Supporting Information

Fluorescent whitening agent stabilized graphene and its composites with chitosan

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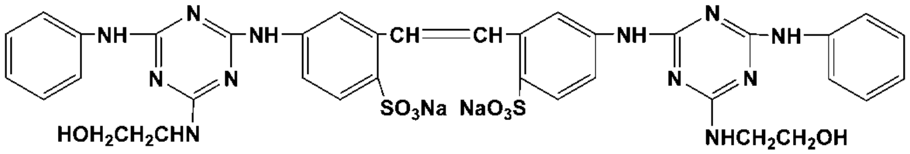
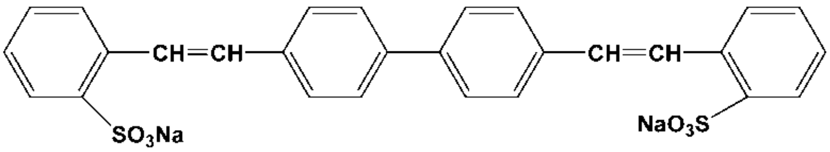
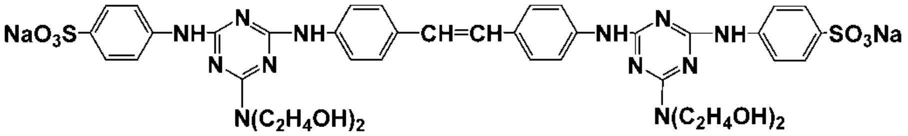
Chemical structures of the FWAs



VBL



CBS



APC

Well-dispersed CBS-G and APC-G in water

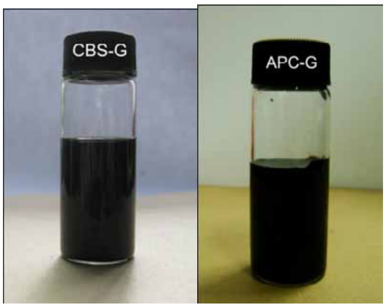


Fig. S1 Photos of CBS-G and APC-G in water

VBL-G paper

The VBL-G paper was prepared by vacuum filtration of VBL-G suspension. The resultant free-standing paper is flexible. The graphene paper prepared by “pristine graphene solution” is porous and fragile[1], and only stable and agglomerate-free graphene colloids could produce uniform and smooth paper. The obtained paper in present work does display a smooth surface and layered structure. The structure of the paper was observed on ZEISS EVO 18 SEM equipment. The cross-sectional view of the paper shows a well-packed layered structure.

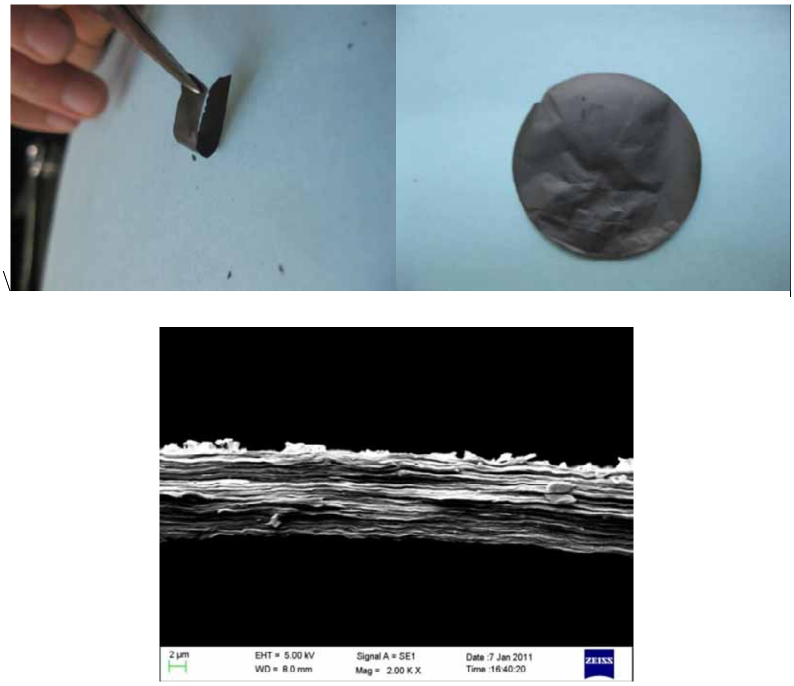


Fig. S2 Digital photos and cross-sectional SEM of VBL-G paper

AFM 3D view of VBL-G

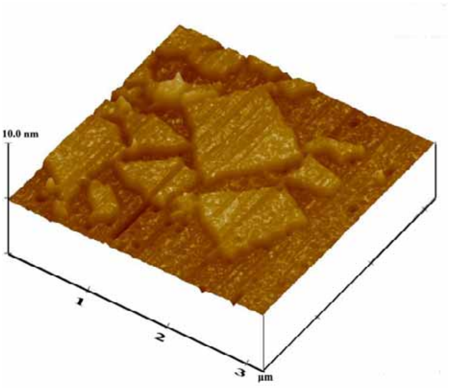


Fig. S3 3D AFM image of VBL-G

Interaction between other FWAs (VBL and APC) and Graphene

The characteristic peak of CBS solution is centered at 350 nm. However, this absorption of CBS-G blue-shifts to 338 nm and broadens. Similarly, the absorption at 349 nm for APC solution shifts to 380 nm for APC-G. In addition, both the fluorescent of CBS-G and APC-G is quenched significantly by graphene. These results indicate the π-π interaction between FWAs and graphene.

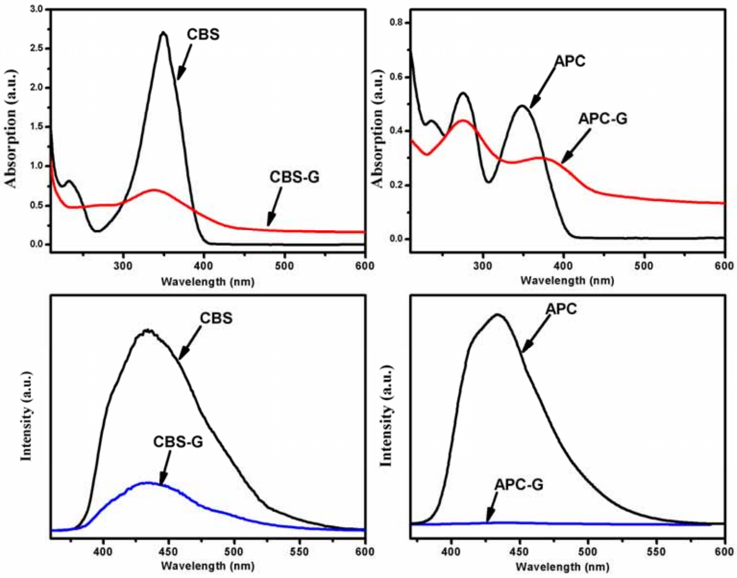


Fig. S4 The UV-vis spectra (upper) and Fluorescent spectra (lower) of CBS, CBS-G, APC and APC-G

The CS/graphene solutions prepared by different methods

First, CS/graphene composites are prepared by adding chemically reduced graphene into CS solution. However, reduced graphene in absence of VBL was agglomerated, which poses the persistent obstacle for its implementation. Alternatively, the GO aqueous solution was firstly added to CS solution, and then the reduction of GO was accomplished *in situ* by adding hydrazine hydrate as reducer. Unfortunately, adding alkaline hydrazine hydrate into acidic CS solution lead to the condensing of CS chains and invalidation of the reducer. To overcome this problem caused by hydrazine hydrate, Vitamin C, which have been reported as an effective reducer for GO, was attempted as the reducer. Still, the reduced graphene by Vitamin C was found to be aggregated in CS solution. Because reduction of graphene will remove the oxygenic groups of GO and recovery the strong van der Waals among graphene sheets. Consequently, the “traditional” preparation of the CS/graphene in absence of modifier is not possible. Photos of the CS/graphene solutions obtained by different methods are demonstrated as following.

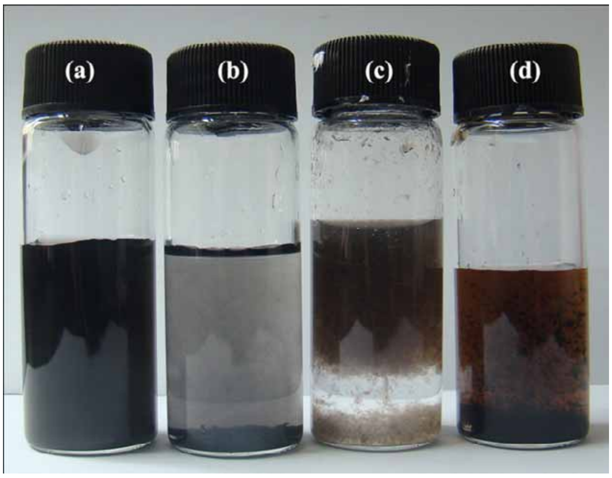


Fig. S5 (a) CS/VBL-G solution, (b) CS/graphene mixture obtained by directly adding chemically reduced graphene, CS/graphene mixture obtained by adding (c) hydrate hydrazine and (d) vitamin C as reducer

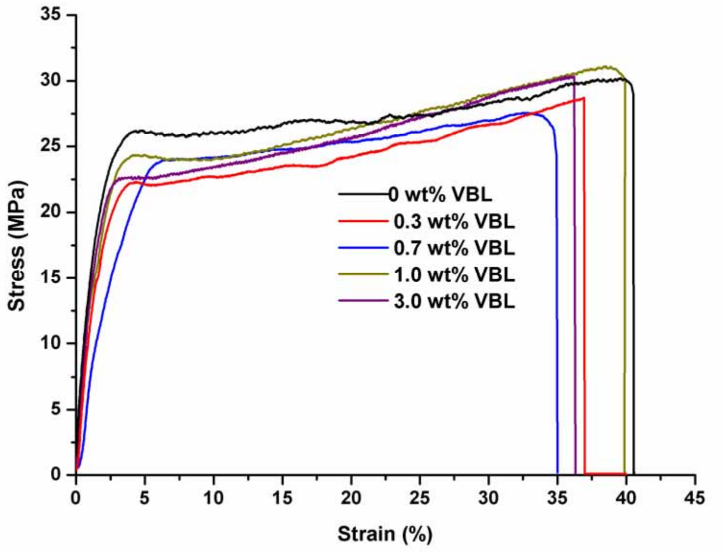


Fig. S6 Typical stress-strain curves of the CS/VBL films. VBL content is the same as that in the composite films

The comparison of the electrical conductivity of graphene prepared by different methods

The graphene prepared by the “top down” methods, such as mechanical exfoliation[1], chemical vapor deposition[2] and epitaxial growth[3], is defect-free. The perfect sp^2 network endows them high conductivity. Especially, the graphene obtained by mechanical exfoliation has the carrier mobilities as high as 200,000 $cm^2\ V^{-1}\ s^{-1}$.[4] However, the “top down” methods suffer from low throughput and poor reproducibility. Liquid-phase exfoliation of graphite can also yield the graphene with few defects, consequently, the conductivity of the graphene film can reach a high value of $\sim 10^4\ S\cdot m^{-1}$. This method is limited by its low efficiency. As for the chemical reduction of GO, the graphitic structure cannot be fully restored after reduction, thus the conductivity of graphene cannot match with that of the “perfect” graphene. In addition, the conductivity of graphene obtained by non-covalent modification is usually much higher than that of graphene obtained by covalent modification.

Table S1 Comparison of the conductivity of graphene obtained by different methods

Method	Condition	Conductivity, ($S\cdot m^{-1}$)	Ref
Liquid-phase exfoliation	Sonication of graphite in NMP	6500	2
	Exfoliation of graphite in water with the assistance of sodium cholate	15000	3
	Exfoliation and functionalization of graphite in ortho-dichlorobenzene in one pot	1500	4
Wet ball milling	Multi-layered graphite dispersed in DMF and subjected to ball milling	1200	5
Reduction of GO based on covalent modification	Coupling azido-terminated long alkyl chain (C-16) onto GO by nitrene chemistry	0.1	6
	Grafting poly(glycidyl methacrylate) onto GO by free radical polymerization	6.5	7
	Grafting poly(ethylene terephthalate) onto graphene by condensation reaction	5.6	8
Reduction of GO based on non-covalent modification	Partial reduction and then anneal at 500°C	35100	9
	Pyrene-1-sulfonic acid sodium[a]	190	10
	Sulfonated polyanilin[a]	30	11
	Pyrenebutyrate[a]	200	12
	VBL[a]	287	Present work
	CBS[a]	1420	
	APC[a]	245	

Note: a, the stabilizer for graphene

Table S 2 Comparison of efficiency of the different stabilizers for suspending graphene

Stabilizers	Weight ratio of stabilizer/GO	Maximum concentration in water (mg/ml)	References
Sulfonated polyaniline	7.2/1	>1	[11]
Pyrene-1-sulfonic acid sodium	4/1	N/A	[10]
Triblock copolymer (PEG-OPE)	57/1	5.2	[13]
Pyrenebutyrate	14.5/1	N/A	[12]
Poly(sodium 4-styrenesulfonate)	10/1	1	[14]
Single-stranded DNA	4.8/1	1	[15]
Lignin and cellulose derivatives	10/1~3/1	0.6~2	[16]
VBL	2/1	6.2	Present work

Table S3 The mechanical properties of neat CS and CS/VBL-G nanocomposites

Samples	Tensile Strength (MPa)	Tensile Modulus (GPa)	Strain (%)	K (J/g)
CS	27.1±2.8	0.30±0.03	36.2±6.0	0.56±0.03
CS-0.3wt%VBL-G	35.1±5.4	0.34±0.05	78.9±8.3	1.20±0.15
CS-0.7wt%VBL-G	38.3±2.8	0.48±0.08	90.3±4.6	1.69±0.20
CS-1.0wt%VBL-G	49.0±3.2	0.65±0.12	68.9±6.3	1.84±0.21
CS-3.0wt%VBL-G	58.0±6.5	0.83±0.08	52.1±2.0	2.02±0.09

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