

Supporting Information to
Poly(tetrabutylphosphonium 4-styrenesulfonate) : a Poly(ionic liquid)
Stabilizer for Graphene being multi-responsive

*Yongjun Men, Xin-Hao Li, Markus Antonietti, Jiayin Yuan**

Materials

Tetrabutylphosphonium bromide (Aldrich 98 %), Sodium 4-vinylbenzenesulfonate (Aldrich >90 %), hydrazine monohydrate (Aldrich 98 %) were used as received. AIBN (Aldrich 98 %) was recrystallized from hexane. Graphene oxide was synthesized from natural graphite according to the Hummers method (W. S. Jr. Hummers, R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339). All other chemicals are purchased from Aldrich for analytic grade and used as received.

Synthesis of TPSS

33.93 g (0.1 mol) of tetrabutylphosphonium bromide, 22.68 g (0.11 mol) of sodium styrenesulfonate and 30 mL water were loaded into a 250 mL reactor. The mixture was stirred at room temperature for 12 h. The product was extracted with dichloromethane (50 mL) for 3 times. The organic phases were combined and washed with water (25 mL×3). After evaporating dichloromethane, the product (TPSS) was dried at room temperature by high vacuum until constant weight.

Synthesis of PTPSS

20 g (0.0452 mol) of TPSS, 371 mg of (2.26 mmol) AIBN and 20 mL ethanol were added into a 100 mL flask. The mixture was sealed with a septum and deoxygenated by flushing with argon for 30 min. The flask was then stirred in an oil bath thermostated at 70 °C for 48h. After cooling down, the PTPSS solution was dialyzed against deionized water exhaustively. After freeze-drying, 19 g of product ($M_n=71,150$ g/L, PDI=1.54 by water GPC) was obtained.

Stabilization of graphene sheets

Graphene oxide was prepared by modified Hummers' method. To stabilize graphene sheets by PTPSS, 1 g of PTPSS was added into 50 mL of graphene oxide suspension (1.3 mg/mL). The graphene oxide was then reduced by hydrazine monohydrate (300 μ L) at 70 °C for 24h (Fig. S3).

A homogenous black solution was obtained after sonication by Branson Digital Sonifier model W450D (40 %, 2 min). To obtain different concentrations of PTPSS in the aqueous dispersion of graphene sheet, desired mounts of PTPSS or water were added into former solution.

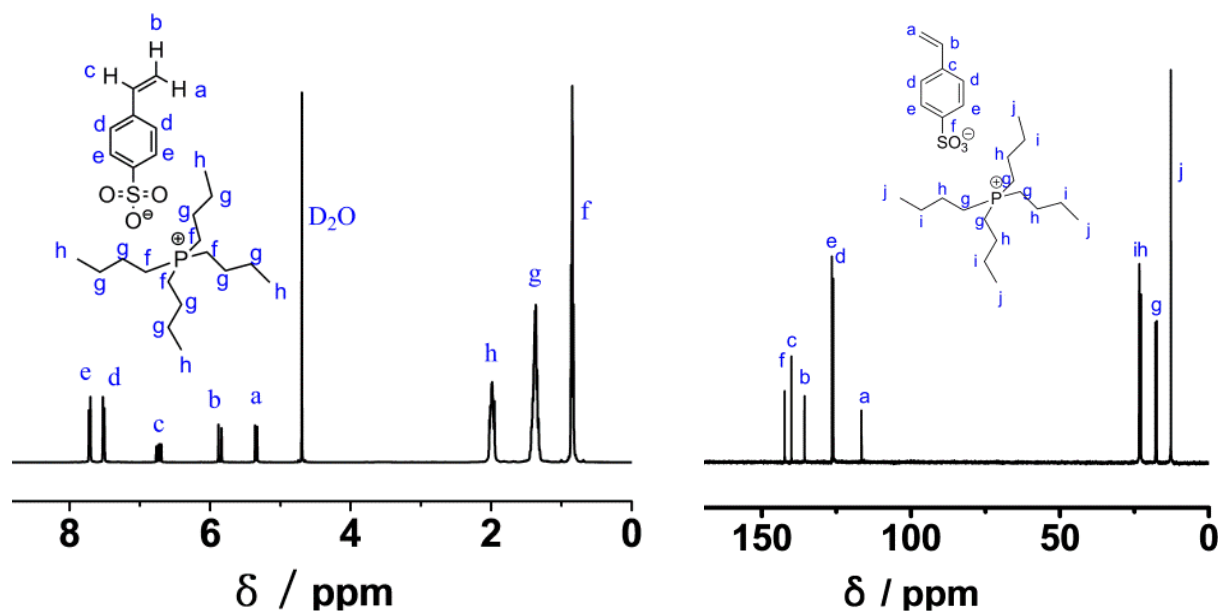


Figure S1. ^1H -NMR (left) and ^{13}C -NMR (right) spectra of TPSS monomer in D_2O .

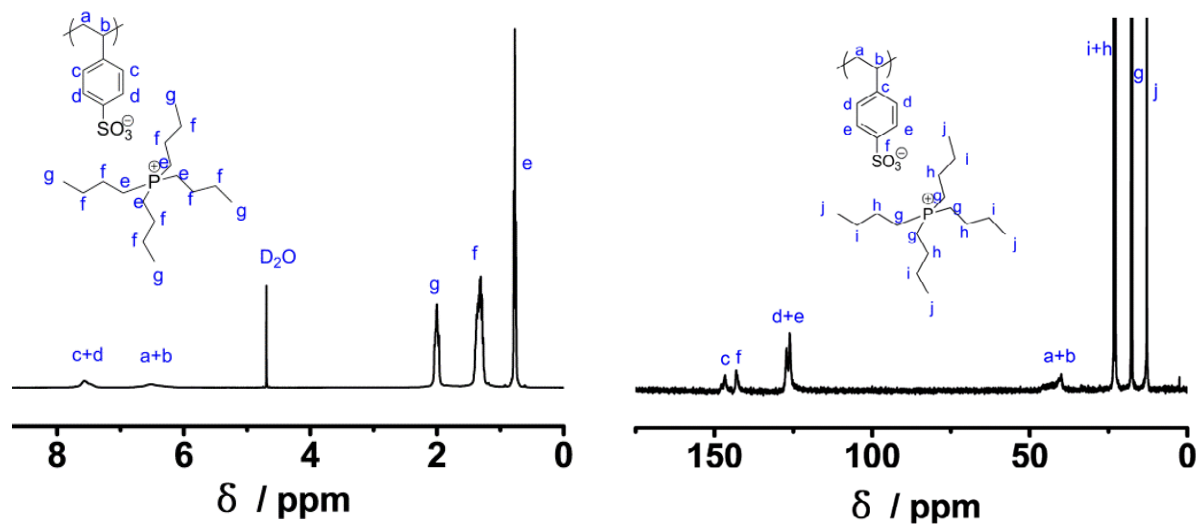


Figure S2. ^1H -NMR (left) and ^{13}C -NMR (right) spectra of PTPSS polymer in D_2O .

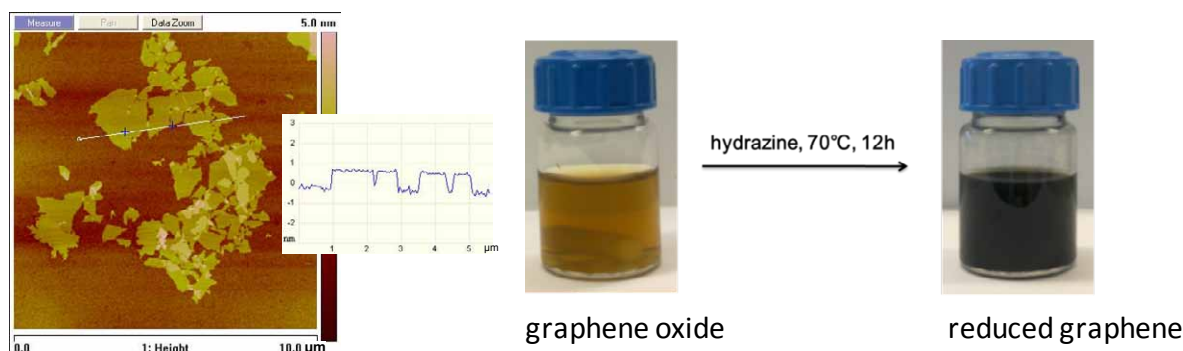


Figure S3. Photographs of dispersions of graphene oxide (left) and reduced graphene (right). The AFM image of the GO sheets shows that the height is ca. 1 nm.

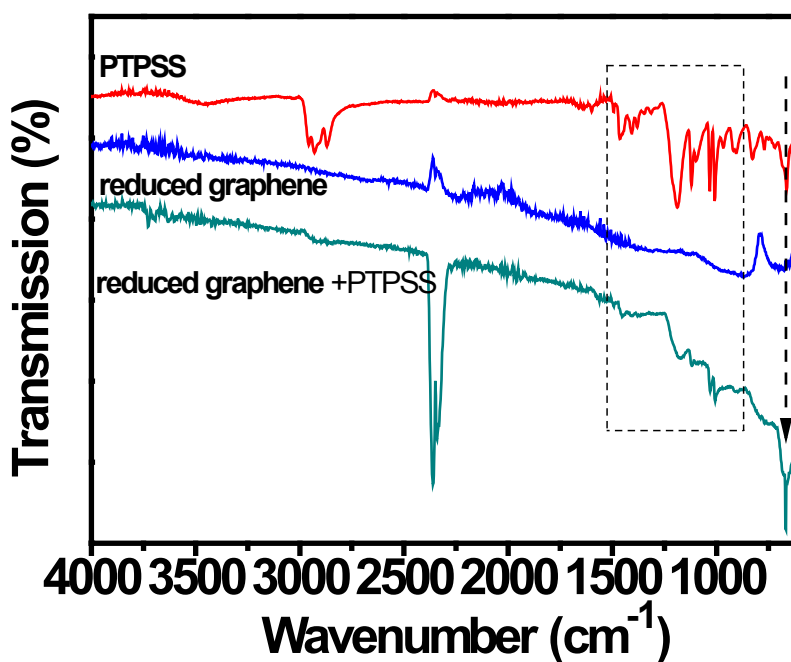


Figure S4. FTIR spectra of PTPSS polymer, reduced graphene, and the composite of reduced graphenen and PTPSS, which was purified by ultracentrifugation and several times of washing with deionized water. It proves that PTPSS stabilizer bonded strongly onto the graphene surface.

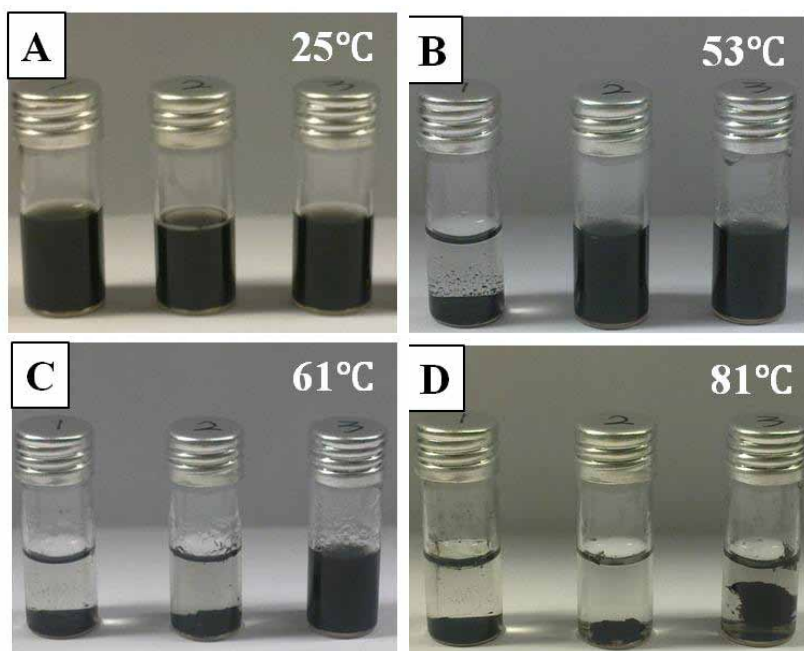


Figure S5. Photographs of destabilization of reduced graphene at different temperatures. In each photograph, from left to right, the PTPSS concentrations are 200, 100 and 20 g/L.

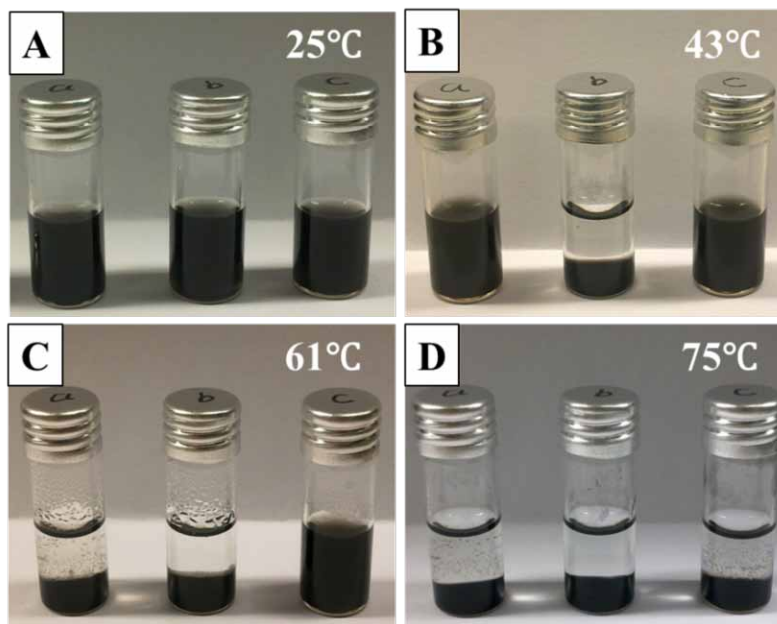


Figure S6. Photographs of destabilization of reduced graphene at different temperatures. In each photograph, the PTPSS concentration is 100 g/L; the left vial is free of salt; the middle one contains 0.3 M of TPB salt; the right one contains 0.3 M of KBr.