Facile preparation of polymer coating on reduced graphene oxide sheets by plasma polymerization

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ABSTRACT
Surface modification was needed in the application of nanoparticles. In this work, a simple method was proposed to prepare polymer coatings on reduced graphene oxide (rGO) sheets. A polymer coating of plasma polymethyl methacrylate (pPMMA) was synthesized on the surface of rGO by plasma polymerization using dielectric barrier discharge plasma equipment. There was good adhesion between the pPMMA coating and the surface of rGO. Furthermore, the pPMMA coating consisted of two layers classified by their interactions with rGO:pPMMA in the outer layer physically adhered to the surface and pPMMA of the under layer interacted with rGO by chemical bonding. The thicknesses of the outer and under layers were 1.5–3 nm and 2–3.5 nm, respectively. Moreover, the morphology and thickness of pPMMA coatings could be effectively regulated by controlling the input voltage and processing time. The process of the deposition of pPMMA coating was preliminarily studied and discussed in this work. We believed that this strategy could open up an avenue for the surface modification of other kinds of nanoparticles.

GRAPHICAL ABSTRACT

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1. Introduction
Nanoparticles have many features which are advantageous for applications in all kinds of fields [1–3]. In the case of graphene, a widely studied and promising inorganic nano material [4, 5], it has been applied to areas of energy storage, sensors, catalyst and so on [6–8]. For applications, we usually hope to introduce some specific performances through surface modification without damaging its bulk properties, besides inherently excellent properties of graphene. For example, Xu’s group prepared a series of GO derivatives including aminated GO, poly(acrylamide)-functionalized GO, poly(acrylic acid)-functionalized GO and poly-(ethylene glycol)-functionalized GO to improve its biocompatibility [9]. Hwang et al. produced an oxygen-functionalized
porous reduced graphene oxide (rGO) by the alkaline treatment with a sodium hydroxide (NaOH) etchant [10]. However, chemical methods for modification always associate with a lot of toxic and corrosive reagents, as well as complex steps and long-time treatments, which would impede its further development and applications. On the contrary, low-temperature plasma [11–14] is an effective technology to compensate for those shortcomings because of its higher energy density compared with conventional chemistry techniques and high concentration of charged and chemical species (electrons, ions, radicals, metastables and photons) to lower the activation energy for chemical reactions [15]. As a useful tool for reactions and synthesis, low-temperature plasma is a dry-chemical method which has features of rapid reaction processes and can induce some unable reactions under traditional chemical systems.

In the modification of carbon-based materials with low-temperature plasma technology, some work has been carried out in recent years. For example, doped carbon materials are of interest when used as electrode or catalytic materials. Neustroev et al. introduced pyrrole-N and pyridine-N doping to the graphene by N₂ plasma [16]. Lai introduced oxygen-containing groups to the surface of electrospun carbon nanofibers using oxygen plasma to improve its capacitive behavior [17]. Except for the functional modification of carbon-based materials, polymerization of organic monomers can also be conducted to prepare an ultrathin film of a few nanometers on materials under plasma conditions. The process can be described that monomers are converted into plasma polymers via the formation of gas-phase radicals and their recombination at radial sites during film growth, denoted as plasma polymerization [18–20]. Especially for low-temperature and low-pressure plasma [13, 21], it has particularly extraordinary advantages for plasma polymerization and deposition. Moreover, plasma polymer films deposited may have a broad range of properties [22–25], like good adhesion, pin-hole-free, high retention of monomer groups, branched, crosslinking to some extent and variable compositions, depending on the energy input [26–28]. Indeed, the energy invested per particle of the gas mixture in the plasma atmosphere (an energy-related dose factor named 'Yasuda factor', \( YF = W/MF \), was proposed to describe it [22]) would significantly influence properties mentioned and the morphology of deposited films. Petersen and his coworkers synthesized plasma polymer films by atmospheric filamentary plasma dielectric barrier discharge (DBD), and they demonstrated molecular structures of siloxane based plasma films could be tuned by the energy assigned per particle [29]. Similarly, Borra et al. presented a route for grafting polyacid and polyether coatings on polymers by post-discharge polymerization of the liquid vinyl monomer. They confirmed both DBD energy density and the time of exposure to plasma would influence coating properties [30]. Moreover, plasma polymer films can also be deposited onto quite tiny matters at nanometer/micron scales by the control of plasma conditions to endow materials with new interfaces and specific performances, such as catalysis, biocompatibility, barrier, wettability and reinforcement interface [29–32], without damaging its bulk properties [33]. Taking carbon materials as an example, Chen and his coworkers deposited heptylamine thin films on carbon fibers by a three-step plasma treatment to enable strong bonding to a matrix. They also demonstrated strong adhesion between the plasma polymer and the CF [34]. Similar work was also conducted by Friedrich’s group [35]. He et al. prepared ultrathin polystyrene film on the surface of carbon nanotubes, and the dispersion of multi-wall carbon nanotubes in polystyrene composites was significantly improved [36]. Carbon black was also modified by plasma polymerization by Mathew to reduce its surface energy and improve the dispersion in rubbers [37]. But in fact, when used for modification of carbon materials by plasma polymerization, plasma is usually served only for the initiation of subsequent polymerization in solution systems [38–40], and relatively few jobs are conducted to study in situ one-step deposition of plasma polymers on nano carbon materials. The former method for preparing polymer coatings still need solvent systems for subsequent polymerization which always has cumbersome procedures and toxicity. Furthermore, the morphology and structure of in situ one-step deposited plasma polymer coatings on nanoparticles are hard to regulate and control [41, 42], and seldom work has been done to discuss it.

Thus, low-temperature plasma used to introduce plasma polymer coatings onto nanoparticles by the method of in situ one-step deposition was studied in this work. In detail, a homebuilt DBD low-temperature plasma equipment was used to modify rGO sheets, with methyl methacrylate (MMA) as reaction precursors being carried into the reactor by Ar gas flow. Subsequently, a homogeneous plasma poly-methyl methacrylate (pPMA) coating of several nanometers on rGO was prepared. The morphology and structure of the coating were effectively regulated. It was further confirmed that the coating adhered tightly to the surface of rGO. Moreover, the structure and composition of the deposited pPMA were characterized by ¹H nuclear magnetic
resonance and gel permeation chromatography. In summary, the method used in this work was efficient and effective to modify nanoparticles with rapid chemical reactions in the plasma environment. In fact, modified nanoparticles were not limited to rGO. Similarly, the coating may also be composed of other components from different precursors, even including inorganic materials [43]. As a prospective technology, plasma processing of nano materials has advantages over traditional wet-processing methods in many aspects, such as efficiency, applicability and environmental protection, and deserves more attentions.

2. Experimental

2.1. Materials

Natural graphite flakes (NG) with an average particle size of 200 meshes and a purity of 99.9% were purchased from Shenhua Research Institute (Changsha, China) and were used without further purification. MMA, acetone, concentrated sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), hydrochloric acid (HCl), potassium permanganate (KMnO₄) and hydrogen peroxide (H₂O₂) were supplied by Haihong Chemical Reagents Company (Chengdu, China). All reagents were of analytical grade. MMA and acetone were distilled to remove impurities.

2.2. Preparation of pPMMA-coated rGO sheets

rGO sheets used in this work were prepared by reducing GO using Vitamin C (Vc) [44]. GO was prepared from NG powder using a modified Hummers’ method [45]. pPMMA-coated rGO sheets were processed by homebuilt DBD plasma equipment with a CTP-2000P plasma generator. The scheme of the DBD plasma setup is illustrated in Figure 1.

In the DBD plasma system, a crafted polycarbonate material box was used as the vacuum reactor with a couple of rectangular electrodes inside, whose length was 33 cm and width was 23 cm. Two dielectric plates were attached to inside faces of electrodes, respectively, with a separation distance of 2 cm. rGO was put into the reactor before the chamber was evacuated using a 2XZ-2 rotary vane vacuum pump and filled with argon for three times to ensure a argon atmosphere (The purity of argon used was 99.999%). MMA monomer was carried into the reactor by Ar gas flow with a flow rate of 5 sccm controlled by a LZB-3WB glass rotor flow meter at 25 °C. The vacuum pump kept working and the pressure of the chamber was maintained at around 700 Pa. Input voltages and processing times were controlled to investigate their influences on the deposition of pPMMA. The frequency was controlled by the plasma generator at 17 kHz.

2.3. Characterization

Fourier transform infrared (FTIR) spectroscopy was performed over the wave number range of 4000–400 cm⁻¹ using a Nicolet 6700 FTIR spectrometer (Nicolet Instrument Company, USA) with a KBr pellet technique. X-ray photoelectron spectroscopy (XPS) measurement was performed on an XSAM800 (Kratos Company, UK) instrument with AlKx radiation (hν = 1486.6 eV) and XPSpeak 41 software (Chemistry, CUHK) was used to calculate the atomic concentrations. Field-emission scanning electron microscopy (FESEM, JSM-5900LV, Japan) and atomic force microscope (AFM, BRUKER NanoScope V) were employed to characterize the morphology of samples. The structural characterization of pPMMA was examined by ¹H nuclear magnetic resonance (NMR) spectroscopy. ¹H NMR spectra was recorded in (CD₃)₂CD at 25°C using a Bruker AV 600 MHz instrument, and peak positions were reported with respect to tetramethylsilane (TMS). The weight average molecular weight (Mw) and molecular weight distribution (PDI: Mw/Mn) of the plasma polymer were determined by gel permeation chromatography (GPC, HLC-8320GPC, Japan). Tetrahydrofuran was used as the eluent at a flow rate of 0.6 mL/min

3. Results and discussion

3.1. Morphology evolution of pPMMA deposited on rGO sheets

FESEM images in Figure 2(a–d) showed the morphology evolution of plasma polymer (pPMMA) on rGO as a function of time (treated for 5, 10, 20 and 40 min and named rGO/MMA-5min, rGO/MMA-10min, rGO/MMA-20min and rGO/MMA-40min) when the input voltage was 85 volts. Compared with rGO (Figure 2(e)) and rGO processed at 85 v without MMA joined (p-rGO) (Figure 2(f)), SEM images of rGO/MMA-5min, 10 min, 20 min and 40 min in Figure 2(a–d) appeared to have apparent pPMMA deposits. The deposits on rGO/MMA-5min and 10 min samples appeared as aggregate structures, while those on rGO/MMA-20min and 40 min samples were presented as homogeneous coatings. Thus, it was easy to find that the morphology of pPMMA deposits tended to develop from aggregate structures to a complete and uniform coating with treating time. What’s more, as shown in Figure 3, we could also observe that pPMMA deposits preferentially grew at the edges or folds of rGO sheets at
first where was rich in defects, such as oxygen-containing groups that could be used as chemically active sites [46]. With further reaction and deposition, complete coatings would form on rGO sheets and the coating grew thicker with time.

Similarly, FESEM images in Figure 4(a–e) showed the morphology changes of pPMMA deposits with input voltages (treated at 65, 75, 85, 95 and 105 volts and named rGO/MMA-65v, rGO/MMA-75v, rGO/MMA-85v, rGO/MMA-95v and rGO/MMA-105v) for 40 min. Similar results were obtained from the images of rGO/MMA-65, 75, 85, 95 and 105 v in Figure 4(a–e) as mentioned above. At low input powers of 65 and 75 v, pPMMA deposits also appeared as aggregates at the edges and folds of rGO. When it increased to 85 v or more, coatings of pPMMA were formed. However, the difference from the one mentioned above was that the pPMMA coating became more smooth instead of growing thicker as the input voltage increased. The reason was that with the increase of input voltages, the discharge power increased, and excited particles with higher energy caused marked etching on the surface of pPMMA coatings which destroyed micro-nano structures of pPMMA film and prevented coating thickening [47]. In brief, for the plasma polymerization of MMA and deposition of pPMMA, processing time and input voltages could be controlled to effectively regulate the morphology and structure of pPMMA coatings. rGO sheets with totally new surfaces (pPMMA coatings) could be produced within a short time.

3.2. Analysis of the pPMMA coating

To further investigate the effectiveness and durability of pPMMA coating on the surface of rGO, rGO/MMA-85v (40 min) was extracted with acetone for 48 h to remove physically adhered pPMMA deposits. The morphology of samples before and after extraction treatment was present in Figure 5. The SEM image of rGO/MMA-85v-w (the sample extracted
with acetone for 48 h) in Figure 5(b) showed obvious change of the surface morphology compared with rGO/MMA-85v (Figure 5(a)), due to the removal of part of physical adsorption pPMMA deposits. However, a layer of pPMMA coating could still be observed (Figure 5(b)) compared with the surface appearance of rGO (Figure 2(e)), which meant good adhesion between the remaining pPMMA and rGO surface. Thus, pPMMA coating on rGO produced through this method had good durability and adhesion.

Besides, FTIR and XPS were employed to further proof the existence of the remaining pPMMA coating on the extracted sample as shown in Figure 6. A peak at 1630 cm\(^{-1}\) which was attributed to C=C stretching vibration from unoxidized graphitic domains could be observed in the FTIR spectra of rGO, rGO/MMA-85v and rGO/MMA-85v-w in Figure 6(a). For rGO/MMA-85v, a narrow vibrational band at 1730 cm\(^{-1}\) was seen due to the C=O stretching vibration caused by the deposition of pPMMA (further explained in supplementary material Figure S1) which was not observed in the FTIR spectrum of rGO. But the peak of C=O stretching vibration at 1730 cm\(^{-1}\) still remained in rGO/MMA-85v-w which implied that pPMMA was residual on...
the surface of the sample. In addition, XPS survey spectra of rGO, rGO/MMA-85v and rGO/MMA-85v-w were shown in Figure 6(b–d). All XPS spectra of C1s signal showed the presence of C–C/H (~284.6 eV), C–O (epoxy and alkoxy, ~286.1 eV) and C=O (carbonyl, ~288.4 eV) groups. Compared with rGO (Figure 6(b)), the intensity of peaks of C=O and C–O in Figure 6(c) increased significantly and the C/O ratio (Table 1) according to the peak areas of C and O elements decreased to 2.03, which was attributed to the deposition of pPMMA on rGO sheets. However, for the sample of rGO/MMA-85v-w in Figure 6(d), the intensity of peaks of C–O and C=O groups decreased obviously compared with rGO/MMA-85v, and its C/O ratio increased to 2.30 which was closer to 2.50 of rGO. The reason was that physically adhered pPMMA deposits were removed after extraction (C/O > 2.03), while the other part of pPMMA chemically bonded to the surface of rGO was still residual (C/O < 2.50).

According to above results, we could deduce that the pPMMA coating on rGO sheets consisted of two parts as shown in Figure 7, classified by their interactions with rGO. pPMMA of the outer layer physically adhered to the surface and pPMMA of the under layer interacted with rGO by chemical bonding. The outer layer was mainly formed by the accumulation of self-polymerization plasma polymer synthetized on the surface of rGO or in the state of gas phase, while the under layer was made up from products that reacted directly with active points on the surface of rGO.

To further explore the structure of pPMMA coating on rGO, AFM images of rGO, rGO/MMA-85v and rGO/MMA-85v-w were shown in supplementary material Figure S2. Moreover, the thickness of samples was measured by AFM depicted in Figure 8. The curves of height changes in Figure 8 corresponded to the thickness of samples at the white horizontal line in supplementary material Figure S2 (mica sheets as the substrate). We could find that the thickness of rGO sheet (Figure 8(a)) was 0.8 nm, slightly larger than the theoretical value of monolayer graphene for not completely reducing GO [48]. However, the thickness of rGO/MMA-85v and rGO/MMA-85v-w increased to 11 nm and 5–8 nm, respectively, as depicted in Figure 8(b,c). According to the above double-layer structure of pPMMA/rGO nanocomposites in Figure 7, changes of the thickness among rGO, rGO/MMA-85v and rGO/MMA-85v-w could be explained by the formation of the pPMMA coating and the removal of physically adhered pPMMA. Comparing rGO/

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**Table 1.** The C/O ratios of rGO, rGO/MMA-85v and rGO/MMA-85v-w.

|          | C (%) | O (%) | C/O |
|----------|-------|-------|-----|
| rGO      | 71.28 | 28.22 | 2.53 |
| rGO/MMA-85v | 67.05 | 32.95 | 2.03 |
| rGO/MMA-85v-w | 69.69 | 30.31 | 2.30 |

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Figure 6. FTIR (a) and XPS (b–d) spectra of rGO, rGO/MMA-85v and rGO/MMA-85v-w.
MMA-85v with rGO/MMA-85v-w, we could measure that the thickness of the physically adhered pPMMA coating (outer layer on one side of rGO) was 1.5–3 nm. Similarly, comparing rGO with rGO/MMA-85v-w, the thickness of the chemically bonded pPMMA coating (under layer on one side of rGO) was 2–3.5 nm. In summary, the pPMMA coating on rGO prepared was as thin as several nanometers and well adhered to rGO.

To gain further insight into pPMMA, \(^1\)H nuclear magnetic resonance (\(^1\)HNMR) was used to characterize the molecular structure of pPMMA. Figure 9 showed the \(^1\)H NMR spectra of the pPMMA product extracted from rGO/pPMMA composites. O–CH\(_3\), C–CH\(_3\) and C–CH\(_2\)–C were denoted as a, b and c, respectively, depicted by the molecular structure formula inset in Figure 9. Peak areas in Figure 9 were calculated based on the rightmost peak (set the area of it to be 1), and their values of the relative area were recorded just below the spectrum. Besides, the inserted spectrum in Figure 9 was the magnification of the curve in the red dotted line. Based on the ratio of peak areas, the ratio of hydrogen atoms at different chemical positions was calculated. Finally, the ratio of O–CH\(_3\):C–CH\(_3\):C–CH\(_2\)–C (a:b:c) of pPMMA was 3.84:3.93:1, totally different from that (1:1:1) of PMMA. According to the mechanism of plasma polymerization [22], it was mainly because monomer molecules became extensively fragmented in high-power plasmas and small fragments then recombined randomly to form products. Moreover, we also found that the ratio of O–CH\(_3\):C–CH\(_3\) (a:b) was close to 1:1, similar with that of PMMA. This suggested that some functional groups of the monomer were preserved during plasma polymerization instead of being totally broken [28]. Such a feature of plasma polymerization was beneficial to keep the same functional groups of plasma polymers as the monomer, which could either be used for graft polymerization, or bring some specific properties.

For example, plasma polymerization technology can be used to synthesize poly(ethylene oxide) (PEO)-like coatings using monomers containing the structural element –CH\(_2\)CH\(_2\)O– [31]. The PEO-like coating shows remarkable resistance to bio-fouling [49]. Thus, nanoparticles (such as rGO) covered by such a non-fouling coating can be fabricated and

\[ \text{Figure 7. Illustration of pPMMA coating on rGO sheets.} \]

\[ \text{Figure 8. The thickness of (a) rGO, (b) rGO/MMA-85v and (c) rGO/MMA-85v-w measured by AFM.} \]
used for the biomedical application [50]. Similarly, nanoparticles coated by non-fouling plasma polymers are also a good choice for the microfluidic application [51]. In addition, nanoparticles coated by specific plasma polymers may have improved compatibility with matrix materials when used as fillers, and the adhesive interaction between nanoparticles and matrix materials can be enhanced. For instance, rGO coated by pPMMA can be used as fillers in the PMMA matrix to enhance the mechanical property of PMMA, just as Sellam’s work [52]. The modified rGO can also serve as conductive fillers to prepare conducting/electromagnetic shielding polymer composites with a low percolation threshold because of its improved compatibility with matrix materials and good electrical conductivity. More possible applications for rGO covered by plasma polymer coatings are depicted in Figure 10. As an efficient and effective method for surface modification of nanoparticles, plasma polymerization deposition deserves more attentions and further applications.

4. Conclusion

In conclusion, an efficient and effective way of preparing pPMMA polymer coatings on rGO sheets by rapid chemical reactions in Ar plasma was proposed. By controlling the input voltage and processing time, a homogeneous pPMMA coating of several nanometers on rGO was prepared at 85v for 40 min. Its morphology and structure could be effectively regulated. The pPMMA coating had good adhesion with the surface of rGO. More importantly, the method could potentially serve for other nanoparticles as well as rGO. The composition and property of the deposited coating could also be tuned by using different monomers because of the characteristics of high energy, high reactivity and low temperature for DBD Ar plasma. Polymer coatings with diverse functions could be designed to endow nanoparticles with new properties by this method. In addition, possible applications of rGO coated by plasma polymers were talked about. Plasma modification for nanoparticles deserves more attention.

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Disclosure statement
No potential conflict of interest was reported by the authors.

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References

1. Hedayatnasab Z, Abnisa F, Daud WMAW. Review on magnetic nanoparticles for magnetic nanofluid hyperthermia application. Mater Design. 2017;123:174–196.
2. Hussain I, Singh NB, Singh A, et al. Green synthesis of nanoparticles and its potential application. Biotechnol Lett. 2016;38:545–560.
3. Luo X, Morrin A, Killard AJ, et al. Application of nanoparticles in electrochemical sensors and biosensors. Electroanalysis 2006;18:319–326.
4. Singh V, Joung D, Zhai L, et al. Graphene based materials: past, present and future. Prog Mater Sci. 2011;56:1178–1271.
5. Zhu Y, Murali S, Cai W, et al. Graphene and graphene oxide: synthesis, properties, and applications. Adv Mater Weinheim. 2010;22:3906–3924.
6. Arvidsson R, Kushnir D, Molander S, et al. Energy and resource use assessment of graphene as a substitute for indium tin oxide in transparent electrodes. J Clean Prod. 2016;132:289–297.
7. Huang X, Zeng Z, Fan Z, et al. Graphene-based electrodes. Adv Mater Weinheim. 2012;24:5979–6004.
8. Higgins D, Zamani P, Yu A, et al. The application of graphene and its composites in oxygen reduction electrocatalysis: a perspective and review of recent progress. Energy Environ Sci. 2016;9:357–390.

9. Xu M, Zhu J, Wang F, et al. Improved in vitro and in vivo biocompatibility of graphene oxide through surface modification: poly(acrylic acid)-functionalization is superior to PEGylation. ACS Nano. 2016;10:3267–3281.
10. Hwang Y-H, Lee SM, Kim YJ, et al. A new approach of structural and chemical modification on graphene electrodes for high-performance supercapacitors. Carbon. 2016;100:7–15.
11. Ostrikov K. Colloquium: reactive plasmas as a versatile nanofabrication tool. Rev Mod Phys. 2008;77:489–511.
12. Bogaerts A, Neyts E, Gijsbels R, et al. Gas discharge plasmas and their applications. Spectrochim Acta B. 2002;57:609–658.
13. Laroussi M. Low temperature plasma-based sterilization: overview and state-of-the-art. Plasma Process Polym. 2005;2:391–400.
14. Fridman A, Chirokov A, Gutso A. Topical review: non-thermal atmospheric pressure discharges. J Phys D Appl Phys. 2005;38:R1–R24.
15. Atti P, Arora B, Choi EH. Utility of plasma: a new road from physics to chemistry. RSC Adv. 2013;3:12540.
16. Neustroe EP, Burshtein EK, Soloviev BD, et al. Modification of graphene oxide films by radiofrequency N2 plasma. Nanotechnology. 2018;29:144002.
17. Lai C-C, Lo C-T. Plasma oxidation of electrospun carbon nanofibers as supercapacitor electrodes. RSC Adv. 2015;5:38868–38872.
18. Wertheimer MR. Plasma polymerization. Thin Solid Films. 1986;144:L107–L108.
19. Choy KL. Chemical vapour deposition of coatings. Prog Mater Sci. 2003;48:57–170.
20. Denes F. Macromolecular plasma-chemistry: an emerging field of polymer science. Prog Polym Sci. 2004;29:815–885.
21. Fouquet T, Girard-Lauriault P-L. Plasma processes and polymers special issue on: a state of the art of analytical techniques for plasma processing and deposition of organic coatings. Plasma Process Polym. 2015;12:844–845.
22. Friedrich J. Mechanisms of plasma polymerization - reviewed from a chemical point of view. Plasma Process Polym. 2011;8:783–802.
23. Friedrich J, Hildre G. Ultra-thin plasma polymer films as a novel class of adhesion promoters: a critical review. Rev Adhes Adhes. 2015;3:1–52.
24. Coulson SR, Woodward IS, Badyl JPS, et al. Ultralow surface energy plasma polymer films. Chem Mater. 2000;12:2031–2038.
25. Mathew AM, Predeep P. Plasma-polymerized elastomer/conducting polymer composite: structural and optical characterization. Polym Compos. 2013;34:1091–1098.
26. Choukurov A, Polonskyi O, Hanus J, et al. PEO-based nanofibers with improved in vitro and in vivo biocompatibility. Adv Mater Weinheim. 2016;28:159–167.
27. Kuzuya M, Ishikawa M, Noguchi A, et al. Nature of plasma-induced radicals on crosslinked methacrylic polymers studied by electron spin resonance. J Polymer Sci A Polym Chem. 1992;30:379–387.
28. Heidger E, Hussain MM, Körner E, et al. Macroscopic description of plasma polymerization. Plasma Process Polym. 2007;4:229–238.
29. Petersen J, Bechara R, Bardon J, et al. Atmospheric plasma deposition process: a versatile tool for the design of tunable siloxanes-based plasma polymer films. Plasma Process Polym. 2011;8:895–903.

30. Borra J-P, Valt A, Arefi-Khonsari F, et al. Atmospheric pressure deposition of thin functional coatings: polymer surface patterning by DBD and post-discharge polymerization of liquid vinyl monomer from surface radicals. Plasma Process Polym. 2012;9:1104–1115.

31. Siow KS, Kumar S, Griesser HJ. Low-pressure plasma methods for generating non-reactive hydrophilic and hydrogel-like bio-interface coatings - a review. Plasma Process Polym. 2015;12:8–24.

32. Lerouge S, Barrette J, Ruiz J-C, et al. Nitrogen-rich plasma polymer coatings for biomedical applications: stability, mechanical properties and adhesion under dry and wet conditions. Plasma Process Polym. 2015;12:882–895.

33. Zhang Z, Liu S, Shi Y, et al. Label-free aptamer biosensor for thrombin detection on a nanocomposite of graphene and plasma polymerized allylamine. J Mater Chem B. 2014;2:1530–1538.

34. Chen Z, Dai XJ, Lamb PR, et al. Coating and functionalization of carbon fibres using a three-step plasma treatment. Plasma Process Polym. 2013;10:1100–1109.

35. Friedrich J, Altmann K, Wettmarshausen S, et al. Coating of carbon fibers with adhesion-promoting thin polymer layers using plasma polymerization or electrospray ionization technique-A comparison. Plasma Process Polym. 2017;14:1600074.

36. He P, Lian J, Shi D, et al. Plasma coating and enhanced dispersion of carbon nanotubes. MRS Proc. 2003;791:Q10.7.

37. Mathew T, Datta RN, Dierkes WK, et al. Plasma polymerization surface modification of carbon black and its effect in elastomers. Macromol Mater Eng. 2011;296:42–52.

38. Song W, Wang X, Wang Q, et al. Plasma-induced grafting of polyacrylamide on graphene oxide nanosheets for simultaneous removal of radionuclides. Phys Chem Chem Phys. 2015;17:398–406.

39. Cheng J, Zhao B, Zheng S, et al. Enhanced microwave absorption performance of polyaniline-coated CNT hybrids by plasma-induced graft polymerization. Appl Phys A. 2015;119:379–386.

40. Yun J, Im JS, Kim H-I. Effect of oxygen plasma treatment of carbon nanotubes on electromagnetic interference shielding of polypropylene-coated carbon nanotubes. J Appl Polym Sci. 2012;126:E39–E47.

41. Rong MZ, Zhang MQ, Shi G, et al. Graft polymerization onto inorganic nanoparticles and its effect on tribological performance improvement of polymer composites. Tribol Int. 2003;36:697–707.

42. Cogal S, Ali AK, Erten-Ela S, et al. Plasma-based preparation of polyaniline/graphene and polypyrrole/graphene composites for dye-sensitized solar cells as counter electrodes. J Macromol Sci A. 2018;55:317–323.

43. Fanelli F, Fracassi F. Aerosol-assisted atmospheric pressure cold plasma deposition of organic–inorganic nanocomposite coatings. Plasma Chem Plasma Process. 2014;34:473–487.

44. Liu Y, Qi G-Q, Liang C-L, et al. Effect of graphite oxide structure on the formation of stable self-assembled conductive reduced graphite oxide hydrogel. J Mater Chem C. 2014;2:3846–3854.

45. Marcano DC, Kosynkin DV, Berlin JM, et al. Improved synthesis of graphene oxide. ACS Nano. 2010;4:4806–4814.

46. Robinson JT, Perkins FK, Snow ES, et al. Reduced graphene oxide molecular sensors. Nano Lett. 2008;8:3137–3140.

47. Fracassi F, Occhiello E, Coburn JW. Effect of ion bombardment on the plasma-assisted etching and deposition of plasma perfluoropolymer thin films. J Appl Phys. 1987;62:3980–3981.

48. Compton OC, Nguyen ST. Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials. Small. 2010;6:711–723.

49. Muir BW, Anna T, Gengenbach TR, et al. Characterization of low-fouling ethylene glycol containing plasma polymer films. Langmuir. 2008;24:3828–3835.

50. Variola F, Troncone F, Richert L, et al. Improving biocompatibility of implantable metals by nanoscale modification of surfaces: an overview of strategies, fabrication methods, and challenges. Small. 2009;5:996–1006.

51. Benjamin T, Mahaveer K, Jun Yan S, et al. Herceptin functionalized microfluidic polydimethylsiloxane devices for the capture of human epidermal growth factor receptor 2 positive circulating breast cancer cells. Biomicrofluidics. 2010;4:032205.

52. Sellam C, Zhai Z, Zahabi H, et al. High mechanical reinforcing efficiency of layered poly(vinyl alcohol)–graphene oxide nanocomposites. Nanocomposites. 2015;1:89–95.