

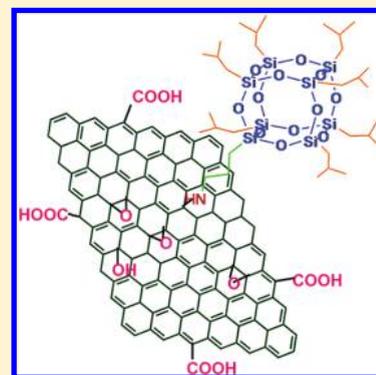
Functionalization of Graphene Oxide with Polyhedral Oligomeric Silsesquioxane (POSS) for Multifunctional Applications

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ABSTRACT: Through the amide formation between amine-functionalized polyhedral oligomeric silsesquioxane (POSS) and oxygen-containing groups (e.g., epoxy and carboxyl groups) in graphene oxide (GO), we have synthesized POSS-functionalized graphene nanosheets (POSS-graphene), which are highly soluble in various organic solvents attractive for multifunctional applications. Thin films from solution casting of the resultant POSS-graphene were found to show superhydrophobic properties with a water/air contact angle of $\sim 157^\circ$, while the superhydrophobic POSS-graphene powder could be used to construct liquid marbles. In addition, the POSS-graphene hybrids were also used as novel nanofillers to increase the glass transition temperature (T_g) and decompose temperature (T_d) for polymers.



SECTION: Physical Processes in Nanomaterials and Nanostructures

Owing to its extremely high surface area as well as fantastic electrical, optical, thermal, and mechanical properties, graphene, a one-atom-thick sheet with honeycomb packed sp^2 -bonded carbon atoms, has attracted a great deal of interest for a large variety of potential applications, including solar cells,¹ supercapacitors,² batteries,³ fuel cells,⁴ sensors,⁵ and actuators.⁶ As the unfunctionalized graphene is insoluble and infusible, however, large-scale practical applications of graphene sheets have been precluded by their poor processability. The recent availability of water-soluble graphene oxides (GOs) by acid oxidation of graphite powder^{7,8} has allowed the functionalization of graphene sheets via various solution reactions. Recently, much effort has been made to prepare organic soluble graphene by incorporating organic moieties onto oxygen-containing groups (e.g., $-OH$, $-COOH$, epoxy) of graphene oxide. Examples include the incorporation of octadecylamine (ODA),⁹ phenyl isocyanate,¹⁰ 5-(4(aminophenyl)-10,15,20-triphenyl porphyrin (TPP)),¹¹ and 2-amino-4,6-didodecylamino-1,3,5-triazine (ADDT)¹² on graphene oxide to increase its solubility in organic solvents. Nevertheless, only a rather limited solubility in common organic solvents (e.g., 15 mg/mL in THF for ODA-modified graphene⁹) has been so far achieved by functionalizing graphene oxide with small organic groups.

On the other hand, polyhedral oligomeric silsesquioxane (POSS) with well-defined organic/inorganic hybrid constituents has received considerable interest due to its unique cage-like molecular structure and interesting physicochemical properties.^{13–15} Having eight organic groups surrounding a cage-like core connected by Si–O–Si bonds, POSS is highly soluble in many organic/inorganic solvents. In addition, the

organic groups in POSS can be used as reaction sites for further functionalization, making POSS an idea modification reagent. Consequently, POSS has been used to modify polymers,¹⁴ nanoparticles,¹⁵ and even carbon nanotubes.¹⁶ Our previous work has demonstrated that certain nanofiber films produced from POSS-modified PMMA exhibited superhydrophobic properties¹⁴ and that POSS-modified Fe_3O_4 nanoparticles showed both superhydrophobic and magnetic properties¹⁵ useful for making magnetically controllable liquid marbles.

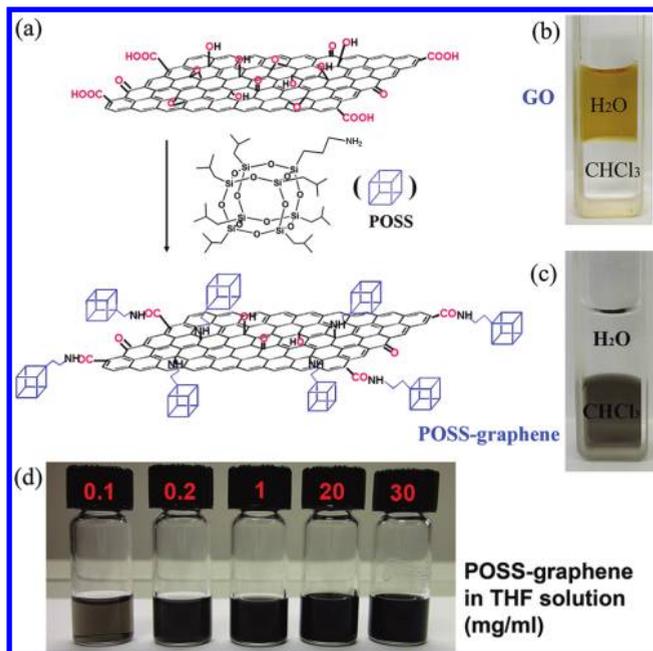
In this study, we have covalently grafted POSS onto graphene sheets via the amide formation between amine-functionalized POSS and oxygen-containing groups (e.g., epoxy and carboxyl groups) of graphene oxide. The resultant POSS-graphene hybrid was found to be highly soluble in many organic solvents, including tetrahydrofuran (THF), hexane, chloroform, acetone, toluene, and dichloromethane. The concentration for the POSS-modified graphene in THF can reach as high as 30 mg/mL. We have also investigated the superhydrophobic properties of the POSS-modified graphene hybrid materials and used them for the construction of liquid marbles. Furthermore, the newly developed POSS-modified graphene was demonstrated to be a useful nanofiller in polymers (e.g., PMMA) to increase their glass transition temperature (T_g) and decompose temperature (T_d).

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As shown in Scheme 1, a typical POSS molecule has eight organic groups surrounding each cubic core, providing POSS

Scheme 1. (a) Schematic Representation of the Route to POSS-Modified Graphene (POSS-Graphene), (b) Photoimages Showing the Starting GO in a Water Phase, Which Transferred into (c) the CHCl_3 Phase upon the Formation of POSS-Graphene, and (d) POSS-Graphene in THF Solutions of Different Concentrations from 0.1 to 30 mg/mL ^a



^aThe data on the caps are the concentrations in mg/mL .

with a high solubility in organic solvents and functionalization capability. In particular, amine-functionalized POSS can be readily attached onto oxygen-containing groups (e.g., epoxy and carboxyl groups) of GO via amide formation in the presence of DCC (Scheme 1a), which also leads to a partial reduction of GO into graphene. The covalent bonding of POSS onto graphene was evident by a phase transfer of the GO starting material from the water phase (Scheme 1b, top) into the CHCl_3 phase (Scheme 1c, bottom) upon the formation of the POSS-graphene hybrid. Unlike most other organic reagents, the covalent bonding of POSS moieties onto graphene sheets can not only change chemical characteristics of the graphene surface but also physically separate graphene layers from each other by the cage-like bulky nanostructure to make graphene sheets highly soluble in organic solvents, such as THF, hexane, chloroform, acetone, and toluene, and to retain graphene surfaces in the solid state for many functional applications (e.g., energy storage).² Scheme 1d indicates that dispersions of POSS-graphene in THF up to a concentration as high as 30 mg/mL are very stable without precipitation even after 24 h standing in an ambient environment.

Apart from the visual observation, the chemical reaction shown in Scheme 1a was also followed by various spectroscopic measurements, including Fourier transform infrared (FTIR) spectroscopy, Ultraviolet (UV-vis) spectroscopy, Raman spectroscopy, and X-ray diffraction (XRD). Figure 1a shows FTIR spectra for the graphene oxide, POSS, and POSS-graphene hybrid. As expected, the FTIR spectrum of graphene

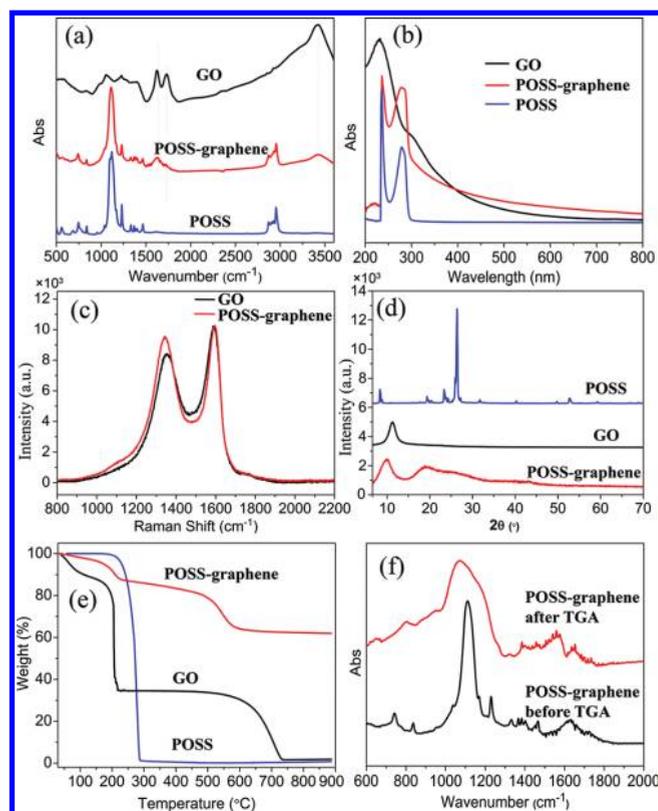


Figure 1. (a) FTIR spectra of GO, POSS, and POSS-graphene, (b) UV-vis spectra of GO, POSS, and POSS-graphene, (c) Raman spectra of GO and POSS-graphene, (d) XRD of GO, POSS, and POSS-graphene, (e) TGA of GO, POSS, and POSS-graphene, and (f) FTIR of POSS-graphene before and after TGA treatment.

oxide shows the presence of hydroxyl (3400 cm^{-1}), epoxy (1228 cm^{-1}), and carbonyl (1731 cm^{-1}) groups. The intensities of these IR peaks decreased significantly after chemical attachment of POSS onto the graphene oxide. In addition, the strong peak at 1110 cm^{-1} characteristic of the Si–O–Si stretching band and the relatively weak bands over $2750\text{--}3000\text{ cm}^{-1}$ associated with the isobutyl groups in POSS were clearly seen in the IR spectrum of POSS-graphene, indicating that POSS has been chemically grafted onto graphene. The UV-vis absorption of GO shows typical bands at 232 and 320 nm, attributable to the $\pi\text{--}\pi^*$ transition of aromatic C–C bonds,¹⁷ while the characteristic UV-vis absorption peaks of POSS are at 236 and 280 nm with no absorption for a wavelength over 300 nm. The characteristic peaks of POSS at 236 and 280 nm also appeared in the UV-vis spectrum of POSS-graphene with strong absorption over 300 nm (Figure 1b). Furthermore, the chemical modification of graphene oxide with POSS was, at least partially, supported by Raman spectra given in Figure 1c, which shows a slight increase in the ratio of the I_D to I_G band intensity upon grafting POSS onto GO due to structural distortions induced by the bulky POSS “cages”. Further evidence for the lattice expansion of graphene oxide induced by the POSS “intercalation” comes from the XRD measurements. Figure 1d shows XRD spectra for POSS, GO, and POSS-graphene. The sharp diffraction peaks seen for POSS indicate a well-defined crystal structure consistent with previous reports.¹⁸ As expected, GO shows a broad band over low diffraction angles ($2\theta = 11.2^\circ$),¹⁹ suggesting some degree of reaggregation of the exfoliated GO sheets. Upon functionaliza-

tion with POSS, the XRD band of GO downshifted to $2\theta = 10^\circ$, indicating that the covalently bonded POSS moieties increased the interlayer space between graphene sheets in the POSS-graphene hybrid. The newly appearing broad amorphous bands over $2\theta = 15\text{--}30^\circ$ in the XRD profile of the POSS-graphene indicate, most probably, that the intercalated POSS moieties, unlike their pristine POSS counterparts, show a largely disordered structure with a low crystallinity.

The thermal stability of the POSS-modified graphene, along with GO and POSS, was measured by thermogravimetric analysis (TGA). As seen in Figure 1e, the initial $\sim 15\%$ weight loss seen for GO up to $\sim 100^\circ\text{C}$ was associated with the thermal desorption of water molecules physically adsorbed onto the hydrophilic GO surface. This was followed by another significant weight loss of $\sim 50\%$ at $\sim 200^\circ\text{C}$, presumably due to the loss of those oxygen-containing groups, before the complete oxidative decomposition of the graphitic substrate over $550\text{--}750^\circ\text{C}$. Interestingly, the thermogravimetric profiles given in Figure 1e show a much better thermal stability for the POSS-graphene hybrid with about 60 wt % POSS, whereas a complete weight loss was observed for POSS at $\sim 300^\circ\text{C}$, presumably due to thermal evaporation. The residue of POSS-graphene after TGA was analyzed by FTIR. As shown in Figure 1f, the Si–O–Si peak of POSS at 1110 cm^{-1} was shift to 1062 cm^{-1} , indicating the occurrence of partial cross-linking of POSS to form a highly dense Si–O structure.

To gain further insights into surface chemical changes associated with the reaction shown in Scheme 1, we have also performed X-ray photoelectron spectroscopic (XPS) measurements. As expected, only C 1s and O 1s peaks were seen in the XPS survey spectrum for GO (Figure 2a). The appearance of the Si 2p (101 eV), Si 2s (152 eV), and N 1s (399.5 eV) peaks, accompanied by the reduced O 1s peak with respect to the C 1s peak, in the XPS survey spectrum of POSS-graphene indicates the successfulness of the covalent bonding of POSS onto GO.

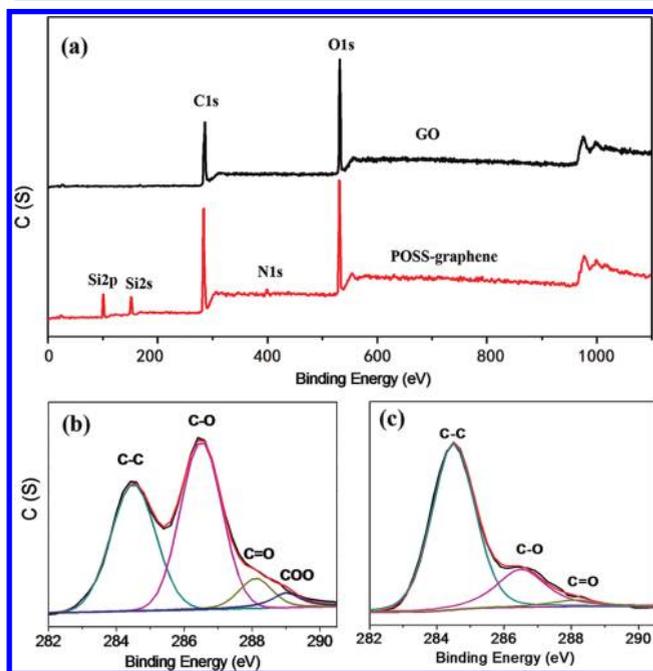


Figure 2. (a) XPS survey spectra of the graphene oxide and POSS-graphene and high-resolution XPS spectra of C 1s for (b) GO and (c) POSS-graphene.

Figure 2b and c reproduces the high-resolution C 1s spectra for GO and POSS-graphene, respectively. As can be seen, the COOH peak at 289.0 eV for GO almost disappeared upon the amide formation with the amine group of POSS. The peak intensity of the C–O (286.5 eV) and C=O (288.1 eV) in GO also significantly decreased. This is because the nucleophilic substitution between GO and amine groups can cause deoxygenation and reduction of graphene oxide.²⁰

Figure 3a represents a typical AFM image for GO, showing the height of $\sim 1\text{ nm}$ (Figure 3c) for a single-layer GO. Upon

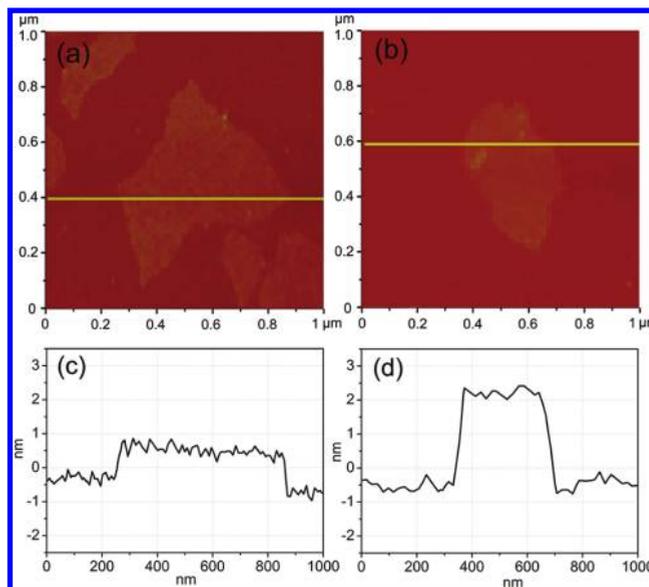


Figure 3. AFM images of (a) GO and (b) POSS-graphene and the corresponding height profiles of (c) GO and (d) POSS-graphene.

the incorporation of POSS on GO, the height of a single-layer POSS-graphene became almost 3 nm (Figure 3b and d), which is much higher than that of GO. The observed increase of the thickness for POSS-graphene could be attributed to the incorporation of POSS on both sides of the graphene sheet.

The unique combination of the hydrophilic GO and POSS with multiple hydrophobic isobutyl groups into a single POSS-graphene hybrid structure could generate unique amphiphilic properties in principle. However, graphene oxides heavily modified with POSS tend to be hydrophobic. Our previous work has shown that superhydrophobic surfaces can be produced by simple solution-coating POSS.^{15,21} In this study, we produce GO films by filtering the GO aqueous solution through a PVDF membrane with pore size of $0.22\ \mu\text{m}$ and POSS-graphene films by filtering a POSS-graphene THF solution through a PVDF film with same pore size. Figure 4a and b reproduces typical SEM images for the GO and POSS-graphene films, respectively, which show a similar surface morphology. As can be seen in Figure 4, however, the POSS-graphene film was hydrophobic (Figure 4e) while the GO film was very hydrophilic (Figure 4d). The observed increase in the air/water contact angle from 30.7° for GO to 111.2° of POSS-graphene is attributable to the surface chemistry change due to the grafting of POSS on GO. However, the increase in the surface roughness could also contribute to the observed hydrophobicity.²² Indeed, a further increase in the contact angle from 111.2° (Figure 4e) up to 157.0° (Figure 4f) was observed for the POSS-graphene film shown in Figure 4b by

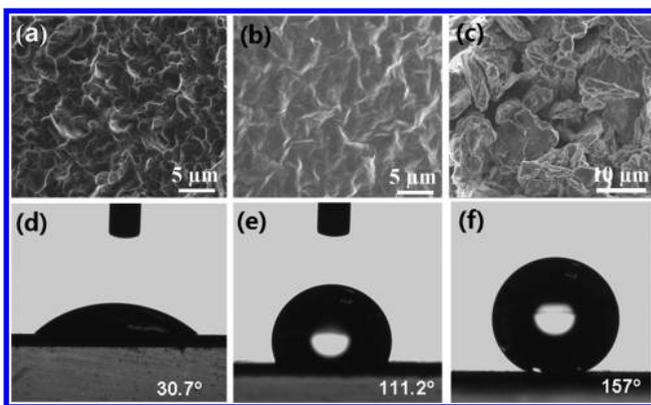


Figure 4. SEM images of (a) a GO film, (b) the as-synthesized POSS-graphene film, and (c) a rough POSS-graphene film prepared from POSS-graphene particles (see text). The corresponding water droplet and air/water contact angles for (d) the GO film, (e) the as-synthesized POSS-graphene film, and (f) the rough POSS-graphene film prepared from POSS-graphene particles (see text).

increasing the surface roughness (Figure 4c). This POSS-graphene film with a relatively high surface roughness (Figure 4c) was prepared by first drying the POSS-graphene, grounding it into particles, dispersing the resultant particles in ethanol, and solution-casting the purified POSS-graphene particle dispersion into the film. Therefore, it is the multiscale roughness, coupled with the low surface tension of POSS-graphene, that makes the film surface shown in Figure 4c be superhydrophobic with a contact angle of 157° (Figure 4f).

Due to its superhydrophobic nature, the POSS-graphene surface can support the free-standing water droplet(s) (Figure 5a). When the water droplet was coated with POSS-graphene

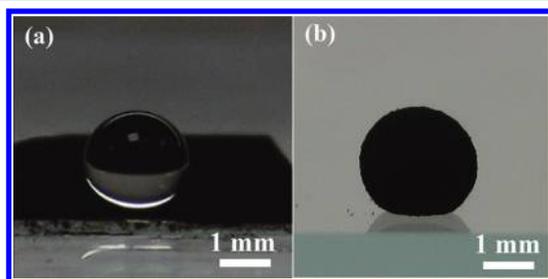


Figure 5. (a) A water droplet on the POSS-graphene surface and (b) POSS-graphene liquid marble on a glass surface.

particles, a POSS-graphene liquid marble was formed (Figure 5b). Much like the liquid marbles made from POSS-modified Fe₃O₄ nanoparticles,¹⁵ the POSS-graphene liquid marble can freely stand on either hydrophilic or hydrophobic surfaces and can be used as miniaturized reactors and other nanoentities for many potential applications.¹⁵

The good solubility in organic solvents and amphiphilic properties characteristic of the POSS-graphene hybrid also make it one of the ideal composite fillers for interfacial reinforcement, for example, with polymers. In this context, we have made POSS-graphene and PMMA composites. As shown in Figure 6, the addition of only 1 wt % POSS-graphene into PMMA can increase T_g of the resultant composite by more than 10° (Figure 6a), along with a significantly increased thermal stability. The decompose temperatures (T_d) at 10 wt %

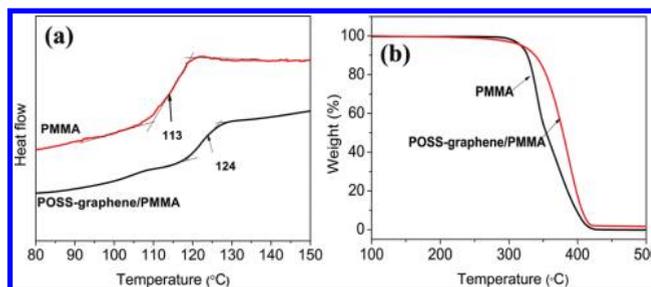


Figure 6. (a) DSC and (b) TGA of pure PMMA and a POSS-graphene (1 wt %)/PMMA composite.

loss are 327 and 338 °C for the PMMA and POSS-graphene PMMA composite, respectively (Figure 6b).

In summary, POSS-functionalized graphene hybrid materials were synthesized by covalently bonding POSS onto graphene oxide via the amide formation between amine-functionalized POSS and oxygen-containing groups (e.g., epoxy and carboxyl groups) in graphene oxide. The chemical reaction was confirmed by various spectroscopic measurements, including FTIR, UV-vis, XRD, XPS, and Raman, while the resultant POSS-graphene hybrid materials were shown to be highly soluble in common organic solvents, including THF, hexane, chloroform, acetone, toluene, and dichloromethane. The unique combination of the hydrophilic graphene oxide and POSS with multiple hydrophobic isobutyl groups into a single POSS-graphene hybrid structure was shown to generate amphiphilic properties for multifunctional applications. Among many potential applications, we have demonstrated that the superhydrophobic POSS-graphene powder with air/water contact angles up to ~157.0° can be used to make liquid marbles free-standing either on hydrophilic or hydrophobic surfaces as a miniaturized reactor. We have also used the POSS-graphene hybrid as a novel composite filler for interfacial reinforcement with PMMA and found that the addition of only 1 wt % POSS-graphene into PMMA could increase T_g of the resultant composite by more than 10 °C, along with a significantly increased thermal stability. Therefore, the newly developed POSS-graphene hybrid materials are promising for a wide range of multifunctional applications.

EXPERIMENTAL SECTION

Materials. Aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS-NH₂) was purchased from Hybrid Plastics and used as received. Other reagents and solvents were purchased from Aldrich Chemical Inc. and used as received.

Preparation of Graphene Oxide. Graphene oxide was prepared by acid oxidation of graphite powder according to the modified Hummers's method.^{23,24} Briefly, 3 g of 300 mesh graphite powder and 1.5 g of sodium nitrate were added to 70 mL of sulfuric acid (98%). The mixture was then cooled down to 0 °C. Thereafter, 9 g of KMnO₄ was carefully added to the reaction bottle with stirring at a temperature below 20 °C; the temperature was then increased up to 35 °C and kept stirring for 1 h. After that, 150 mL of water was added, and the mixture was stirred at 90 °C for 15 min. Then, an additional 500 mL of water was added into the reaction vessel, followed by the addition of 15 mL of 30% H₂O₂. The reaction mixture was filtered through a PVDF filter membrane with a pore size of 0.22 μm, washed consecutively with 1 M HCl and DI water, and further purified by dialysis. Finally, the resultant dispersion

in water was ultrasonicated for 1 h, followed by centrifugation at 4000 rpm for 30 min to produce the graphene oxide.

Preparation of POSS-Graphene. In a 250 mL round-bottom flask, 100 mg of graphene oxide, 2 g of POSS-NH₂, and 100 mg of DCC (as a catalyst) were dissolved in 50 mL of THF, followed by ultrasonication for 10 min. The mixture was then refluxed for 48 h. Once the reaction was completed, the resultant solution was evaporated, and the solid product was subjected to further heat treatment at 120 °C for 8 h. The product was then dissolved in 50 mL of THF and poured into methanol (500 mL) to precipitate POSS-graphene, and this process was repeated three times to remove unreacted POSS. Then, the methanol solution was vacuum filtered through a 0.22 μm PVDF membrane; the filtered solid was further dissolved in 50 mL of THF and poured into methanol (200 mL) to precipitate POSS-graphene, and this repeated three times to remove unreacted POSS. After filtration, the solid was dried in a vacuum oven (80 °C) to collect the final product. The final product yield was 0.171 g.

Characterization. X-ray photoelectron spectroscopic (XPS) measurements were carried out on a VG Microtech ESCA 2000 using a monochromic Al X-ray source (97.9 W, 93.9 eV). Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer spectrum GX FTIR system. The UV–vis absorption spectra were measured with a Shimadzu UV1800 spectrometer. The thermogravimetric analysis was performed on a TA Instruments with a heating rate of 10 °C. The Raman spectra were collected using a Raman spectrometer (Renishaw) with a 514 nm laser. Scanning electron microscopic (SEM) images were taken on a Nova nanoSEM 600, while X-ray diffraction (XRD) was measured on a Miniflex II Desktop X-ray diffractometer.

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Notes

The authors declare no competing financial interest.

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