (e.g., epoxy, carboxyl, and also hydroxyl). Indeed, the fast Fourier transform (FFT) (Figure 2b) of the STM image exhibits two different frequencies. The lower frequencies (central ring) are connected to the brighter and distorted regions, whereas the higher frequencies are characteristic of the hexagonal structure observed in graphenic regions. The inverse Fourier transform image considering only the higher frequencies (Figure 2c) clearly shows groups of
broken bonds on the bright spot regions in Figure 2a. Two typical dI/dV spectra were measured on different locations of the as-purchased flakes, demonstrating that the band structure can be locally different on the same flake due to unsystematic distribution of oxygen atom clusters (Figure 2a).

The red dI/dV curve of Figure 2d shows a wide parabolic shape characteristic of dI/dV measured on an oxygen group. The black dI/dV curve in Figure 2d is flat, with a shoulder at 0.2 eV attributed to a STS conducted on a site with a close-lying oxygen surrounding as seen in the studies by Harthcock et al. and Katano et al.\(^{33,34}\) dI/dV spectra taken at low temperature (25 K) exhibit a very similar behavior to that shown in Figure 2d (see Figure S3, Supporting Information). The XPS spectrum shown in Figure 2e, of as-purchased GO flakes deposited from the solution, can be deconvoluted into three main peaks corresponding to C=C (284.78 eV, \(\approx 47.08\)%), C=O (287.03 eV, 46.19%), and C = O (288.67 eV, 6.73%) bonds. Thus, the overall oxygen concentration in as-purchased GO is 52.92%.

2.2.2. Dilution and Sonication (15 min) of the As-Purchased GO

To achieve GO single layers, the GO solution was first diluted and then sonicated for 15 min, before drop-casted onto an
Au/mica substrate. Worth noting that the dilution is expected to reduce the flake agglomeration, however, without altering the oxygen concentration. Various sonication durations were applied, and the products were evaluated by examining topography of the flakes in the AFM images. The results revealed an optimal sonication time of 15 min, whereas an extended procedure (~1 h) led to a breakage of the flakes into tiny fragments (see Figure S2, Supporting Information).

Two different frequencies can be observed on the Fourier transform of the HR-TEM image shown in Figure 3b (which is a zoom in on Figure 3a). The high frequency (outer ring) corresponding to a graphenic region, as shown by the blue-circle in Figure 3b. The lattice atomic distance extracted from the hexagonal Fourier pattern is 0.146 nm. The low frequency (central region) is associated with distorted regions on a flake, as shown by the green-circle in Figure 3b. It should be noted that the graphenic regions appear much sharper than the distorted ones. It is most probable that the OD and oxygen functional groups concentrate on those distorted regions. The XPS spectrum (Figure 3d) measured after 15 min sonication treatment, of the as-purchased GO flakes deposited from the solution, exposed a decrease in the ratio between the C─O (286.58 eV, 20.45%) and C─C (284.81 eV, 70.60%) peaks’ intensity with respect to the unsonicated (Figure 2b) samples, however, the ratio of C=O (288.65 eV, 8.95%) to C─C remained the same. The XPS observations are shown in Table 1, reflecting an overall decrease in the oxygen concentration, originating from the C─O group. Actually, it is not clear at this moment whether the C─O group is directed bonded to the flakes’ surface, or clustered as a fragment on to the debris. Indeed, the HRTEM (Figure 3a) exhibits pronounced ODs after the sonication stage, and therefore the type of the removed oxygen groups will be further elucidated in the following sections. We attempted to further decrease the concentration of OD by performing water rinsing.

2.2.3. Surplus Treatment by Water Rinsing, After the Sonication Process

The GO flakes deposited on Au/mica substrates were treated by water rinsing process (as given in Experimental Section) after the 15 min of sonication. The as-obtained layers were examined by AFM and Kelvin probe force microscopy (KPFM). Figure 4a shows the AFM topography of a representative sample with a few different GO flakes’ sizes. Figure 4b shows KPFM contact potential map of the same surface as shown in panel (a), indicating clearly the location of GO layers. Line profiles plotted in

![Figure 3](image-url)

**Figure 3.** Characterization of the GO samples after dilution and short sonication: a) HR-TEM topography image in real space of a single GO layer suspended on a TEM grid, after the 15 min sonication treatment of a diluted solution; b) a zoom-in of the image in (a); c) Fourier transform of image in (b), showing two distinct regions: an inner part at low frequency, corresponding to a distorted region as framed by a green line in (b); an outer-ring at a higher frequency, related to the “graphenic” region marked by blue line in (b); d) C 1s XPS spectrum of GO after 15 min sonication.
Figure 4c show layer thickness of 1–2 nm, thus proving the existence of single or double layers after the combined treatment.

The STM image in Figure 5a resembles, at a first glance, that of a pristine graphene, with substantially less-distorted regions with respect to images of unrinised samples. However, the image in Figure 5a shows variations in bond lengths and appearance of some rippling after rinsing. Typical $dI/dV$ curve measured after the double treatment is shown in Figure 5b. The spectrum displays a parabolic shape with shoulders at negative and positive voltages, characterizing, and oxygen lying atoms in the surrounding. However, the spectrum is narrower than that obtained in Figure 2d on purchased GO and wider than that taken on a freshly cleaved highly oriented pyrolytic graphite (HOPG) shown in Figure S4, Supporting Information. It should be noted that this type of $dI/dV$ is obtained on most of the GO flake independently of the tip location, confirming an average lower density of oxygen functional groups, as compared with the as-purchased GO flakes. The XPS spectrum (Figure 5c) of the diluted and sonicated GO flakes treated with water rinsing demonstrates a weak intensity of the C–O peak (286.00 eV, 4.95%) relative to that of C–C peak (284.67 eV, 87.19%). The C–O/C–C ratio was further reduced with respect to that found in as-purchased and as-sonicated samples, thus revealing an additional loss of oxygen atoms. In contrast, the contribution of the C=O band (287.96 eV, 7.86%) remained almost unchanged upon rinsing (see Table 1).

By analyzing the results shown in Figure 5, several things can be noticed. The rippling seen in the STM image can be due to oxygen functional groups entrapped between the GO layer and the substrate, whereas the different bond lengths can be associated with oxygen functional group bonded to GO surface. The XPS results along with the diminution of the distorted regions in the STM image, suggest that part of the C–C bonds have recovered upon a removal of weakly (e.g., van der Waals) bonded oxygen groups by the water rinsing, but the covalently connected oxygen groups (e.g., C=O) stayed intact. This finding is in agreement with those published by Bonanni et al.\cite{42}

Further clarification about the involved oxygen species was done using FTIR spectroscopy, complementing the information gained from the XPS spectroscopy. Figure 6 shows FTIR spectra of as-purchased, sonicated (15 min), and sonicated and...
Figure 7. Model for GO of as-purchased multilayer and after dilution, sonication and rinsing (monolayer). The blue balls are the oxygen clusters (also known as debris).

water-rinsed GO flakes, deposited on Au/mica substrates, as given in the indent of the figure. For comparison, the spectra were normalized with respect to the C–C peak intensity. The spectrum of the as-purchased GO sample comprised a few vibration modes, identified as the C=O, C–C, C–OH, and C–O–C groups. The C–C is related to the graphene flakes. The C=O more likely exists at the flake rims, and other oxygen species maybe attached to defect sites or to ODs. The FTIR spectra of the sonicated GO flakes (green curve) showed some reduction of the C–OH and C–O–C, with minor influence on the C=O stretching mode. More important, the surplus water rinsing after sonication, induced a substantial drop of C=O and C–O–C peak intensity, along with minor effect on the strong C=O bond. The FTIR observations are compatible with the trend seen in the XPS experiments, as well as in the pronounced recovery of graphene morphology seen in the STM image (Figure 5a). The fact that water rinsing diminished the presence of the C–OH and C–O–C groups, suggests that these species already existed as fragments held weakly on top of OD.

Although, a substantial reduction of oxygen concentrations was shown in the XPS and FTIR measurements when progressing from as-purchased to the fully treated (sonication and water rinsing) samples, oxygen-containing residues remained. As suggested earlier, those residues can be related to ODs entrapped between single flakes and the Au/mica substrate. This assumption is further supported by the appearance of rippling, as well as by the fact that unoxidized regions on a flake are compatible with pure graphene. This can happen when a flake is suspended by the OD legs, avoiding direct contact with the substrate, which would normally induce strained graphene. The scheme presenting the GO flakes, which underwent evolution from the as-purchased to that found after full treatment, is shown in Figure 7.

3. Conclusion

This study analyzed the morphology, chemical composition, and local electrical properties of GO flakes, which were treated by simple procedures, including short-time sonication in ethanol of the as-purchased solutions, their deposition onto precleaned Au/mica substrates and finally a surplus wash with distilled water. The evolution of the flake properties under various stages were examined by microscopy (TEM, HR-TEM, STM, AFM, and KPFM) and spectroscopy (STS, XPS, Raman, and FTIR). The microscopy investigations of the GO flakes before treatments exhibited regions with a close resemblance to pristine graphene and at the same time, showed distinct islands composed from oxygen-related fragments (named ODs). Following the simple sonication and water wash treatments, the damaged island regions vanished. The XPS and FTIR uncovered gradual loss of oxygen content from the as-purchased sample to that of the water-rinsed ones; in particular the amount of C=O, C–OH, and C–O–C groups had been reduced, albeit that of C=O nearly remained unchanged. The locations of the C=O groups were assigned before to terminating bonds along the flakes’ rims. The preservation of graphene-like regions across the studied flakes occurred due to their suspension by OD legs, entrapped between them and the Au substrate. The STS spectra before the treatments displays bandgap energy typical of oxidized graphene. In contrast, beyond all treatments, the STS spectra are characteristics of graphene with uneven distribution of oxygen on the surface. The study exposed simple and mild treatments for the regulation of GO character, which can be implemented for various graphene derivatives or other layered materials.

4. Experimental Section

Extended Sample Preparation: Single layer GO dispersion in ethanol, 5 mg mL$^{-1}$, was purchased from ACS Material. The solution was diluted in ethanol absolute 99.8% H.P. and sonicated for 15 min, at half frequency. Au(111)/mica substrate was purchased from PHASIS and was cleaned in ethanol and DI water. GO flakes (from a solution) were deposited on Au/mica substrate by drop casting method. After overnight deposition, some samples were washed in distilled water to remove debris, and all samples were dried in an oven before microscopy and spectroscopy measurements. For transmission electron microscopy (TEM) measurements, suspended GO flakes were deposited by drop-casting diluted and sonicated GO solution on top of ultrathin holey carbon grids precleaned with plasma cleaner.

The presence of oxygen in the films was detected by Raman and FTIR spectroscopy. The number of deposited GO layers was checked by a combination between atomic AFM and KPFM means. The distribution of the oxygen functional groups and/or OD across GO flakes was investigated by...
STM and HR-TEM. STM measurements were carried out on a GO film deposited over a continuous Au/mica substrate chosen for achieving low-noise STM measurements. All the d/dV curves shown are averaged over tens of d/dV and normalized to I/V. HR-TEM measurements were carried out on a GO film, suspended (without substrate) over holes of a TEM grid. Information about the chemical nature of the oxygen functional groups adsorbed to the surface from GO flakes of different treated solution, were obtained by performing XPS and FTIR spectroscopy.

Characterization Methods: Raman spectra were obtained using a micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR), equipped with a Nd:YAG laser for excitation at 532 nm. The HR-TEM images were acquired using a monochromated and double corrected Titan Themis G2 60-300 (FEI/Thermo Fisher) operated at 60 keV.

The STM/STS measurements were carried out in an ultrahigh-vacuum variable temperature AFM/STM ScientaOmicron system using electrochemically prepared tungsten tips. Differential conductance dI/dV curves were directly obtained using a lock-in amplifier operated at a modulation voltage of 5 mV and a time constant of 30 ms. The shown SSTS spectra are the result of averaging tens of dI/dV curves taken at the same location and further normalizing them to I/V.

AFM and KPFM measurements were carried out with an Asylum research MFP-3D AFM system in ambient air. The resonance frequency of the cantilever is around 70 kHz, the conductive Ti/Ir (5/20)-coated silicon tip radius is $\approx$28 nm. The KPFM was carried out in dual-pass mode. XPS measurements were carried out in an analysis chamber (UHV—210-10 Torr during analysis) using a Versaprobe III—PHI Instrument (PHI, USA). The sample was irradiated with a focused X-ray Al Kx monochromated X-rays source (1486.6 eV) using (X-ray beam size 50 pm, 12.5 W, and 15 kV). The resulting photoelectrons are directed to a spherical capacitor analyzer (SCA). The sample charging was compensated by a dual beam charge neutralization based on a combination of a traditional electron flood gun and a low energy argon-ion beam. High-resolution X-ray photoelectron spectroscopy (HR-XPS) was measured for the CsI line; HR-XPS measurements were carried out using a pass energy of 20 eV and step size of 0.05 eV. The core-level binding energies of the different peaks were normalized by setting the binding energy for the result of averaging tens of dI/dV curves taken at the same location and further normalizing them to I/V.

FTIR spectroscopy measurements were carried out using Jasco 6800 FTIR Spectrometer (Tokyo, Japan). The sample was deposited on the diamond attenuated total reflection (ATR) crystal. The measurement taken with a resolution of 4 cm$^{-1}$. Each scan was accumulation of 64 runs. Background of Au substrate spectrum was reduced.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors acknowledge the financial support from the Israel Council for Higher-Focal Area Technology (No. 872967), the Volkswagen Stiftung (No. 88116), the Israel Science Foundation (No. 2528/19), the Israel Science Foundation (No. 1045/19), USA National Science Foundation – US/Israel Binational Science Foundation (NSF-BSF, No. 2017/637).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
graphene oxide, high-resolution transmission electron microscopy, oxygen debris, scanning tunneling microscopy, X-ray photoelectron spectroscopy

Received: September 18, 2020
Published online: October 25, 2020

[1] P. R. Wallace, Phys. Rev. 1947, 71, 622.
[2] A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183.
[3] Y. Zhang, L. Zhang, C. Zhou, Acc. Chem. Res. 2013, 46, 2329.
[4] H. Tetlow, J. P. De Boer, I. J. Ford, D. D. Vvedensky, J. Coraux, L. Kantorovich, Phys. Rep. 2014, 542, 195.
[5] A. Douglas, C. L. Pint, ECS J. Solid State Sci. Technol. 2017, 6, M3084.
[6] P. Yu, S. E. Lowe, G. P. Simon, Y. L. Zhong, Curr. Opin. Colloid Interface Sci. 2015, 20, 329.
[7] G. G. Gebregziabher, A. S. Asemahegne, D. W. Ayele, M. Dhakshnamoorthy, A. Kumar, Mater. Today Chem. 2019, 12, 233.
[8] B. C. Brodie, Philos. Trans. R. Soc. Lond. 1859, 149, 249.
[9] H.-P. Boehm, A. Claus, G. O. Fischer, U. Hofmann, Z. Anorg. Allg. Chem. 1962, 316, 119.
[10] W. S. Hummers Jr., R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339.
[11] S. V. Tkachev, E. Yu. Buslaeva, A. V. Naumkin, L. S. Kotova, I. V. Laure, S. P. Gubin, Inorg. Mater. 2012, 48, 796.
[12] H. Shen, L. Zhang, M. Liu, Z. Zhang, Theranostics 2012, 2, 283.
[13] M. Choudhary, V. Kumar, A. Singh, M. P. Singh, S. Kaur, G. B. Reddy, R. Parshica, S. P. Singh, K. Arora, J. Biosens. Bioelectron. 2013, 4, 1.
[14] S. Priyadarsini, S. Mohanthy, S. Mukherjee, S. Basu, M. Mishra, J. Nanostruct. Chem. 2018, 8, 123.
[15] S. M. Coman, I. Podolean, M. Tudorache, B. Cojocaru, V. I. Parvu, M. Puche, H. Garcia, Chem. Commun. 2017, 53, 10271.
[16] M. Favaro, L. Ferrighi, G. Fazio, L. Colazzo, C. Di Valentin, C. Durante, F. Sedona, A. Gennaro, S. Agnoli, G. Granazzo, ACS Catalysis 2014, 5, 129.
[17] Y. Liu, in IOP Conference Series: Earth and Environmental Science, IOP Publishing, Bristol 2017, p. 12060.
[18] T. A. Amollo, G. T. Mola, V. O. Nyamori, Sol. Energy 2018, 171, 83.
[19] G. Kucinskis, I. Podolean, M. Tudorache, B. Cojocaru, V. I. Parvu, M. Puche, H. Garcia, Chem. Commun. 2017, 53, 10271.
[20] Z. Li, S. Gadielli, Y. Yang, G. He, J. Guo, J. Li, Y. Lu, C. A. Howard, D. J. Brett, I. P. Parkin, Energy Storage Mater. 2019, 17, 12.
[21] H. Luo, G. Aucberlonie, J. Zou, J. Appl. Phys. 2017, 122, 145101.
[22] A. Lerf, H. He, M. Forster, J. Klinowski, J. Phys. Chem. B 1998, 102, 4477.
[23] B. Yuan, C. Bao, X. Qian, P. Wen, W. Xing, L. Song, Y. Hu, Mater. Res. Bull. 2014, 55, 48.
[24] J. Tian, H. Cao, W. Wu, Q. Yu, Y. P. Chen, Nano Lett. 2011, 11, 3663.
[25] M. Z. H. Khan, S. M. F. Shahed, N. Yuta, T. Komeda, J. Electron. Mater. 2017, 46, 4160.
[26] S. Abdolhosseinzadeh, A. Gharbadeh, H. S. Kim, Sci. Rep. 2015, 5, 10160.
[27] K. Krishnamoorthy, M. Veerapandian, K. Yun, S.-J. Kim, Carbon 2013, 53, 38.
[28] N. R. Wilson, P. A. Pandey, R. Beanland, R. J. Young, I. A. Kinloch, L. Gong, Z. Liu, K. Suenaga, J. P. Rourke, S. J. York, ACS Nano 2009, 3, 2547.
[29] C. G. Navarro, J. C. Meyer, R. S. Sundaram, A. Chuvilin, S. Kurash, M. Burghard, K. Kern, U. Kaiser, Nano Lett. 2010, 10, 1144.
[30] Y. Zhu, X. Li, Q. Cai, Z. Sun, G. Casillas, M. Jose-Yacaman, R. Verduzco, J. M. Tour, J. Am. Chem. Soc. 2012, 134, 11774.
[31] K. A. Mkhoyan, A. W. Contrryman, J. Silcox, D. A. Stewart, G. Eda, C. Mattevi, S. Miller, M. Chhowalla, Nano Lett. 2009, 9, 1058.
[32] H. O. Doğan, D. Ekinci, Ü. Demir, Surf. Sci. 2013, 611, 54.
[33] C. Harthcock, A. Jahanbekam, Y. Zhang, D. Y. Lee, J. Phys. Chem. C 2017, 121, 20051.
[34] S. Katano, T. Wei, T. Sasajima, R. Kasama, Y. Uehara, Phys. Chem. Chem. Phys. 2018, 20, 17977.
[35] D. Pandey, R. Reifenberger, R. Piner, Surf. Sci. 2008, 602, 1607.
[36] R. Rozada, J. I. Paredes, M. J. López, S. Villar-Rodil, I. Cabria, J. A. Alonso, A. Martínez-Alonso, J. M. D. Tascón, Nanoscale 2015, 7, 2374.
[37] S. T. Wang, Y. F. Lin, Y. C. Li, P. C. Yeh, S. J. Tang, B. Rosenstein, T. H. Hsu, X. Zhou, Z. Liu, M. T. Lin, W. Bin Jian, Appl. Phys. Lett. 2012, 101, 183110.
[38] H. R. Thomas, S. P. Day, W. E. Woodruff, C. Vallés, R. J. Young, I. A. Kinloch, G. W. Morley, J. V. Hanna, N. R. Wilson, J. P. Rourke, Chem. Mater. 2013, 25, 3580.
[39] A. M. Dimiev, T. A. Polson, Carbon 2015, 93, 544.
[40] H. R. Thomas, C. Vallés, R. J. Young, I. A. Kinloch, N. R. Wilson, J. P. Rourke, J. Mater. Chem. C 2013, 1, 338.
[41] A. Naumov, F. Grote, M. Overgaard, A. Roth, C. E. Halbig, K. Nørgaard, D. M. Guldi, S. Eigler, J. Am. Chem. Soc. 2016, 138, 11445.
[42] A. Bonanni, A. Ambrosi, C. K. Chua, M. Pumera, ACS Nano 2014, 8, 4197.
[43] D. W. Kim, J. Jang, I. Kim, Y. T. Nam, Y. Jung, H.-T. Jung, J. Phys. Chem. C 2018, 122, 17507.
[44] T. M. McCoy, G. Turpin, B. M. Teo, R. F. Tabor, Curr. Opin. Colloid Interface Sci. 2019, 39, 98.
[45] X. Chen, B. Chen, Environ. Sci. Technol. 2016, 50, 8568.
[46] S. J. Tjung, S. M. Hollen, G. A. Gambrel, N. M. Santagata, E. Johnston-Halperin, J. A. Gupta, Carbon 2017, 124, 97.
[47] W.-X. Wang, Y.-W. Wei, S.-Y. Li, X. Li, X. Wu, J. Feng, L. He, Phys. Rev. B 2018, 97, 85407.
[48] A. Criado, M. Melchionna, S. Marchesan, M. Prato, Angew. Chem., Int. Ed. 2015, 54, 10734.
[49] J. J. Navarro, F. Calleja, R. Miranda, E. M. Pérez, A. L. V. de Parga, Chem. Commun. 2017, 53, 10418.
[50] A. Pélinkás, P. Súle, M. Szendrő, G. Molnár, C. Hwang, L. P. Biró, Z. Osváth, Carbon 2016, 107, 792.
[51] J. B. Wu, M. L. Lin, X. Cong, H. N. Liu, P. H. Tan, Chem. Soc. Rev. 2018, 47, 1822.