

Ionizable Star Copolymer-Assisted Graphene Phase Transfer between Immiscible Liquids: Organic Solvent/Water/Ionic Liquid

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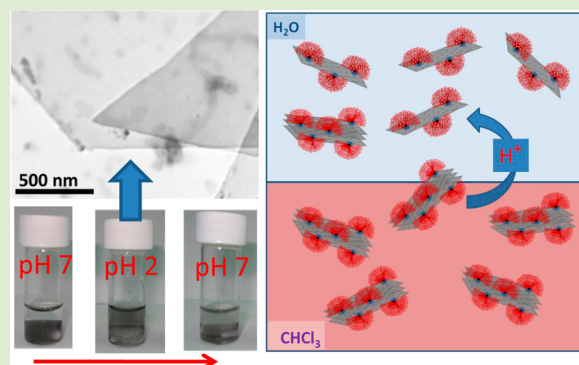
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S Supporting Information

ABSTRACT: The present study reports on the development of a simple two-step process toward the isolation of nearly defect-free mono- and few-layer graphenes in various media. This was achieved by liquid phase pre-exfoliation of pristine graphite in the presence of an ionizable PS_nP2VP_n heteroarm star copolymer in an organic solvent and subsequent graphene shuttle between immiscible media, that is, organic solvent/water and water/ionic liquid. This polymer-assisted phase transfer of graphene sheets gave rise to enrichment of suspended nanostructures in monolayers, especially in an aqueous environment. The exfoliation efficiency was assessed through Raman and electron microscopy. Relatively high concentration suspensions of efficiently exfoliated graphene sheets of large size and in high solubilization yield, could be prepared in any kind of solvent, that is, organic low boiling point medium, aqueous environment, or ionic liquid, whereas the shuttle transfer was found to be a reversible process between organic and aqueous phases.



The process of transport of substances (molecules, supramolecular assemblies, particles, etc.) across interfaces between two immiscible liquids is of great importance in numerous applications including phase transfer catalysis,¹ separations,² reactions,³ and drug delivery.⁴ Thus, there is growing interest to develop strategies for reversible and quantitative shuttling of substances between two immiscible liquid phases. An appealing strategy to induce a phase transfer process is the utilization of responsive polymers that may undergo structural/conformational changes in variation of various trigger parameters. In this regard, a series of important contributions have been reported recently. Representative examples include the transfer of inorganic nanoparticles capped with polymer chains across water/organic solvent interfaces,⁵ as well as thermoresponsive polymeric micelles shuttled between ionic liquid and water.⁶ Currently, nanostructures that have been shown to act as efficient shuttles are mainly limited to polymer or metal-based nanoassemblies. Thus, it is of interest to extend the study of shuttle concept onto more complex composites, such as the ones based on graphitic nanostructures.

Graphene, the two-dimensional carbon allotrope, has attracted great attention due to its single-atom thickness, flexibility, and exceptional electronic, optical, thermal and mechanical properties.^{7,8} For most graphene-based applications, high concentration dispersions of adequately exfoliated platelets in specific solvents are often desired.⁹ Although high graphene concentrations, up to 63 mg/mL, have been achieved after

prolonged sonication times of graphite in *N*-methyl-2-pyrrolidone (NMP), these suspensions suffer from continuous flake size scission, rather low exfoliation quality, and difficult processability due to the high boiling point of the solvent.^{9d} Thus, it is imperative to develop a versatile procedure (avoiding prolonged sonication) toward the preparation of relatively concentrated graphene suspensions, highly enriched in monolayer graphenes. An additional parameter that should be taken into account is the solubilization yield of graphene dispersion (mass ratio between suspended graphene and starting graphite). Except the typical amphiphilic surfactants used for liquid-phase graphene exfoliation through a non-covalent approach,^{9a} substances, such as stimuli-responsive block copolymers, have been studied as both graphene exfoliation agents and stabilizers.^{10–13} Depending on the chemical nature and composition of the block copolymer and the molecular weight ratio between solvophobic/solvophilic domains, the resulting exfoliated pristine graphene sheets may be suspended in either aqueous,^{10,13,14} organic,^{13,14} or ionic liquid media.^{15,16} Taking advantage of the progress achieved by polymer chemistry in controlling the synthesis of specific macromolecular architectures,¹⁷ the development of graphene exfoliation strategies by macromolecules with a more complex

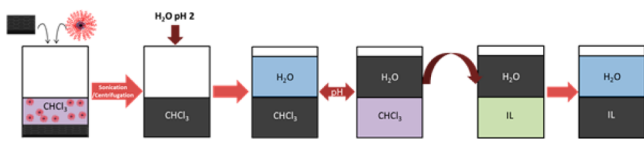
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structure could open new pathways toward the preparation of suspensions highly enriched with monolayer sheets. To this end, we demonstrate herein a pH-induced shuttle process between CHCl_3 and water, which leads to higher quality graphene dispersions, as well as phase transfer from water to hydrophobic ionic liquids (Scheme 1). As a noncovalent stabilizer, we used a heteroarm star copolymer bearing n polystyrene and n pH-responsive poly(2-vinylpyridine) arms, $\text{PS}_n\text{P2VP}_n$ ($n = 22$; Table S1).

Scheme 1. Transfer Scheme of the Graphene/ $\text{PS}_n\text{P2VP}_n$ Nanohybrid Shuttle between CHCl_3 , H_2O , and $[\text{BMIM}][\text{PF}_6]$



Recently, star polymers with similar architecture were used to successfully disperse carbon nanotubes in water^{18a} and to fabricate polymer-modified graphene oxide (GO) flakes at the air–water interface by the Langmuir–Blodgett process.^{18b} Concerning the stabilization of pristine graphene sheets in solution, a linear diblock copolymer counterpart (with high PS percentage) was recently used to obtain stable graphene dispersions in organic as well as in aqueous medium, by diluting a graphene suspension in NMP with excess of acidic water.¹³ Yet, the authors provided only qualitative results.

In this work we attempted a novel route to disperse graphene through phase transfer between immiscible liquids with the aid of a $\text{PS}_n\text{P2VP}_n$ star copolymer. We demonstrate for the first time that shuttle transfer between CHCl_3 and acidic water affords graphene sheets, enriched in monolayers. In addition, utilization of the same polymeric stabilizer resulted in the formation of stable graphene suspensions, in good yield in a variety of different media, that is, organic solvent, aqueous media, or ionic liquid.

At first, a graphene suspension in CHCl_3 (good solvent for both arms) was prepared through short time (1.5 h) sonication-assisted exfoliation of pristine graphite in the presence of $\text{PS}_n\text{P2VP}_n$ star copolymer with a polymer/graphite weight ratio of 0.75. After centrifugation, a black-colored dispersion of the exfoliated graphene was obtained, which was stable for more than 1 month (Figure 1A). By using a combination of filtration and weighting protocol, we estimated that the centrifuged organic suspension contained graphene at concentration up to 0.312 mg/mL in the presence of $\text{PS}_n\text{P2VP}_n$ star copolymer (Table S2). It is noted that, in the absence of stabilizer, CHCl_3 is an ineffective medium for graphite exfoliation under the specific experimental conditions. Only at prolonged sonication

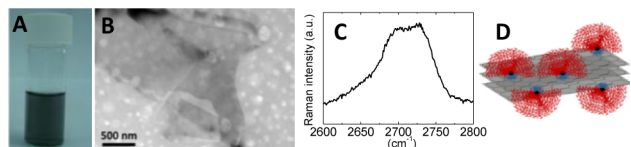


Figure 1. (A) Digital image showing stable graphene suspension; (B) TEM image; (C) Raman spectrum of deposited 3-layered graphene sheet; and (D) Schematic representation of the 3-layered graphene sheet prepared in CHCl_3 .

times (48 h), concentrated suspensions of few-layer graphenes may be prepared, as shown in the work of Coleman and co-workers.¹⁹

In order to further assess the exfoliation efficiency of graphene nanostructures, we conducted TEM analysis. Figure 1B showed a representative image of deposited graphene platelets, where rather few-layer structures were observed with sizes in the μm scale. The layer number distribution was monitored by Raman spectroscopy. The shape of the so-called 2D band of the deposited flakes offers some direct indication of the graphene layer number.²⁰ A mapping procedure demonstrated that few-layer graphenes (layer number from 3 to 8) were isolated (Figures 1C and S2). The integration ratio of 2D and G bands (2D/G) was found to be 2.63, whereas the corresponding ratio D/G was about 0.16. The values of both parameters are typical for few-layer graphene. This combination of enhanced values of graphene concentration as well as large surface area of graphene sheets, could be the result of efficient binding of PS arms (mainly) onto the graphite surface via π – π stacking interactions, with the assistance of short time sonication treatment (Figure 1D).

In a following step, we have attempted the phase transfer of the graphene/ $\text{PS}_n\text{P2VP}_n$ nanohybrids from CHCl_3 to aqueous phase. Examining appropriate pH conditions for the aqueous phase (see SI), pH 2 was chosen, close to maximum P2VP arm ionization, which allowed the pyridine units of P2VP arms to be protonated at the CHCl_3 /water interface and impart a positive charge ($\text{p}K_a$ of P2VP ≈ 5.2).²¹ With the two liquids being immiscible, the lower layer is the CHCl_3 phase containing the graphene/ $\text{PS}_n\text{P2VP}_n$ nanohybrids and the upper layer the aqueous phase. After stirring at moderate rates for 72 h, the graphene/polymer hybrid was transferred almost quantitatively to the aqueous phase, as confirmed by the black coloration of the upper layer (Figure 2A). In order to determine the

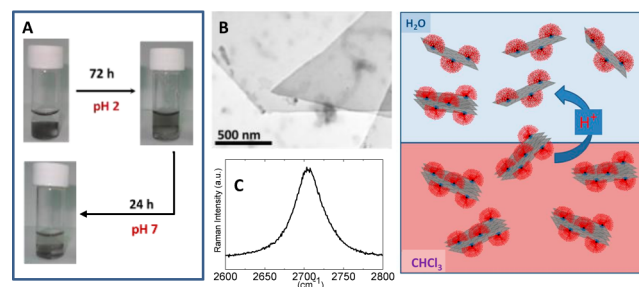


Figure 2. (A) Digital image showing the two-phase shuttle of the graphene/ $\text{PS}_n\text{P2VP}_n$ nanohybrids from CHCl_3 to the H_2O (pH 2) and back to CHCl_3 phase; (B) TEM image; (C) Raman spectrum of monolayer graphene in H_2O phase; (D) Schematic illustration of the graphene shuttle and simultaneous exfoliation.

graphene concentration, optical absorbance measurements were performed (Figure S4). The graphene concentration in the aqueous phase was estimated about 0.219 mg/mL (Table S3). It should be noted here that we performed a control experiment, in which exfoliation of graphite flakes was attempted in an aqueous $\text{PS}_n\text{P2VP}_n$ solution at pH 2. In this condition, an appreciably lower concentration of dispersed graphene was obtained, corresponding to a value of 0.042 mg/mL, yet, higher than the one achieved in a sodium cholate/water system (~ 0.005 mg/mL).^{20c} Such low efficiency of $\text{PS}_n\text{P2VP}_n$ star copolymer to act as graphite exfoliation agent directly in aqueous environment could, be explained due to

polymer micellization in this medium, resulting in caging of PS arms into a hydrophobic core, thus, decreasing significantly the interactions with the graphene surface.²¹

The aqueous suspension of graphene/PS_nP2VP_n nanohybrids after the phase transfer was further characterized by TEM and Raman. The microscopic structure of graphene/PS_nP2VP_n hybrids was presented in Figure 2B. As can be seen, the graphene sheets are quite transparent (see the three overlapping sheets in the right edge of the image), suggesting monolayers.

TEM images showed also black-gray spots scattered on the deposited graphene sheets. Since the system was exclusively composed of graphene and PS_nP2VP_n stars, we therefore infer that the black spots derive from the polymer physically adsorbed onto the graphene planes, in the form of nano-segregated stars,²¹ as illustrated in Figure 2D (see also SI).

Figure 2C shows a representative Raman 2D band of exfoliated graphene flakes deposited onto SiO₂/Si wafer by spin-coating an aqueous suspension. As a guide to distinguish the layer number of graphene structures, the full width at half-maximum (fwhm) of the 2D band positioned at $\sim 2710\text{ cm}^{-1}$ was calculated.²⁰ Its value ranged between 30 and 35 cm^{-1} , suggesting the presence of monolayer graphenes corroborating the TEM observation. An additional parameter supporting the presence of monolayer structures is the value of 2D/G integration ratio, which was estimated about 7.05 (Figure S5). The relative population of sp³ carbon defects (D/G ratio) was found to be about 0.32. The somewhat enhanced value of D/G ratio could be ascribed to the defective carbon atoms at the periphery of the monolayer structure. Statistical analysis by Raman analysis showed that the fraction of monolayer graphenes was about 15%, with the remaining population of sheets identified as bi-, tri-, and four-layered ones. Thus, we could conclude that large surface few-layer graphenes were successfully enriched with monolayer structures during the shuttle process from CHCl₃ to the aqueous phase. This conclusion is consistent with the polyelectrolyte character of P2VP at acidic pH²¹ and the composition of the star copolymer ($\sim 80\%$ P2VP). Specifically, upon interfacial protonation of P2VP chains (Figure 2D), the affinity of the polymeric stabilizer for the aqueous medium becomes higher than it is for CHCl₃, which leads to thermodynamically favorable phase transfer. In addition, the highly charged adsorbed polymer chains promote further exfoliation and stabilization of the graphene flakes through electrostatic repulsive interactions in accordance with other findings.¹³ In order to investigate any possible effect of polymer architecture, the same protocol was followed with a linear block copolymer PS-P2VP (88 wt % P2VP), using equimolar quantities with the star counterpart. Preliminary results showed better dispersibility (up to 0.293 mg/mL) but worse exfoliation efficiency (few layers graphene) for the linear sample. To the best of our knowledge, this is the first report concerning exfoliation of graphite into high yield monolayer graphene with the aid of an amphiphilic star-shaped block copolymer by a shuttle process.

Recently, the successful exfoliation of pristine graphite into mono- and few-layer structures in exclusively organic media was demonstrated by the utilization of an amorphous crystalline block copolymer, poly(vinyl cyclohexane)-polyethylene-poly(vinyl cyclohexane).¹¹ However, therein mono- and few-layer graphene flakes of lateral size $< 500\text{ nm}$ were obtained. It has been established that the size of the graphene flakes represents a critical parameter for several applications. The large

monolayer graphene presented herein (lateral size of several μm) can be used as functional filler material in polymer composites for enhancement of mechanical and electrical properties.

Further on, we studied the reversibility of shuttle process between organic and acidic aqueous media. Upon rising pH to 7, the water-dispersed graphene hybrids were transferred back to a renewed CHCl₃ phase at relatively fast rate, about 24 h (Figure 2A). Inspection by Raman spectroscopy suggests that the two-phase back transfer of carbon nanostructures occurs without detectable aggregation and quality reduction. The reversible phase transfer of the mono- and few-layered graphene/polymer nanostructures upon raising the pH is due to the deprotonation of P2VP arms which become hydrophobic and subsequently “drag” the graphene sheets into the nonselective CHCl₃ phase.²¹ The successful dispersion of the graphene sheets into low boiling solvents is highly desirable in order to integrate impurity-free graphene in various applications.

Finally, we have investigated the phase transfer of graphene/PS_nP2VP_n sheets from acidic aqueous environment to 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] ionic liquid. [BMIM][PF₆] and water are immiscible media with the upper layer being the aqueous phase, containing the graphene/protonated copolymer nanohybrids.

The phase transfer was taken place instantaneously and quantitatively, as seen by optical observation (Figure 3A) and

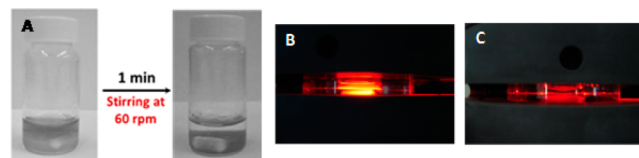


Figure 3. (A) Digital images displaying the phase transfer of graphene/PS_n-P2VP_n sheets in [BMIM][PF₆] and the corresponding images displaying a laser beam passing through the aqueous upper phase in the light scattering apparatus, before (B) and after the transfer (C).

the complete suppression of the Tyndall effect in the upper water phase after transfer (Figure 3B,C). Note that direct exfoliation of graphite to IL in the presence of PS_nP2VP_n under the same conditions was not stable. This easy transfer could be ascribed to the much higher affinity of graphene sheets with the hydrophobic imidazolium-based IL versus water and the good solubility of protonated P2VP. The use of an ionic liquid, exhibiting high ion conductivity and negligible volatility, as dispersing media of graphene opens up new possibilities for novel applications as ion gel for electrochemical devices.

In conclusion, we have demonstrated for the first time a shuttle process for preparing enhanced quality graphene (mono- and few layers) with the aid of a pH responsive PS_nP2VP_n star copolymer. Graphite exfoliation was first, accomplished in CHCl₃ (a common good solvent for the different arms of the star copolymer dispersing agent) followed by phase transfer to the immiscible acidified water phase. At the CHCl₃/H₂O (pH 2) interface, protonation of P2VP arms of the star copolymer, physisorbed onto graphene surface by π - π stacking interactions of the PS arms, takes place, promoting further graphene exfoliation and stabilization in aqueous environment through electrostatic repulsive forces. This procedure is reversible since the graphene is transferred intact

back to the CHCl_3 phase upon raising pH to neutral values. This shuttle-based methodology exhibits great potential in producing aqueous dispersions of nearly defect-free graphene, remarkably enriched in monolayer graphene sheets (ca. 15%) at concentration of 0.219 mg/mL and remarkable solubilization yield (11%). Yet the polymer architecture (star vs linear) seems to affect the exfoliation efficiency. More importantly the obtained concentration is about 5 \times higher than that of direct exfoliation in acidified water in which the copolymer dispersing agent self-assembles due to selectivity of the solvent (i.e., bad solvent for PS). Thus, the novel two-step exfoliation procedures proposed herein seems to be advantageous regarding direct exfoliation using amphiphilic block copolymers. A technical drawback of the method is the relatively long time for transfer completion which needs further investigation to accelerate the process.

Interestingly, graphene can be transferred in a variety of different media by using the same copolymer as dispersing agent in relatively high concentrations and good solubilization yield either in nonselective low boiling point organic solvents, aqueous media or ionic liquid. Furthermore, the mean size of suspended graphenes remains to the μm scale, due to the short duration of sonication used, whereas the material is highly enriched in monolayer sheets (especially for the aqueous batches). It should be also underlined that the overall exfoliation yield, including concentration, solubilization yield, monolayer percentage, and large graphene size, is among the highest observed so far using polymeric stabilizers.

Additional potential of these graphene/star polymer nano-hybrids relies on the fact that the P2VP arms can be used as templates for growing inorganic nanoparticles, for example, Pd, Au, and so on,^{18a,22} thus, fabricating graphene/polymer/inorganic particle hybrids, which will be demonstrated in a forthcoming paper. Such noncovalently modified graphene monolayers have a great potential in a wide range of applications, such as fillers in polymer nanocomposites for enhancement of mechanical, electrical, and thermal properties, as well as components in biomedical devices by choosing appropriate biocopolymers.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, absorption spectra of graphene-based suspensions, and Raman spectra of deposited graphenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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