High-Concentration Self-Cross-Linkable Graphene Dispersion

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ABSTRACT: The formation of a homogeneous graphene dispersion is a fundamental prerequisite for the preparation of high-performance graphene-based materials, yet it remains a challenge to obtain, particularly at high concentrations, meanwhile possessing a film-forming ability. In the present work, a new TSiPD+ molecule, consisting of a conjugated core and terminal silanol groups, was synthesized. With the aid of the TSiPD+, a stable graphene dispersion in water was obtained with a concentration up to 10 mg/mL. More interestingly, the graphene dispersion was able to self-cross-link, after direct casting on substrates, forming highly conductive graphene films with good mechanical strength and excellent solvent resistance. The outstanding performance of the graphene films is owed to the condensation of the silanol groups in the TSiPD+ molecules. The use of the aqueous graphene as conductive ink for paper, glass, and even polymer films was demonstrated.

INTRODUCTION

Because of its excellent electrical, thermal, and mechanical properties, graphene has been widely studied in various fields, such as electronics, energy, composite materials, and bioapplications.1–4 For the acquisition of high-performance graphene-based materials, the formation of a homogeneous graphene dispersion is a key issue; however, the nanosheets tend to aggregate because of the existence of strong van der Waals forces and π−π interactions between the large sp2-conjugated structures.5,6 The noncovalent functionalization of graphene, namely, the use of specific polymers, surfactants, or conjugated aromatic molecules as stabilizers, has been extensively adopted to prepare graphene dispersions, because of the convenience of the process and its low impact on the intrinsic properties of graphene.7–13 Nevertheless, in most cases, these chemicals only work as stabilizers, without a self-cross-linking function. Another polymer has to be added to aid film-formation from the graphene dispersion. This both causes a compatibility problem between the dispersant-attached graphene sheets and the polymer matrix, and deteriorates the electrical conductivity of the graphene film, because of the increased amount of nonconductive components in the film.5,14

So far, two strategies have generally been adopted to solve the above challenges. The first consists of employing functional polymers that simultaneously favor the film-forming ability and the dispersion of graphene.15–17 For example, Huang et al.15 prepared a composite film by drop-casting a reduced graphene oxide (rGO)/polyvinylpyrrolidone (PVP) aqueous dispersion onto Scotch tape. Ali et al.16 deposited a PVP/graphene film on a silicone substrate by electrospraying the dispersion. Secor et al.17 produced a graphene/cellulose film by ink-jet printing the ethyl cellulose/graphene dispersion. In the cases mentioned above, PVP or ethyl cellulose functioned not only as a stabilizer of the graphene dispersion, but also as a binder in the composites. The second strategy involves the use of dispersants that possess reactive groups. With the help of these reactive groups, the dispersant-stabilized graphene can chemically interact with the matrix to avoid incompatibilities. For instance, a dispersant containing epoxy groups, reported by both Ding et al.18 and Teng et al.,19 and one with vinyl groups, reported by Otieno et al.,20 were used to enhance the interfacial interaction of graphene sheets with the epoxy resin and polyurethane matrix, respectively. The drawback of the first strategy is that the polymer dispersants are not cross-linkable, so that the obtained graphene films have poor solvent resistance. Under these conditions, the erosion of the solvents could cause a serious deterioration of the mechanical strength of the graphene-based composite films, and possibly lead to their total breakdown. In the second case, additional cross-linking agents are indispensable, resulting in difficulty in fabrication of composites with a high graphene content, which is essential for electrical conductive applications such as conductive inks or coatings.21,22 Sometimes, the additional cross-linking agent may destroy the graphene dispersion stability.23,24 Therefore, the development of new dispersants...
with self-cross-linking ability is still in demand for high-performance graphene-based films.

Herein, we report a new efficient graphene dispersant that can not only stabilize high-concentration graphene (10 mg/mL) in water, but also self-cross-link when cast on a substrate. The molecular structure of the dispersant (TSiPD**), as shown in Scheme 1a, was easily synthesized from the cheap, commercially available chemicals, (3-glycidoxypropyl)-trimethoxysilane (GPTMS) and p-phenylenediamine (PDA). Conductive composites with high graphene content were obtained by directly drying the TSiPD**-stabilized dispersion. The composites have good mechanical strength and are durable in water, hydrochloric acid, and various organic solvents. More importantly, the conductivity of the composite was less influenced by the presence of TSiPD**, benefiting from the presence of tightly stacked graphene sheets.

Experimental Section

Materials. PDA, anhydrous methanol, and formic acid (HCOOH, 88%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). GPTMS (97%) and \(N,N,N',N'\)-tetramethyldiphenylenediamine dihydrochloride (TMPPD, 98%) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used as received without further purification. Graphene powders (XF001W, thermally reduced, lateral size of 0.5–5 \(\mu\)m, 7.0–7.5 at% oxygen, BET surface area of 500–1000 m\(^2\)/g, and electrical resistivity <50.30 \(\Omega\) cm) were purchased from Nanjing XFNANO Materials Co., Ltd. (Nanjing, China).

Synthesis of TSiPD. PDA (1.08 g, 10 mmol) was first dissolved in anhydrous methanol (25 mL) under sonication, and GPTMS (9.75 g, 40 mmol) was subsequently added to the solution. The mixture was then left to react at the reflux temperature for 48 h in a dark and anhydrous environment (the condenser was equipped with a drying tube). Finally, methanol was removed by vacuum rotary evaporation. TSiPD was obtained as a brown liquid after drying in a vacuum oven under anhydrous environment (the condenser was equipped with a drying tube). It is well-known that an effective graphene dispersant can not only stabilize high-concentration graphene (10 mg/mL) in water, but also self-cross-link when cast on a substrate.

Preparation of Self-Cross-Linking Graphene Films. The graphene films were synthesized on a glass slide, the cartoons and Chinese character on polyethylene terephthalate (PET) films, and the molecular structure of graphene films was obtained by directly writing with a 10 mg/mL TSiPD**-stabilized graphene dispersion on the corresponding substrates. A plastic pipet tip (1000 \(\mu\)L) was used to contain the graphene dispersion employed. The graphene–PVP and graphene–TSiPD** films for electrical conductivity measurement and mechanical strength test were prepared by drop-casting the corresponding dispersion on glass slides and drying them at 60 °C in an oven.

Characterization. NMR experiments were conducted on a Bruker AVANCE III spectrometer. FT-IR spectra were obtained from a Bruker VERTEX 70 spectrometer (Madison, WI), using KBr pellets as supports. Mass spectrometry (MS) data was obtained from a Waters 3100 mass detector (Milford, MA). UV–vis absorption spectra were measured using a Hitachi U-4100 spectrophotometer (Tokyo, Japan) in a quartz cell of path-length 10 mm. The electronic paramagnetic resonance (EPR) was recorded at room temperature using a Bruker EMX-8/2.7 instrument, with 9866 MHz frequency and 6.373 \(\mu\)W power. \(\zeta\)-potential and size-distribution of the graphene dispersion solution were obtained from a Zetasizer Nano ZS90 instrument (Malvern). Prior to measurement, each sample was diluted to 0.01 mg/mL by gentle shaking. The surface and cross-sectional morphology of the composites was characterized by scanning electron microscopy (SEM, VEGA 3 XMU, TESCAN). Transmission electron microscopy (TEM) images of the graphene sheets were obtained using a Tecnai G2 20 TWIN microscope (Hillsboro, OR) operated at an accelerated voltage of 200 kV. Atomic force microscopy (AFM) was performed on a Bruker Dimension edge-scanning probe microscope (Santa Barbara, CA) in tapping mode under ambient conditions; the sample was prepared by spin-coating a drop of graphene dispersion (0.5 mg/mL, graphene/TSiPD** = 1:0.8) on freshly cleaned mica. Electrical conductivities were measured with a RTS-9 four-point probe meter (Guangzhou, China).

The mechanical strength test was as follows: Graphene dispersions (2 mL, 2 mg/mL) with different TSiPD** contents were first deposited on glass slides (25 mm × 35 mm) and dried at 60°C in an oven. The mechanical strength of the obtained coating films was measured by a pencil hardness tester (BY type, Shanghai Pushen Chemical Machinery Co., Ltd., China) equipped with pencils having different hardnesses (CHUNG HWA 101, 6B–6H). Before the test, the lead of the pencil was ground with sandpaper until it became flat and was held firmly against the coating film at a 45° angle. The mass loaded on the pencil tips was 1000 g, and it was pushed away from the operator for no less than 10 mm.

Results and Discussion

Design and Synthesis of the Self-Cross-Linkable Dispersant (TSiPD**). It is well-known that an effective...
Dispersant for graphene must meet two criteria, that is, high affinity toward graphene sheets and good compatibility with the dispersing medium. Large conjugated molecules, such as perylene bisimides, diazaperopyrenium dications, pyrenes, flavin mononucleotides and naphthalene dimides, have been developed because they can physically attach to the graphene surface via strong π−π interactions. In addition to these polycyclic aromatic structures, we noticed that the tetracyanoquinodimethane anion (TCNQ− in Scheme 1b), a small conjugated molecule, is also capable of stabilizing graphene dispersions. Furthermore, it was demonstrated that a para-quinone parent with an extended conjugate structure effectively interacts with graphene. On the basis of these observations, we surmise that a similar structure, a radical cation form of TMPD (TMPD•; Scheme 1b), could also interact with graphene via π−π interactions since the electrons are delocalized within the central benzene ring and the two nitrogen atoms. TMPD• is a stable radical cation that can be easily obtained from one-electron oxidation of TMPD. Because its derivatives can be easily synthesized from the cheap PDA and other reactive agents, we chose the as-TMPD• structure as the affinity site for graphene.

GPTMS was chosen to react with PDA to form a TMPD derivative. The residual trimethoxysilyl groups can hydrolyze in water, forming the hydrophilic silanol groups (Si−OH) and thus making the molecule soluble in water and some polar organic solvents. More importantly, the Si−OH groups can form strong Si−O−Si bonds through inter-/intramolecular dehydration condensation, so as to endow the graphene dispersion with self-cross-linking ability and the high mechanical strength of the finally obtained graphene films. The multifunctional character of the TSiPD• dispersant is illustrated in Figure 1.

In our experiment, TSiPD was first obtained by the reaction of PDA with GPTMS, with a 97.5% yield. The detailed characterization spectra are provided in the Supporting Information. For the acquisition of the aqueous TSiPD• solution, TSiPD was first hydrolyzed in deionized water at room temperature. Nevertheless, the hydrolyzation rate was found to be too low to form a homogeneous solution. A 0.1 M formic acid solution was hence used to accelerate the hydrolyzation of the alkoxy silanes. TSiPD gradually dissolved in the acidic media and formed a clear solution under stirring conditions, demonstrating the generation of hydrophilic Si−OH groups. Beyond our expectation, the color of the solution simultaneously turned to light blue during the hydrolytic process. The solution displayed strong UV−vis absorption peaks centered at 576 and 626 nm (Figure 2a), with a band profile in accordance with that of the TMPD• solution. This phenomenon indicated that TSiPD• was generated in the hydrolytic process. To further confirm this formation, an EPR measurement was conducted. A strong EPR signal, with g = 2.0030, was observed (Figure 2b), making solidly evident the formation of TSiPD•.

**Performance of TSiPD** as Graphene Dispersant. To verify the capability of TSiPD• as a stabilizer for graphene in water, a 0.5 mg/mL dispersion was first tested by tip-sonication of graphene powders in this solution. The weight ratio between graphene and TSiPD• was 1:0.8. It should be noted that we hypothesized that the methoxyl groups were completely hydrolyzed, but without condensation between the silanol groups. As expected, a stable and homogeneous dispersion was obtained simply by carrying out tip-sonication for 30 min (Figure 3a). After either settling for one month or centrifuging at 2000 rpm for 30 min, only very small amounts of sediments appeared at the bottom. By contrast, graphene sheets without TSiPD• settled completely within a short time (Figure 3b). The ζ-potential of the dispersion was found to be +35.7 mV which explains the excellent stability of the dispersion. TEM images in Figure 3c provide direct evidence...
for the dispersion state of the graphene sheets with TSiPD** in water. The presence of sheets consisting of one or a few layers was clearly observed. Figure 3d shows a typical AFM image of the graphene−TSiPD** hybrid. The sample was prepared by spin-coating the dispersion on a freshly cleaved mica surface. The cross-section analyses indicated that the average thickness of a one-layered graphene−TSiPD** hybrid is ~2 nm; the thickness of the two-layered hybrid is ~3.2 nm. Since the dispersant acted on both surfaces of the sheets, we reasonably concluded that the TSiPD** thickness on the surface is ~0.4 nm, and the thickness of the graphene sheet is ~1.2 nm, which is consistent with most previous reports.9,11,12,37 The TEM and AFM results demonstrated that the graphene sheets were uniformly dispersed, and that TSiPD** effectively prevented the agglomeration of the commercial graphene in water. Dynamic light scattering (DLS) was also used to evaluate the dispersion results. Only a single peak, centered at 157 nm, appeared (Figure 3e), indicating the homogeneity of the dispersion.38,39

Upon a further increase of the graphene content to 2.5 mg/mL, a stable and homogeneous dispersion was still obtained with a graphene-to-TSiPD** weight ratio of 1:0.8. On the other hand, the dispersion became metastable when the graphene concentration was increased to 3 mg/mL. Agglomeration took place a few hours after the freshly prepared dispersion had settled. Several previous works reported in the literature have demonstrated that the dispersion concentration of graphene depends on the stabilizer concentration.5,7 We thus tried to

Figure 3. Photographs of a 0.5 mg/mL graphene dispersion (a) with and (b) without TSiPD**. Typical (c) TEM and (d) AFM images of the TSiPD**-stabilized graphene sheets. (e) DLS measurement results of the 0.5, 3, and 10 mg/mL graphene dispersions. Inset: 10 mg/mL graphene dispersion (left) and 1 000 times diluted (right).

Figure 4. (a) Surface (left) and cross-sectional (right) SEM images of the “Graphene” pattern deposited on a glass slide (inset). (b) Pencil hardness test results on graphene−TSiPD** composite films at different weight ratios. Inset: the testing apparatus. (c) Optical microscope images of the 1:1.2 composite after stroking by 3H and 4H pencils. (d) “Graphene” pattern soaked in different solvents for 24 h. (e) Graphene−PVP and graphene−TSiPD** composite line deposited on a glass slide (left), and sonication for 5 s after dipping in water (right).
increase the amount of TSiPD** to obtain a stable dispersion. If the weight ratio of graphene-to-TSiPD** was increased to 1:1.2, the 3 mg/mL graphene dispersion could be stored stably. Even after having been stored for one month, the DLS measurement continued to show a single peak (Figure 3e) with a size distribution similar to that of the 0.5 mg/mL graphene dispersion. With a graphene-to-TSiPD** weight ratio of 1:1.2, stable graphene dispersions could be obtained for graphene concentrations up to 10 mg/mL. A small peak occurred for large particle size (Figure 3e), but its integrated intensity is negligible relative to that of the peak at small size. The 10 mg/mL dispersion (Figure 3e; inset, left) can transform into a translucent dispersion without the formation of any visible agglomerates after being diluted by 1000 times merely by gentle shaking (Figure 3e; inset, right), in accordance with the DLS result. It should be noted that the concentration of 10 mg/mL is much higher than that using conventional surfactant or polymer as stabilizer, where it is usually below 1 mg/mL. TSiPD** can make the nanosheets extend fully. Since TSiPD** exhibited good mechanical strength. The TSiPD** dispersion was first coated on glass slides and dried at 60 ºC, and a pencil hardness tester (the inset in Figure 4b) was then used to perform the experiments. The results are shown in Figure 4b. When the weight ratio of graphene-to-TSiPD** was 1:0.8, the coating film hardness was 2H, indicating a moderate mechanical strength. When the ratio was changed to 1:1.2, the film hardness dramatically increased to 3H. The film surfaces obtained after stroking by a 3H or 4H pencil were observed using an optical microscope, as shown in Figure 4c. Although the mass loaded on the pencil tips was as high as 1000 g, the surface was still intact, with only slight scratches on it, demonstrating the high mechanical strength of the graphene–TSiPD** composite film. This may be due to the formation of an integrated film with high TSiPD** content. An additional increase in the TSiPD** content did not bring appreciable improvement in the hardness, which remained at 3H for weight ratios becoming 1:1.6. Only when the graphene–TSiPD** ratio was down to 1:2.4 did the mechanical strength increase to 4H.

The graphene–TSiPD** composites also exhibited good solvent resistance. Figure 4d shows the “Graphene” pattern soaked in either water, ethanol, acetone, tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), dimethylformamide (DMF), or 2 M HCl solutions for 24 h. The pattern remained intact even after soaking followed by 20 min of sonication. Only the pattern immersed in the 2 M NaOH solution for 12 h was gradually deteriorated and partially peeled off from the glass substrate. This was mainly due to the breaking, in the alkaline media, of the Si–O–Si bond that existed within the composite and at the interfaces between graphene and the glass substrate. A PVP-stabilized graphene film on glass substrate was used as a comparison. Because no covalent bond existed, the film broke down within 5 s after soaking and sonication in water (Figure 4e). Therefore, the self-cross-linkable TSiPD** dispersant was proven to efficiently improve the solvent resistance of graphene films.

The TSiPD**-stabilized graphene dispersion could be used directly as conductive ink on printer paper. As shown in Figure 4f.
Sa, the molecular structure of TSiPD** on paper was composed of graphene, of which the connected part is conductive, with a resistance of 3.42 kΩ. Because of the reaction of the Si−OH of TSiPD* with the hydroxyl groups of the paper cellulose fiber, the pattern on paper is so strong that it cannot be eliminated by moderate erasing. Its resistance was not noticeably changed even after repeated abrasion. Figure 5b shows a hand-drawn Chinese character and two cartoon animals on flexible PET films using the graphene dispersion as ink. Because the graphene sheets could be uniformly stacked on the smooth substrate, the pattern has a much lower resistance, dropping to 0.458 kΩ. More interestingly, the resistance did not vary even when the film was bent arbitrarily, suggesting the potential application of the graphene dispersions in flexible circuits.

The influence of TSiPD** on the electrical conductivity of graphene was investigated. PVP-K30, the most commonly used polymer dispersant for graphene, was chosen for comparison. Figure 5c displays the conductivities of the graphene composites measured by the four-point probe method. It is obvious that all conductivities decreased when increasing the amount of dispersant, since it blocked the connection between graphene sheets. Nevertheless, even with a graphene-to-TSiPD** weight ratio of 1:0.8, the graphene−TSiPD** film still exhibited a high conductivity (531 S/m), equal to about 45.4% of that of the pure graphene film (1169 S/m). In contrast, the conductive value of the corresponding graphene−PVP film was 102 S/m, only 8.7% of that of the pure graphene film. When the graphene-to-dispersant weight ratio was 1:2.4, the conductivity of the graphene−TSiPD** film was 128 S/m, about 10.5 times higher than that of the graphene−PVP film (11.1 S/m). These results indicated that the electrical conductivity of the graphene film is less impacted by the presence of the TSiPD** dispersant compared to PVP-K30.

The great difference in the conductivities of these two composites is most likely due to the different packing density of graphene. When using TSiPD** as dispersant, dehydration condensation takes place between the Si−OH groups, resulting in a weight loss of about 12%. This weight loss caused the formation of a denser composite film, as revealed from the film thickness shown in Figure 5d,e. At the same graphene-to-dispersant ratio of 1:2.4, the graphene−TSiPD** film has a thickness of ~9.3 μm, while the thickness of the graphene−PVP film is ~11 μm. This suggests that in the former film the graphene volume fraction is higher than in the second. Since the electrical conductivity of composite materials (σ) is related to the volume fraction φ of the conductive filler by the power-law expression,42,43 $\sigma = \sigma_0 (\phi - \phi_c)$, it is reasonable for the graphene−TSiPD** film to possess a higher electrical conductivity.

Different stacking of the graphene sheets is another reason responsible for the difference in conductivity. As seen from Figure 5f, no large embossment was observed on the surface of the graphene−TSiPD** film. In contrast, the surface of the graphene−PVP film was quite rough. These micrometer-scale embossments (Figure 5g) could remarkably impact the electron transfer in the composite, and thus result in a lower conductivity. The morphology difference is mainly due to the different dispersion mechanisms. In the case of TSiPD**, most of its molecules could uniformly attach to the graphene surface in the dispersion via π−π interactions, and graphene sheets could cross-link in a flat form after condensation. On the other hand, for PVP-K30, the long polymer chains could not be adsorbed on the graphene surface as uniformly as the small molecules, and a slight phase separation may have taken place during the drying process, resulting in an uneven stacking of graphene.

**CONCLUSIONS**

In summary, we have synthesized a new graphene dispersant, TSiPD**, using cheap, commercially available chemicals. The radical cation of a tetra-alkyl-substituted PDA on the nitrogen atoms was demonstrated for the first time to be effective in interaction with graphene. The dispersant can stabilize graphene in water with a concentration up to 10 mg/mL, being superior to the commonly used surfactants or polymers. More importantly, the dispersant possesses plenty of reactive silanol groups, which endow the graphene dispersion with a self-cross-linking ability via the dehydration condensation among silanol groups. Highly conductive films with good mechanical strength and excellent solvent resistance were obtained by directly casting the graphene dispersion on various substrates. The impact of TSiPD** on the electrical conductivity of graphene film is quite small compared with the commonly used PVP. The outstanding performance of the self-cross-linkable graphene dispersion makes it a potential candidate for use in fields including conductive ink and coatings, electrodes, flexible circuits, and printable electronics.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b00884.

**1H NMR, 13C NMR, FT-IR, and MS characterization spectra of TSiPD, and the calculation of the yield (PDF)**

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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