

Electronic Supplementary Information (ESI)

Ultra-low gas permeability and efficient reinforcement of cellulose nanocomposite films by well aligned graphene oxide nanosheets

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The optical image of GONS/cellulose nanocomposite films

As shown in Figure S1, neat regenerated cellulose film is substantially transparent to the naked eyes, while the addition of GONSs remarkably blocks the light transmission. This probably permits our nanocomposite films to serve as packaging materials for protecting perishable goods vulnerable to degradation from light, for example, some chemical reagents (nitric acid, silver halide, etc.) and some light sensitive foods (juice, vitamin, sport drink, dairy product, edible oil, etc.).



Fig. S1 Optical image of ~0.09 mm-thick GONS/cellulose nanocomposite films as a function of GONS loadings.

Preparation of glycerol toughened cellulose films

The wet cellulose films without any NaOH and urea were initially prepared as reported in the Experimental Section, and then immersed in the 5 wt% glycerol aqueous solution for 12 h at room temperature. The resultant films were further dried under a certain pressure at 150 °C for 10 min to obtain glycerol toughened cellulose films, which could be successfully applied to barrier measurements. In order to estimate the glycerol content, the toughened cellulose films were preconditioned at 150 °C for 10 min and weighed (W_1). Subsequently, warm water at about 60 °C was used to etch the glycerol for a sufficient time. Finally, the etched cellulose films were dried at 150 °C for 10 min and weighed (W_2). The glycerol content in the toughened cellulose films summarized in Table S1 was calculated by the following equation:

$$\text{Glycerol content (wt\%)} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (\text{S1})$$

Table S1 The content of glycerol in the toughened cellulose nanocomposite films

GONS loading (vol%)	0	0.17	0.41	0.83	1.64
Glycerol content (wt%)	13.8 ± 3.1	12.7 ± 1.1	15.3 ± 2.9	17.0 ± 0.5	15.6 ± 1.4

The dispersion of GONSs in the preparation process of cellulose nanocomposite films

It is well known that graphite oxide can be easily exfoliated as individual GONSs by sonication in water (Fig. S2a).¹ In the well-dispersed aqueous suspension, GONSs are highly negatively charged, apparently arising from the ionization of the carboxylic acid and phenolic hydroxyl groups on their basal planes and edges. The result indicates that GONSs dispersed in water as colloids should be attributed to electrostatic repulsion, rather than just the hydrophilicity of GONSs.² However, the electrostatic repulsion can be easily destroyed by the addition of electrolytes due to their high ionic strength.³ Similarly, in our preparation of cellulose nanocomposite films, the inclusion of NaOH and urea in the GONS suspension has an adverse effect on the GONS dispersion and consequently results in a large amount of GONS aggregations (Fig. S2b). After dissolving cellulose at low temperature, GONSs could be uniformly re-dispersed in the solvent system (Fig. S2c).⁴ The phenomenon may be ascribed to the intermolecular interactions between GONSs and cellulose molecular chains.

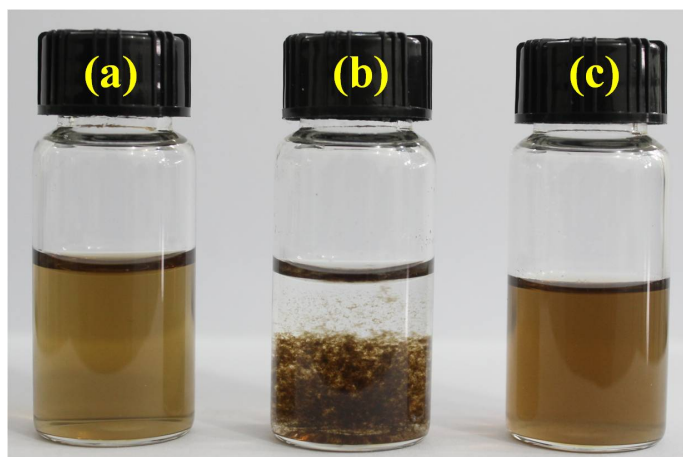


Fig. S2 Digital picture of dispersion of GONSs in water (a) and then added into NaOH/urea (b) for dissolving cellulose at low temperature to obtain GONS/cellulose NaOH/urea aqueous solution (c).

The crystalline structure of regenerated cellulose

Fig. S3 shows representative 2D-WAXD patterns with uniform diffraction rings of original cotton linter and RC film, implying the randomly distribution of cellulose crystals. The intensity profile of original cotton linter exhibits a crystal structure of cellulose I with typical diffraction peaks for the plane (200) at 20.2° , (101) at 14.7° , and $(10\bar{1})$ at 13.2° .⁵ While the RC film displays the two distinct diffraction peaks at 17.8° and 19.2° , which is considered as the crystalline form of cellulose II.⁶ The polymorphic transformation of cellulose I into cellulose II by treating with an alkali solution suggests that the original cotton linter containing native cellulose is well dissolve in the precooled NaOH/urea solution in our work.

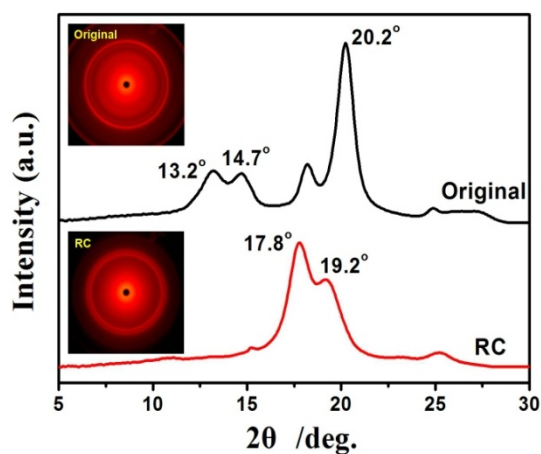


Fig. S3 Representative 2D-WAXD patterns and the corresponding 1D-WAXD intensity profiles of original cotton linter and RC film.

Table S2 Mechanical properties of neat regenerated cellulose and its nanocomposite films incorporated withgraphene-based materials⁷⁻¹¹

Sample	Tensile strength		Young's modulus		Processing solvent	Ref.
	Experimental data (MPa)	Increment (%)	Experimental data (MPa)	Increment (%)		
RC	54.6 ± 2.9	--	1.19	--	NaOH/urea aqueous solution	7
7.5 wt% GONSs	83.1 ± 3.8	52	1.91	61		
RC	73.1 ± 10.1	--	4.5 ± 0.6	--	NMMO monohydrate	8
5 wt% GONSs	97.8 ± 8.2	34	5.5 ± 0.2	22		
RC	89	--	3.4	--	DMAC/LiCl solution	9
1.6 wt% GNSs	148	66	7.2	110		
RC	60.0 ± 3	--	3.3 ± 0.3	--	ionic liquid	10
0.5 wt% GONSs	98.8 ± 6	65	3.7 ± 0.4	12		
RC	--	--	--	--	ionic liquid	11
3 wt% GNP	--	34	--	52		
RC	50.1 ± 1.0	--	3.8 ± 0.2	--	NaOH/urea aqueous solution	this study
1.64 vol% GONSs	83.5 ± 3.8	67	6.4 ± 0.3	68		

GNSs: graphene nanosheets; GNPs: graphene nanoplatelets.

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