Carbon Nanotubes/Polymer Nanocomposites -- From Fundamental to Application

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Outline

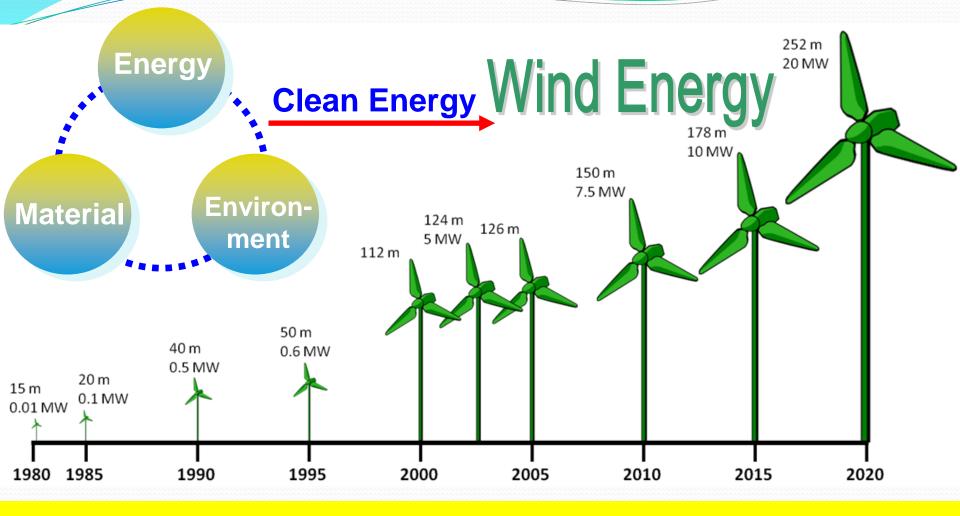
Engineering application of CNT/polymer nanocomposites

- -- Perspectives for wind blade materials
- -- Sensory materials for defect monitoring in FRPs
- Environmental application of (CNT)/polymer nanocomposites
 - -- Materials for oil-water separation
 - -- Multi-functional textiles
- Concluding Remarks
- > Acknowledgement

Engineering Applications of CNT/Polymer Nanocomposites

Perspectives for Wind Blade Materials

Introduction



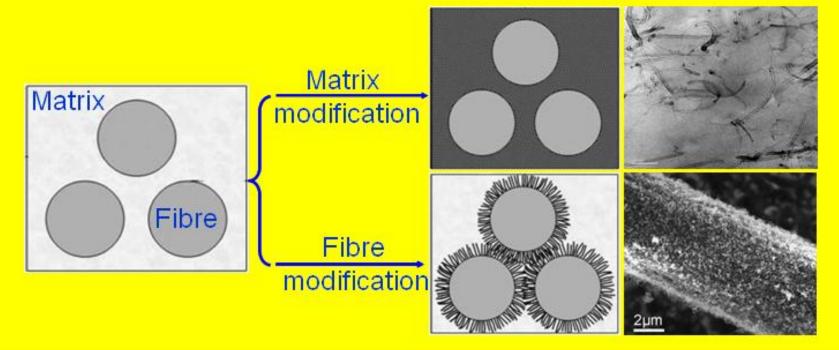
Requirements for Wind Blades

Larger Size Higher Strength Better Stability

Material Selection for Wind Blades

FRP Structures for Wind Blades

How to improve FRP performance?





-- Environmental aspect: Lighting strike, humidity, thermal stability...

Ma, et al. Renew Sustain Energy Rev, 2014, 30, 651

Multi-functionality of CNTs in Polymer (I) – Mechanical Reinforcement

Importance of Mechanical Properties for Blades

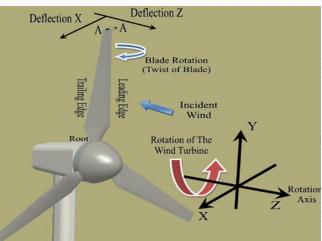
- -- Blade length >40 m, structural integrity
- -- Blade loading under different conditions
- -- Properties: Modulus, strength, toughness, fatigue...

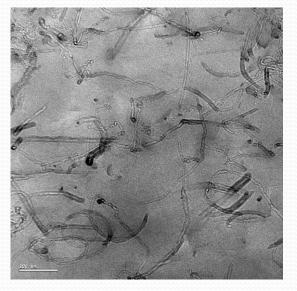
Modulus and strength of CNT/Epoxy Nanocomposites

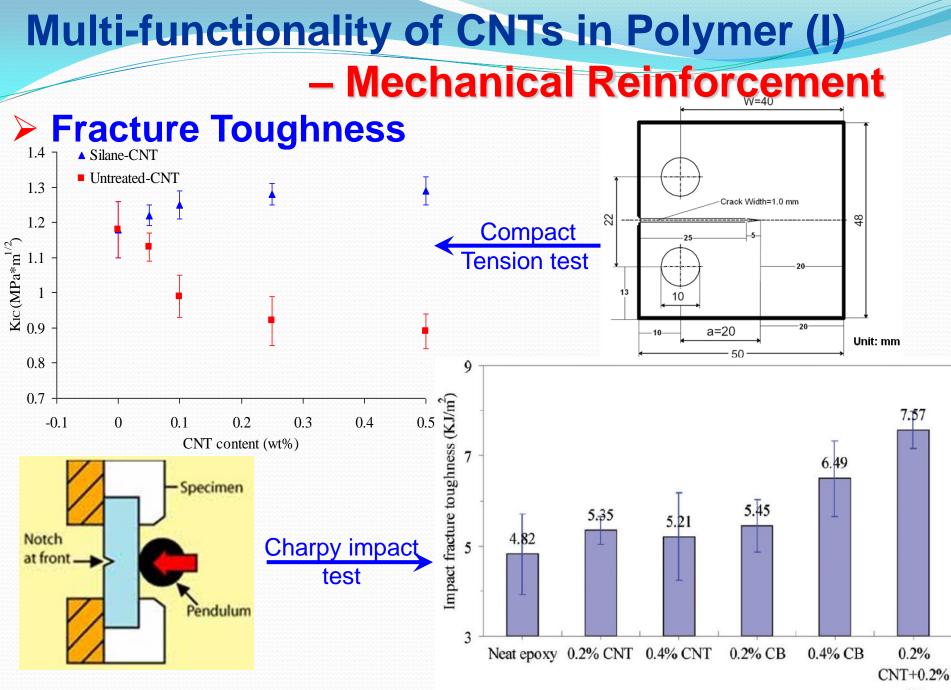
	Flexural modulus	Flexural strength	
	(GPa)	(MPa)	
Ероху	2.91±0.03	106.6±2.2	
CNT/Epoxy	3.56±0.05	125.3±1.2	

CNT content: 0.25%; 3-point bending test;
 Epoxy: DGEBA (Epon-828) & m-phenylenediamine

Ma, et al. Compos Sci Technol, 2007, 67, 2965







Ma, et al. Compos Sci Technol, 2007, 67, 2965; ACS App Mater Interfaces, 2009, 1, 1090

CB

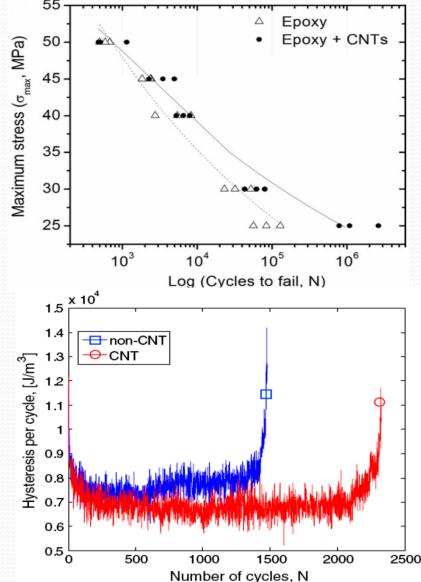
Multi-functionality of CNTs in Polymer (I) – Mechanical Reinforcement

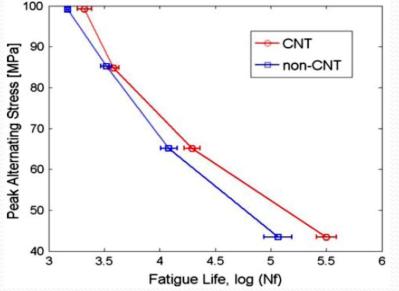
Matuin	CNT content		Enhancement on mechanical properties*		
Matrix			Modulus (%)	Strength (%)	Toughness (%)
Thermo-plastic	PA	1.0 wt.%	6.1 (42)	-5.3 (18)	_
	PB	1.5 wt.%	18 (91)	-27 (61)	-40(67)
	PE	1.5 wt.%	22 (75)	-17 (33)	-69 (61)
	PI	7.0 wt.%	39 (61)	19 (31)	-
	РР	1.5 wt.%	55 (84)	-10 (13)	-
	PS	0.25 wt.%	-8.3 (25)	2.1 (50)	-
	PVA	2.5 wt.%	35 (40)	-4.8 (17)	-
	PMMA	0.10 wt.%	57 (104)	-2.7 (86)	-
Thermo-set	EP	0.10 wt.%	2.1 (6.7)	-2.2 (3.1)	17 (19)
		0.25 wt.%	8.6 (24)	6.8 (20)	35 (60)
		0.25 wt.%	8.7 (22)	3.6 (18)	-22 (8.5)
*	PU	0.7 wt.%	48 (178)	27 (23)	-
Data in bracket: Enhancement by employing		10 wt.%	340 (500)	51 (111)	-
	VR	25 phr	444 (594)	175 (244)	-
functionalized Cl	NT s	1 phr	35 (28)	-7.8 (25)	-

Ma, et al. Compos A, 2010, 41, 1345

Multi-functionality of CNTs in Polymer (I) – Mechanical Reinforcement

Fatioue properties: Cumulative damages due to the cyclic loading





CNTs inhibit the formation of cracks: A large density of nucleation sites by CNTs

Contribution from the fracture of CNTs bridging across nanoscale cracks and CNT pull-out from polymer matrix Grimmer, et al. J Mater Sci 2008, 43, 4487; Loos, et al. Polym Eng Sci 2012, 52, 1882; Ma, et al. Renew Sust Energ Rev, 2014, 30, 651

Multi-functionality of CNTs in Polymer (II) - Electrical Conductor Lightning strike to blades $\sigma = 10^4 - 10^5 \text{ S/m}$ CNTs on glass fibre Application of conducting composites 1.00E+02 Conducting adhesive and coating Electrical conductivity (S/cm) 1.00E+00 Thermal interface and electromagnetic shielding materials 1.00E-02 А Conducting thin film, elastic electrode Down Receptor conductor 1.00E-04 Down Metal mesh conductor Antistatic coatings and films 1.00E-06 Metal wire Semiconducting materials, papers and 1.00E-08 textiles, household appliances shell 1.00E-10 Insulating material Ma, et al. CNTs for polymer reinforcement, CRC Pres⁵⁰.

Multi-functionality of CNTs in Polymer (II)

CNT/Epoxy Nanocomposites

-- Transition from the insulator to conductor;

-- More pronounced increase in conductivity for Ag@CNT nanocomposites: From 2.2×10^{-13} to 0.81 S/cm (CNT=0.50 wt%).

Synergistic effect in CNT/CB/Epoxy nanocomposites 1.0E-02 1 1.0E-02

Filler content (wt%)

--- A: CNT only

B: CB only

2

1.5

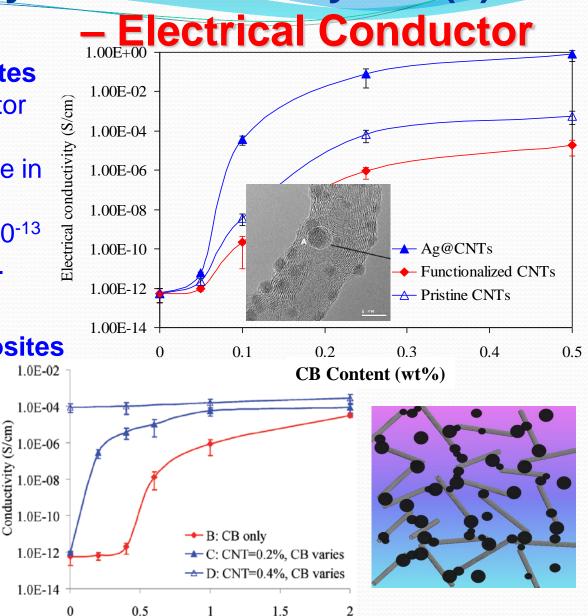
1.0E-04

1.0E-06 Conductivity (S/cm) 1.0E-08 1.0E-10

1.0E-12

1.0E-14

0.5



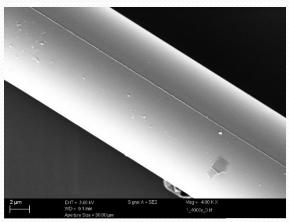
Ma, et al. Carbon, 2008, 46, 1497; ACS App Mater Interfaces, 2009, 1, 1090

CB content (wt%)

Multi-functionality of CNTs in Polymer (III) – Functional Coating for Fibres

Problem of glass fibre used in FRPs

- -- Lower strength than the theoretical prediction
- -- Small defects in surface scratches, cracks and internal flaws
- -- Environmental stability: -Si-O-Si- structure, chemical and humidity affected



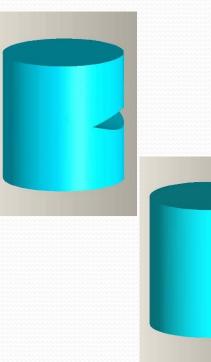
CNT/Polymer Nanocomposite coating for fibres

- -- Healing of fibre surface
- -- Multi-functional glass fibres
- -- Role of nanocomposites in properties of glass

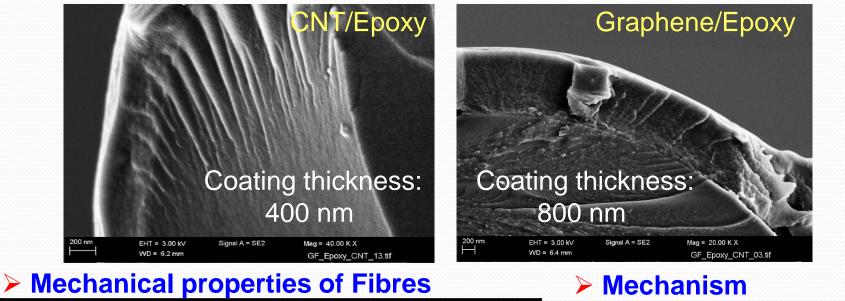
fibres

How & Why?

- -- Polymer: Fill the micro-cracks on fibre surface
- -- CNTs: Bridge and resist the opening of cracks

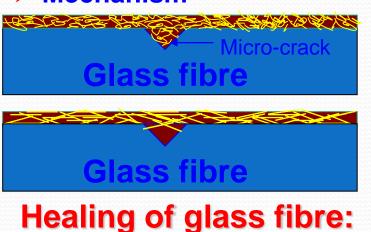


Multi-functionality of CNTs in Polymer (III) – Functional Coating for Fibres Fibres with nanocomposites coating



Coating	Strength (MPa)	Weibull modulus
No coating	2094±299	6.29
Ероху	2231±238	6.45
CNT/epoxy	2404±310	8.43
Graphene/epoxy	2289±380	6.98

Ma, et al. Compos A, 2013, 44, 16



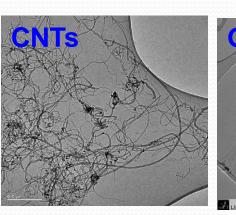
CNT > Graphene 13

Multi-functionality of CNTs in Polymer (III) - Functional Coating for Fibres

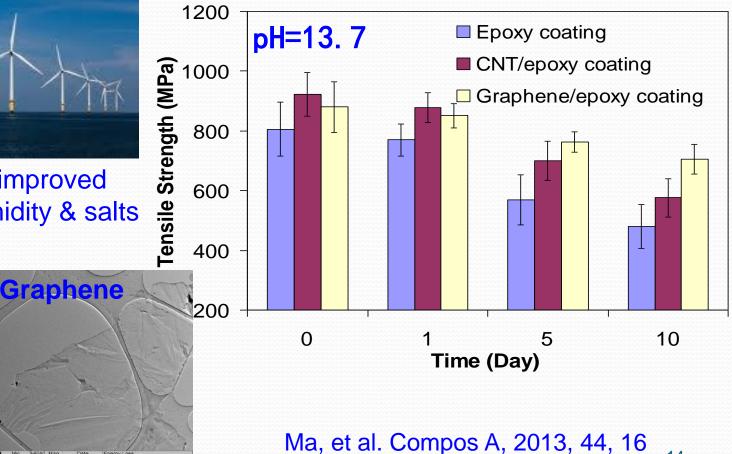
Offshore wind turbine



Materials with improved resistance to humidity & salts



Barrier performance of fibres to humidity and alkali



14

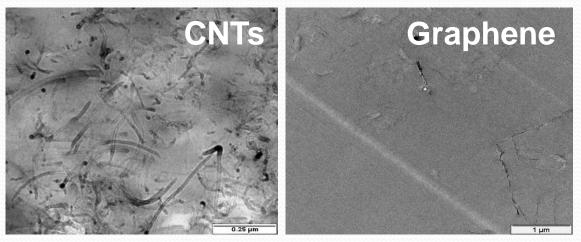
Multi-functionality of CNTs in Polymer (III)

Functional Coating for Fibres

Conducting glass fibres with coating

Coating	Measured length 5 mm	Measured length 5 mm	Measured length 5 mm
Ероху	> 1000 MΩ	> 1000 MΩ	> 1000 MΩ
CNT/epoxy	10-100 MΩ	100-800 MΩ	100-800 MΩ
Graphene/epoxy	10-100 ΚΩ	100-500 KΩ	500-1000 ΚΩ

Distribution of nanofillers in coating





Mechanical induced Graphene Alignment in nanocomposites coating

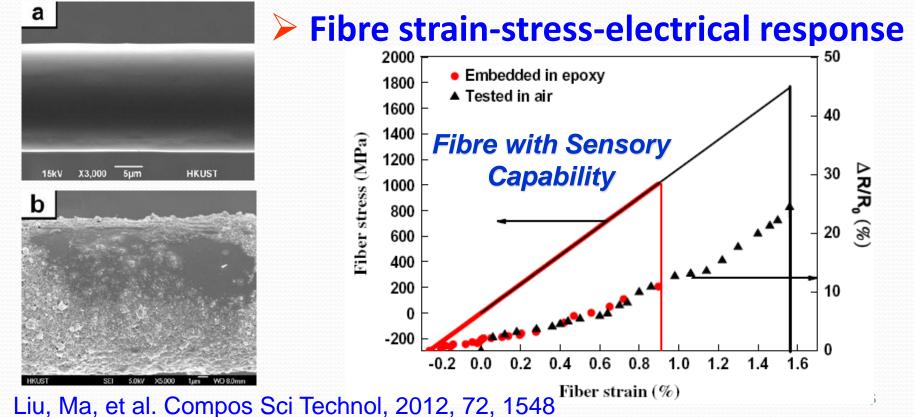
Ma, et al. Compos A, 2013, 44, 16

Multi-functionality of CNTs in Polymer (IV)

– Damage Sensor for FRPs

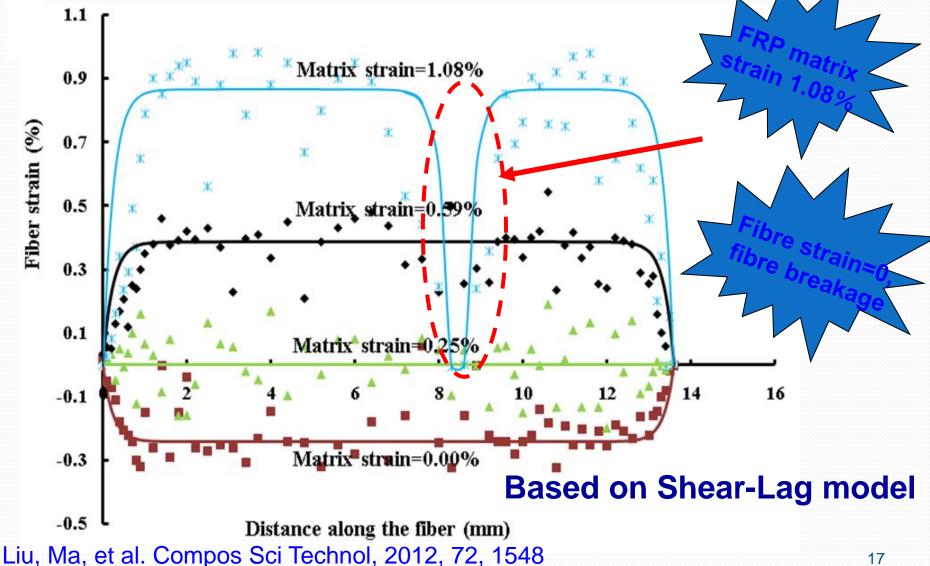
Specific discrete build-up makes maintenance and damage analysis of FRPs a challenging task.

- Advanced warning of defects in composites using CNTcoated glass fibres
- Fibres without/with CNT coating



Multi-functionality of CNTs in Polymer (IV) – Damage Sensor for FRPs

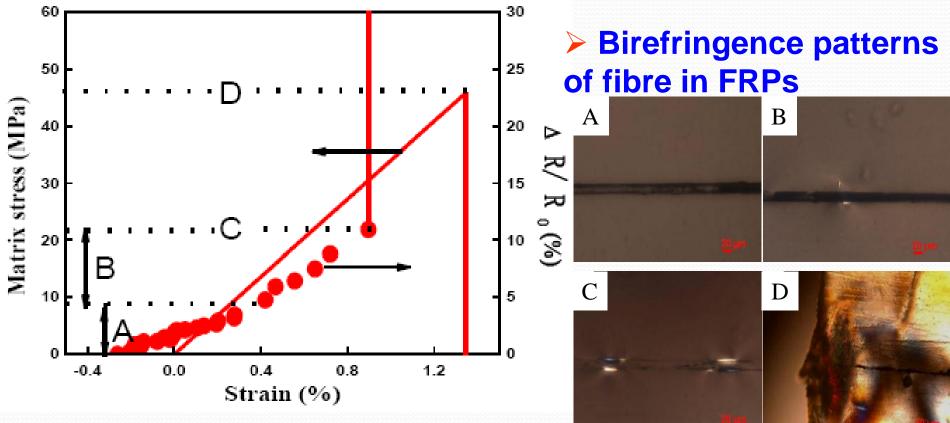
Distribution of fibre strain in FRPs



Multi-functionality of CNTs in Polymer (IV)

- Damage Sensor for FRPs

Matrix stress-strain-fibre resistance



Earlier fibre breakage than matrix failure: Warning of damage process in FRPs

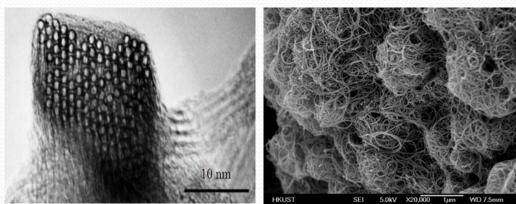
Liu, Ma, et al. Compos Sci Technol, 2012, 72, 1548

Summary

CNTs

Multi-functional modifier for FRP components:
 Polymer matrix: Improved mechanical, electrical, damping properties
 Fibre: Surface healing and sensory capability

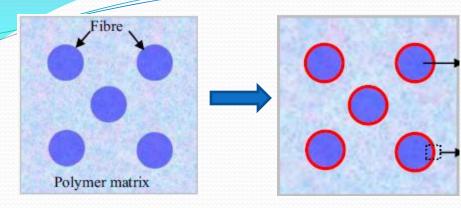
- Challenges
 - -- Dispersion
 - -- Functionalization
 - -- Cost: ~ 2 US\$/g
 - -- FRP processing



Engineering Applications of CNT/Polymer Nanocomposites

Sensory Materials for Defect Monitoring in FRPs

Introduction

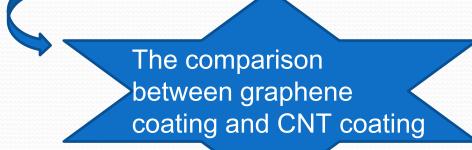


Key role of interphase

Much investigation in the interphase of GFRP: interfacial strength, other functions by CNT and Graphene.

CNT: 1 Dimension

Graphene: 2 Dimension

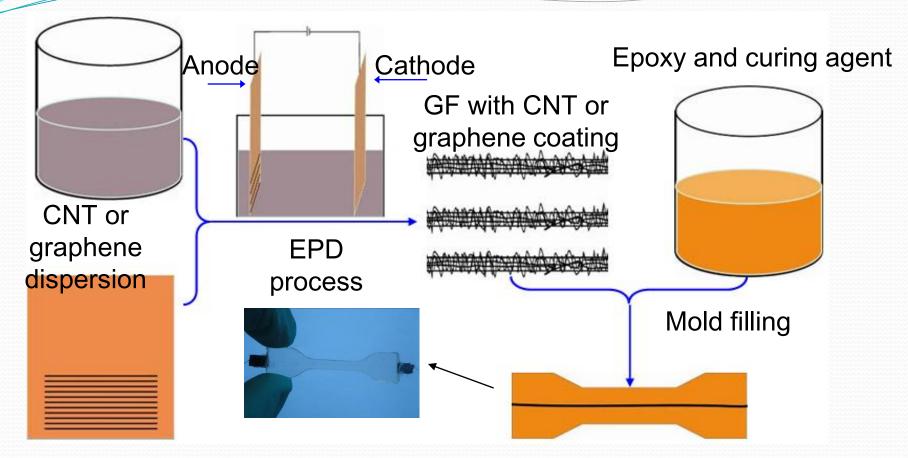


 H_2N NH₂ H₂N NH₂ H₂N NH₂ Bonding between H_2N NH₂ fibre and matrix **Modification** GF-NH₂ b 1.1 Matrix strain=1.08 Matrix strain - Tensile strengt -AR/R 0.06 0.04 0.04 0.02 0.00 1.5 2.0 2.5 3.0 3.5 4.0 0.0 0.5 1.0

Zhang J, Carbon, 2010 Ma PC, Renewable&Sustainable Energy Reviews, 2014

Strain (%)

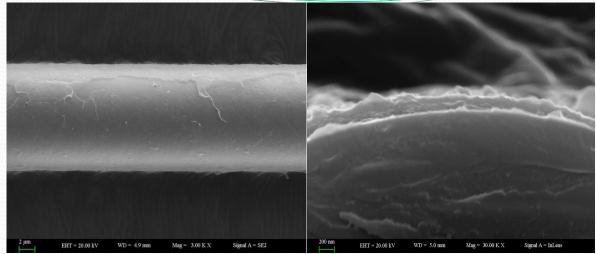
Experimental Setups



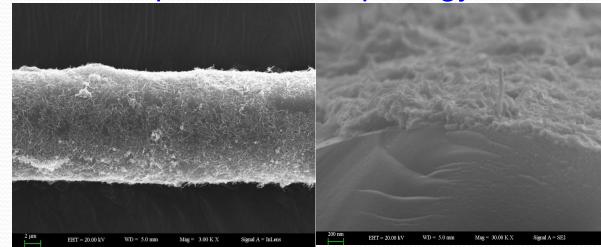
GFs on Cu plate Model GFRPs with single GF

Process of Sample preparation

Graphene coating: ~ 10^2 nm 10^{-2} ~ $10^{-1} \Omega$ •cm

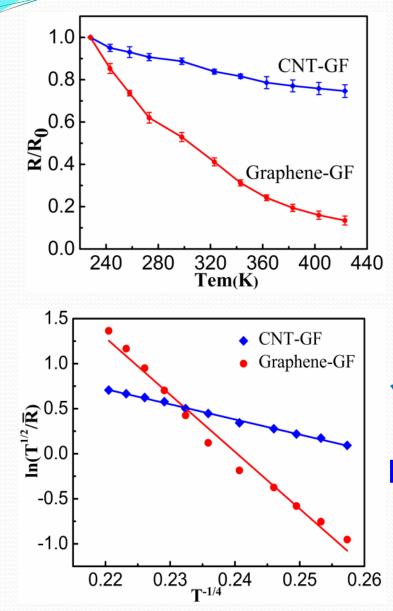


Graphene/GF morphology



CNT/GF morphology

CNT coating: ~ 10²nm 10⁻²~10⁻¹ Ω•cm



- Negative temperature coefficient (NTC)
- ✓ Change ratio

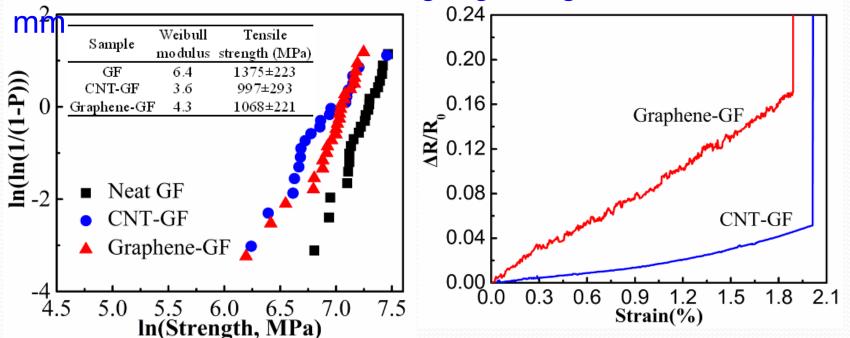
Graphene/GF-80%, CNT/GF-20% ✓ Variable range hopping (VRH)

model:

$$\ln(T^{1/2}/\overline{R}) \propto T^{-1/2}$$

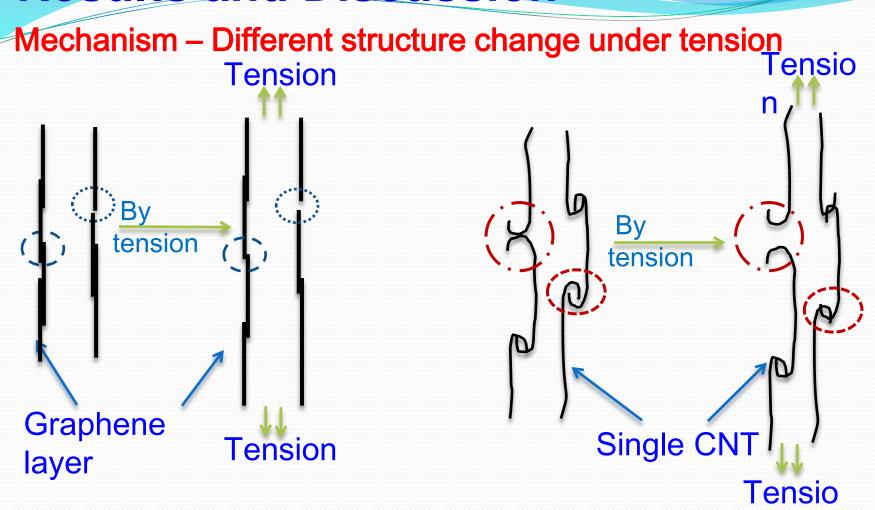
Hopping efficiency
 Graphene/GF: B=63.3; CNT/GF:
 B=16.8
 Reason
 Structure difference
 Graphene/GF: More contacting area

-Tension rate - 0.5 mm/min, gauge length - 40



Results: - Lower tensile strength -Resistance increases with strain -Sensitity: Gauge factor $K = \frac{R(\varepsilon) - \varepsilon}{1 - \varepsilon}$

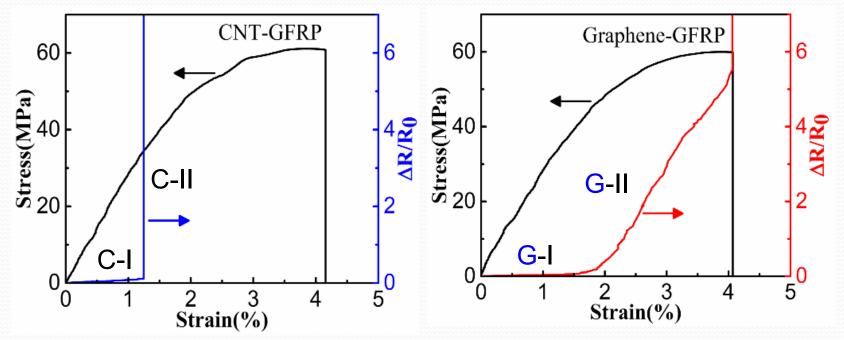
-Sensitity: Gauge factor $K = \frac{R(\varepsilon) - R_0}{R_0} / \varepsilon$ CNT/GF: 2.3±0.1, Graphene/GF: 9.5±0.4



Graphene coating: contacted area was reduced under tension

CNTs coating: rebuilt of the conductive paths

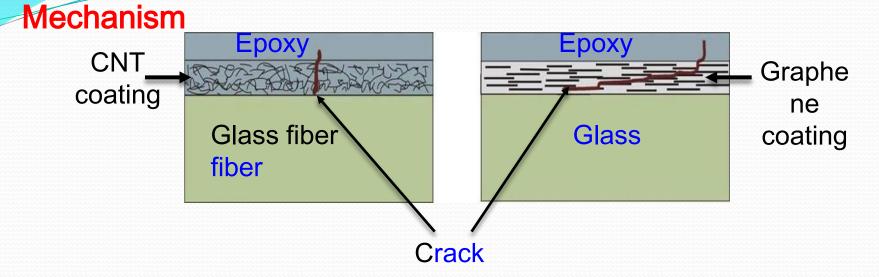
Model GFRP tension test



✓No change in tensile strength after combining with single fiber.

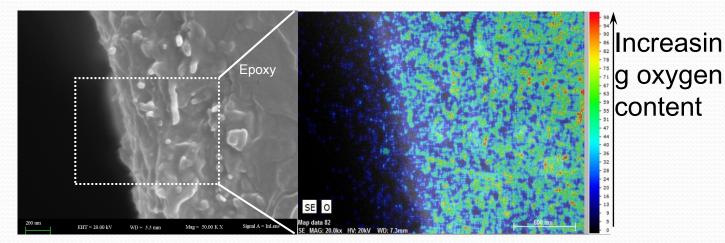
✓CNT-GFRP: non-conductive (Strain=1.3%) before breakage of matrix (4.2%)

 ✓ Graphene-GFRP: resistance change in two different slope, remained conductive until break of matrix

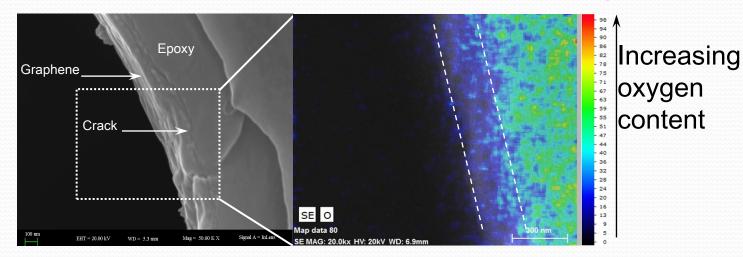


Structure of coating in GFRP CNT-GFRP: nanocomposites made of epoxy and CNT Graphene-GFRP: mainly made of Graphene layers Different paths of crack

Different performance in resistance change

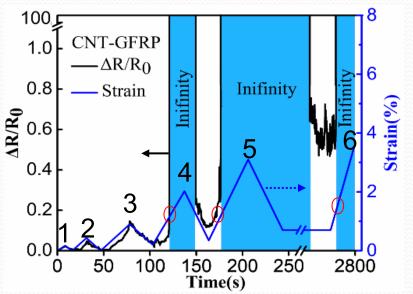


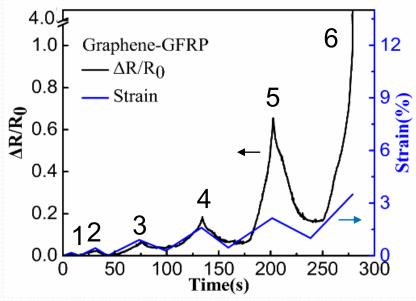
CNT-GFRP: nanocomposites made of epoxy and CNT



Graphene-GFRP: nanocomposites and Graphene layers

Piezoresistive responses of GFRPs under cyclic mechanical loadings





Stage 1, 2 (below 0.5%): reversible Stage 3 (strain peak was 0.9%): irreversible Stage 4 (strain peak was 2%): Switch effect, starting strain =1.14% Stage 5 (strain peak was 3.1%): Delayed switch effect Stage 6: Break of GFRP

Stage 1, 2 (below 0.5%): reversible Stage 3,4,5: irreversible Stage 6: Break of GFRP

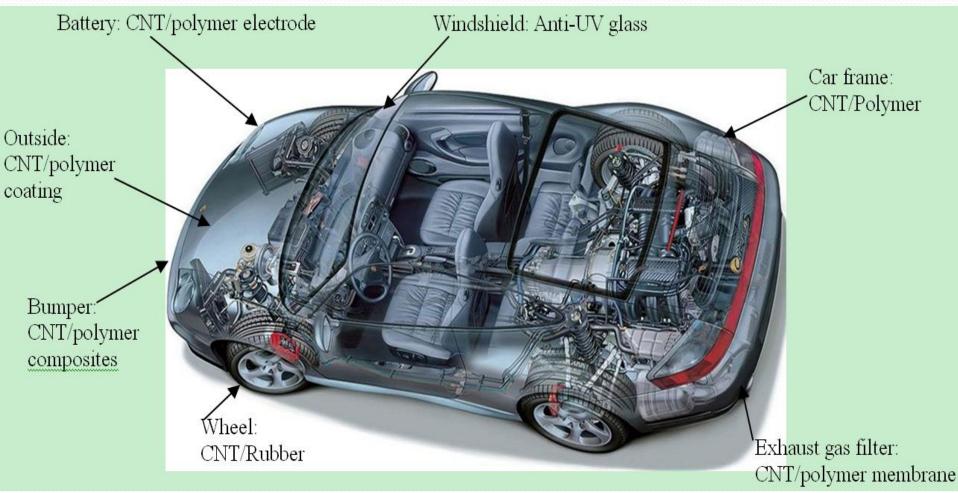
Summary

- Successful deposition of CNT or graphene on glass fibre
- ✓ Single fibre test:
 - Graphene-GF: more sensitive to T and tension
- Different interphase structure in GFRP
 Graphene-GFRP: mainly made of graphene layers
 CNT-GFRP: nanocomposites by CNT and matrix
- ✓ Different piezoresistive responses

Graphene-GFRP: conductivity could be remained until break of matrix CNT-GFRP: nonconductivity before break of matrix

Other Engineering Applications of CNT/Polymer Nanocomposites (I)

Automobile Industry



Ma, et al. CNTs for polymer reinforcement, CRC Press.

Other Engineering Applications of CNT/Polymer Nanocomposites (II)



Environmental Applications of (CNT)/Polymer Nanocomposites

Materials for Oil-water Separation

Where is Xinjiang?



Where is Xinjiang?





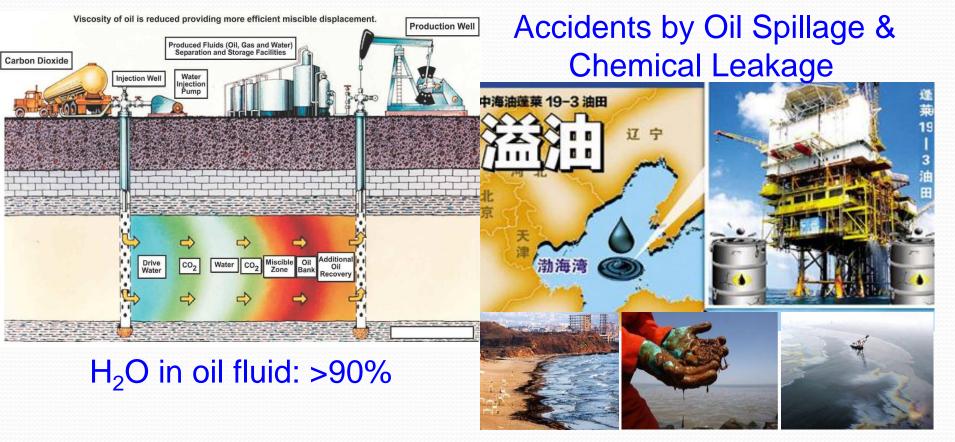




Oil-Field in Xinjiang

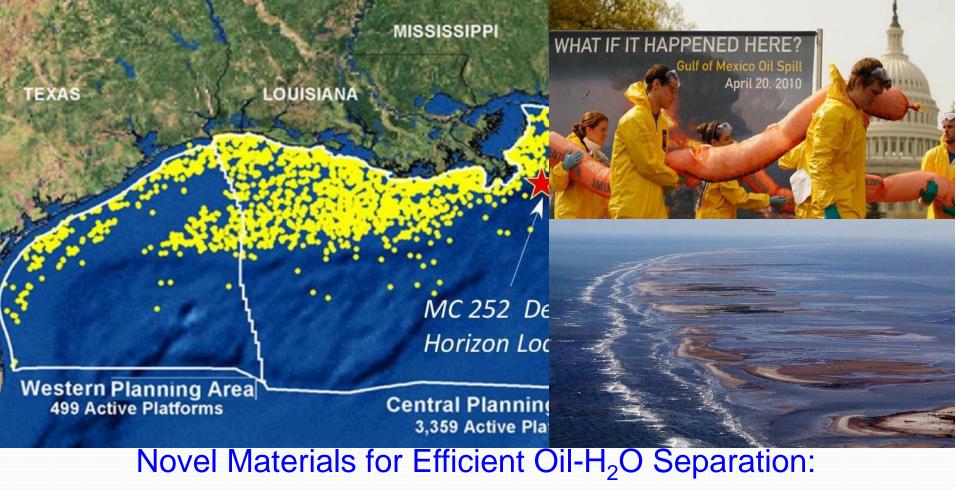
Oil-Water Separation

Enhanced Oil-Recovery Technique



Oil-Water Separation

Accidents by Oil Spillage & Chemical Leakage



<u>Enhancement</u> for Energy Production and <u>Protection</u> for Environmental and Ecological Systems

Outline

Introduction

- -- Materials for oil-water separation
- -- C-based nanomaterials
- -- Research objectives

Experiment and Results

- -- Preparation (Materials, method...)
- -- Characterization (Morphology, surface chemistry...)

> Application of Polymer Nanocomposites

- -- Oil-water separation (Adsorption capacity, recyclibility...)
- -- Oil collector (Design, performance...)
- -- Perspectives
- Concluding Remarks

Materials for Oil-H₂O Separation (I)

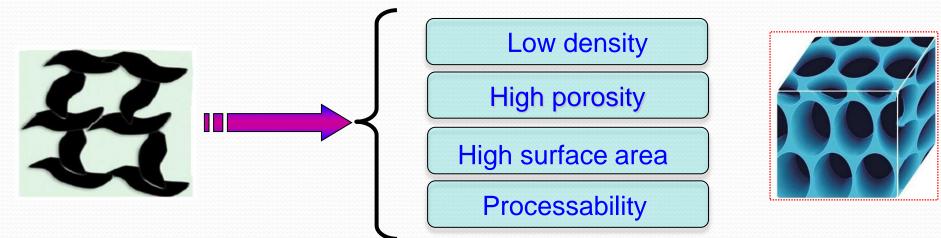
Traditional materials for Oil-Water Separation

Parameter	Natural materials (Wool, cotton)	Inorganic materials (Clay, graphite)	Polymers (Fibre, foam…)
Adsorbate	Oil and water	Oily compounds	Oils & chemicals
Capacity (g/g)	< 10	5-10	> 10
Material cost	High	Low	Medium
Operation convenience	Hard (Fabrics)	Hard (Powders and particles)	Easy (Flexible)
Reusability	No	Yes	Yes
Dimension stability	Instable	Instable	stable
Regeneration of adsorbate	No	Yes	Yes



Materials for Oil-H₂O Separation (II)

C-based nanomaterials (CNTs, CNFs, Graphene)



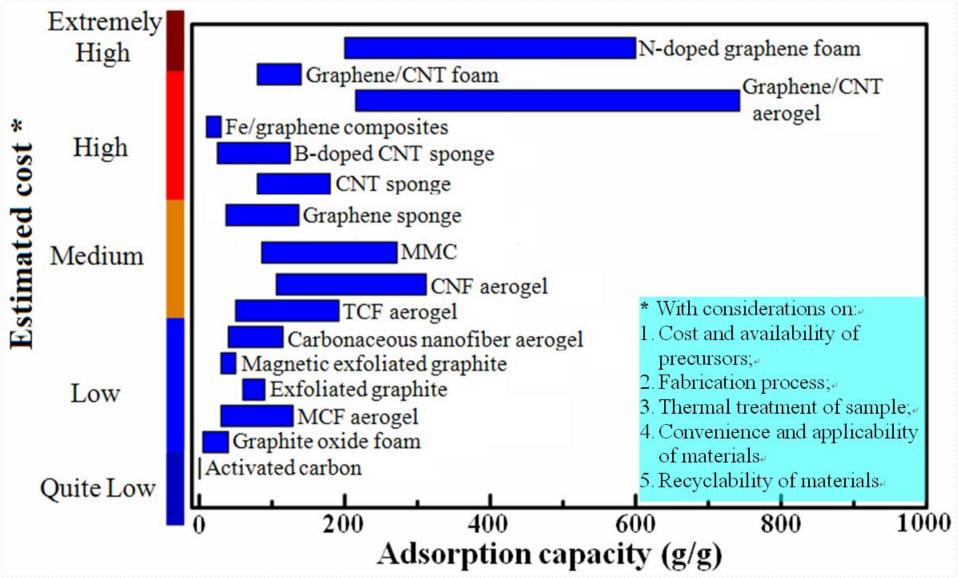
Inherent hydrophobic nature of carbon makes C-based nanomaterials ideal material for oil-water separation



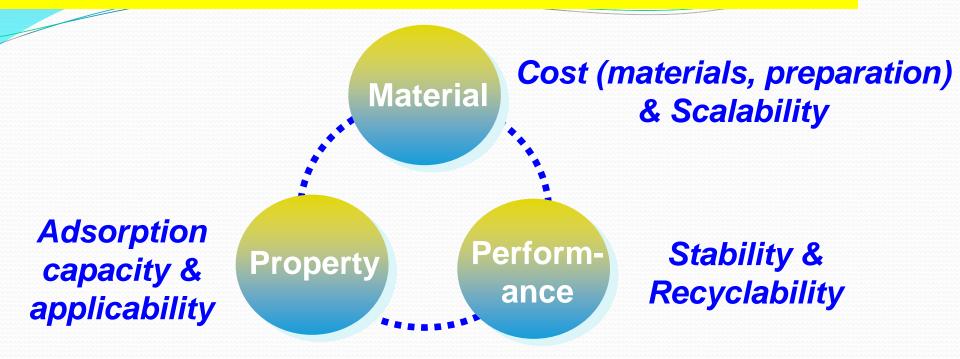
Foam, Sponge, Aerogel, Membrane...

Materials for Oil-H₂O Separation (III)

Adsorption Capacity of C-based Nanocomposites



Research Objectives

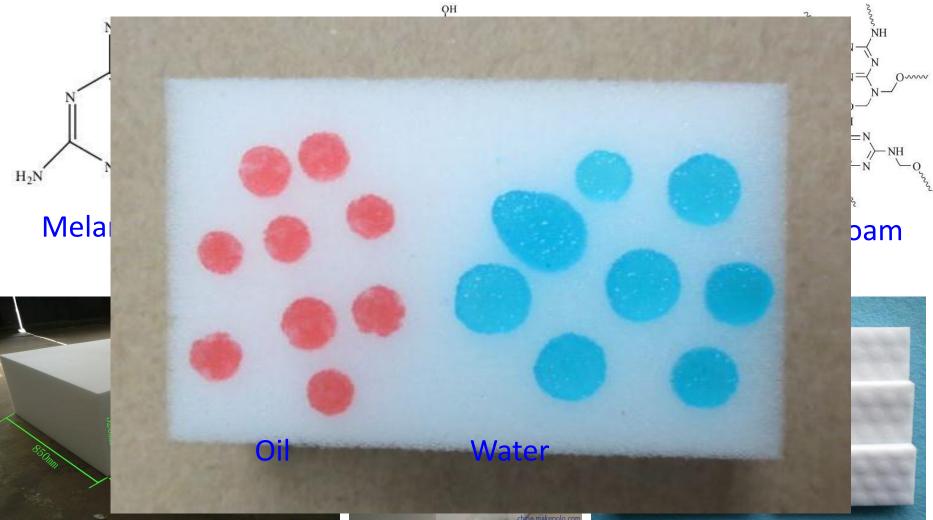


How?

- -- Chemical modification for commercial available polymer foams
- -- Changing on surface and structural properties of foams
- -- Macro-, meso- and micro-pores for oil-H₂O separation What?
 - -- Polymer foams with nanocomposites coating
 - -- Oil collector using polymer nanocomposites as key components

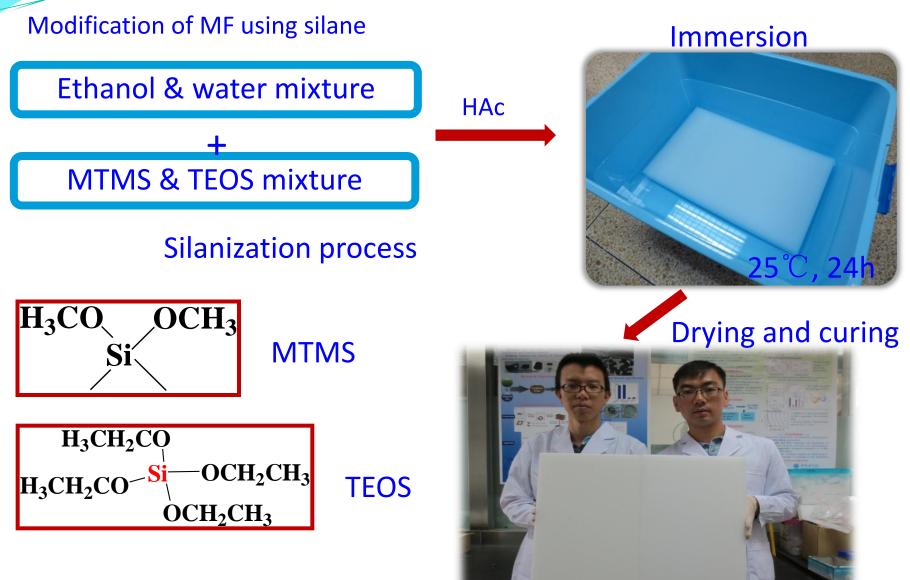
Experimental Setups (I)

Material-- Melamine foam (MF)

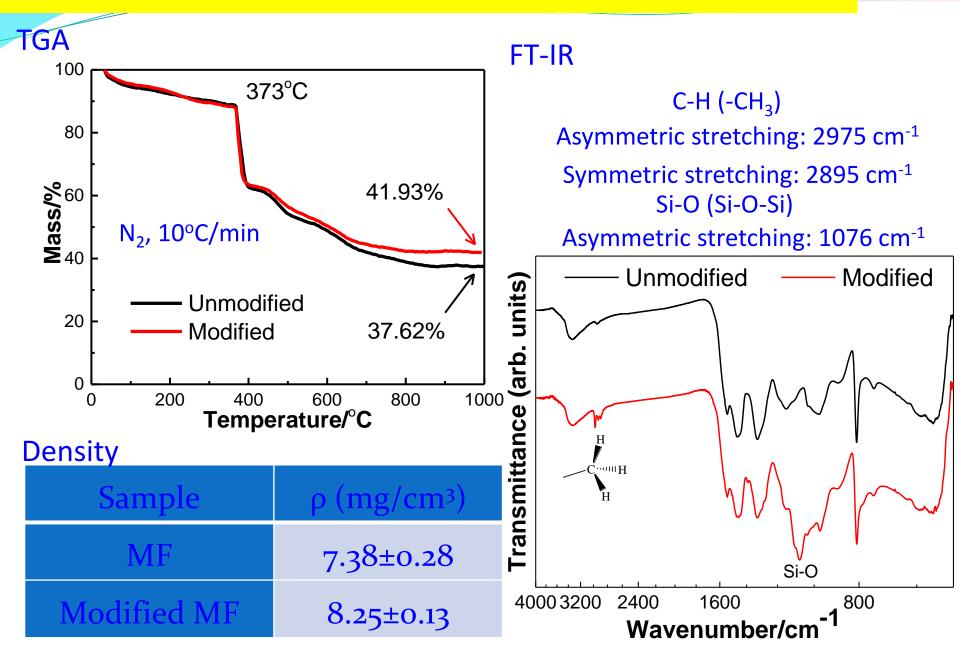


Porosity > 99%, Density < 10mg/cm³, Super-Light materials

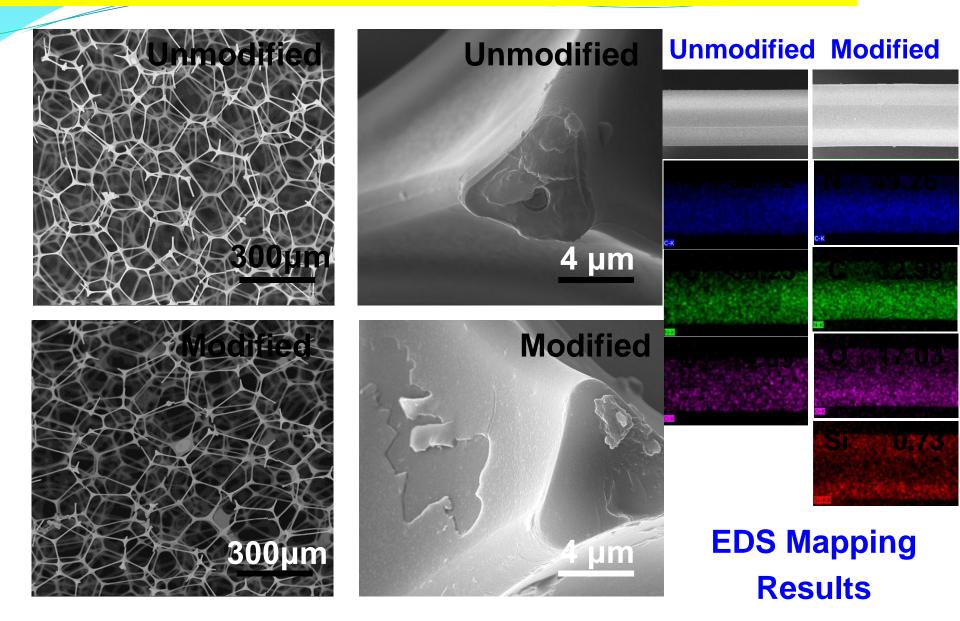
Experimental Setups (II)



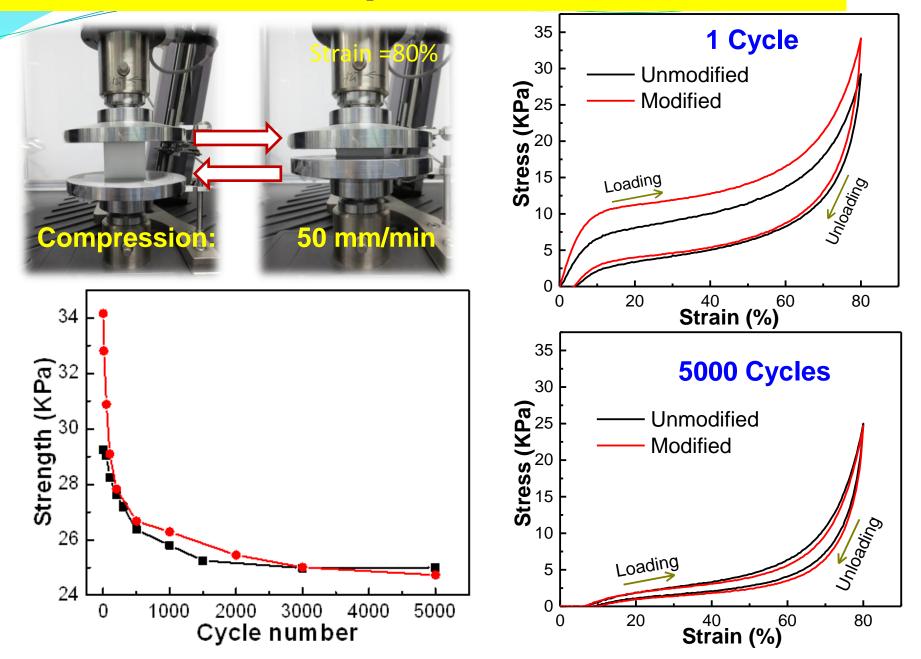
What Happens for MF with Silane?



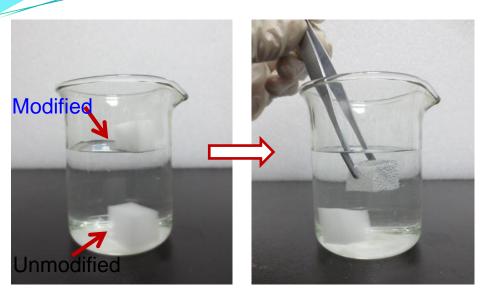
Morphology & Composition of MF

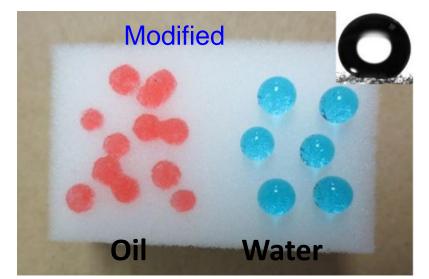


Mechanical Properties of MF



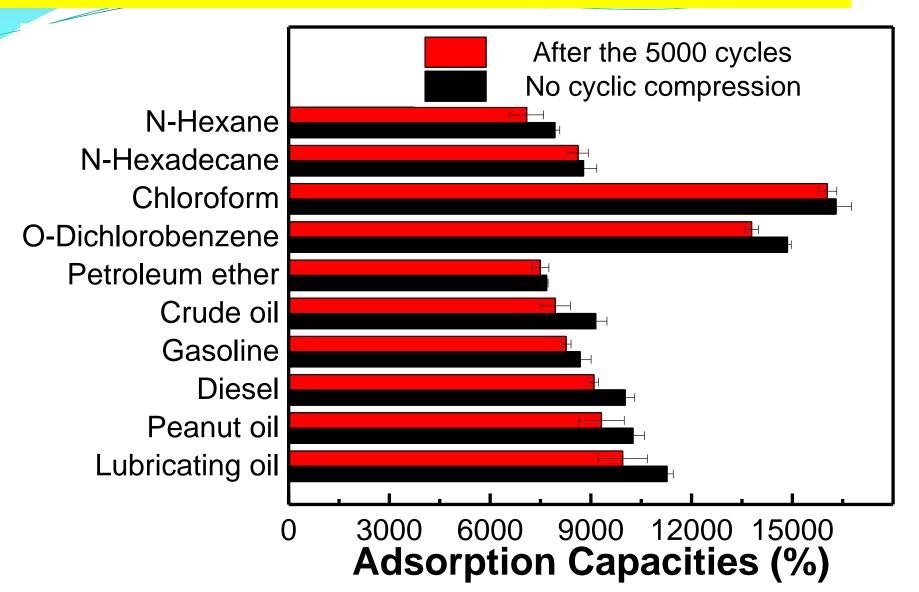
Wettability of MF



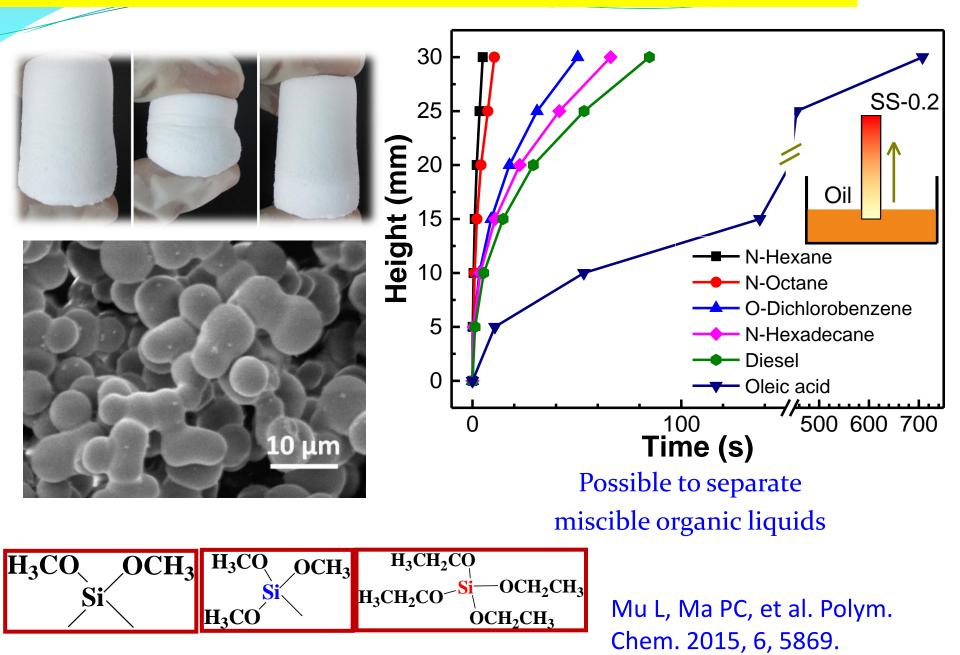


Contact angle of MF with	η Η ₂ Ο	
Modified MF	Contact Angle/º	
Before compression	156.4±1.9	
After 5000 cycles Parallel to compression	153.0±3.2 🗲	
After 5000 cycles Vertical to compression	150.2±2.1 ←	

Adsorption Capacity of MF



Novel Application of Polymer Foam



Comparison: Cost Vs. Performance

Surface modification of various sponges

Parameter	PU sponge	MF sponge	MF
Modification <i>methods</i>	Oxidation & immersion	Solution immersion	Solution immersion
Modifier	PDMS, CNTs, fluorinated silane	PDMS, CNTs, graphene, fluorinated silane	Common silane (MTMS & TEOS)
Adsorbate	Oils & Organic solvent	Oils & Organic solvent	Oils & Organic solvent
Capacity (g/g)	10-25	40-180	40-180
Material cost	Cheap/High	Cheap/High	Cheap/Cheap
Cyclic used times	300	~ 10	>1000

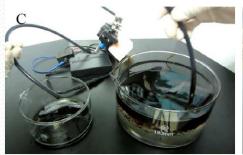
Practical Application of Modified MF (I)

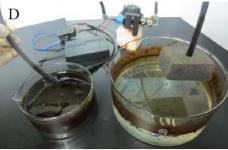
Oil-collector (EN-0) Using MF as Key Material









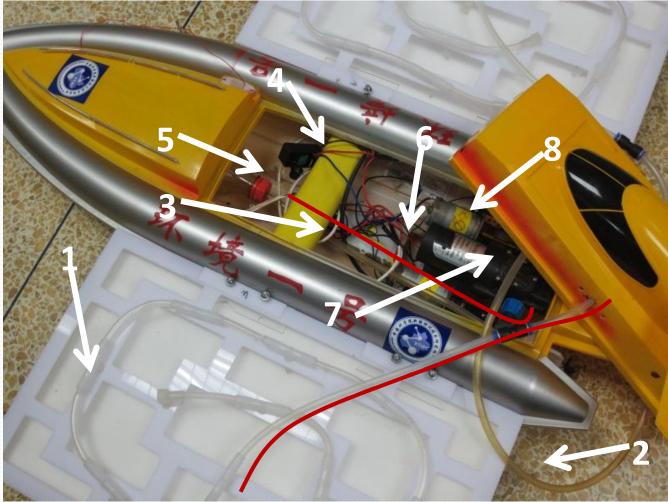






Practical Application of Modified MF (I)

Oil-collector (EN-1) Using Nanocomposites as Key Material



1: Polymeric Sponge 2: Oil Pipe Network 3: Power (Battery) 4: Power Divider 5: Oil Storage 6: Remote Controller 7: Pump 8: Motor

Practical Application of Modified MF (I)

Oil-collector (EN-1) Using Nanocomposites as Key Material



Perspectives (I)

Oil Collector: Environmental No. X Series

EN-1: Remote control prototype (Accomplished)

EN-0: Portable (Accomplished)





EN-2: Remote controllable oil



http://www.lamor.com/products/

Perspectives (II)

EN-3: Recovery for Oil Spill & Chemical Leakage Integrated System and Solution Offshore: Remote control, monitoring and support Inshore: Leakage site, mothership and collectors (EN-2) Overhead: Monitoring using UAV, GPS navigation and

wireless controlling for EN-2

Perspectives (III)









Conclusions

A simple and efficient method for the modification of MF using silane-derivated nanocomposites

> MF with nanocomposite modification:

- -- Superhydrophobic and superlipophilic behaviors
- -- High adsorption capacities with stable cyclic operations
- -- Excellent thermal stability and mechanical properties
- Design and verification of oil collector for oil-H₂O separation using polymer nanocomposites as key <u>component</u>





Black

Environmental Applications of (CNT)/Polymer Nanocomposites

Multi-functional Cotton Fabrics with Nanocomposite Coating

Introduction

Functional cotton materials



Research Background

Characteristic of pristine cotton

- Hydrophilic and strong absorption capability
- High specific surface and porous structure
- Bio-degradable
- Available in different form and relatively less cost

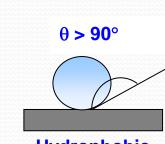
Limitations for advanced application

- High superhydrophilicity
- Impotent antimicrobial property
- Poor UV protection property
- Low strength for some applications

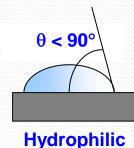


Microbial growth on cotton





Hydrophobic





Cotton Fiber



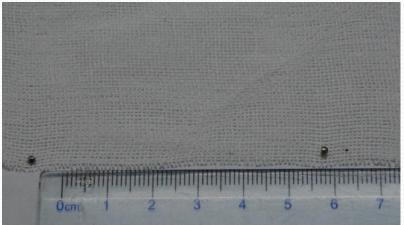
Cotton Yarn



Cotton Fabric

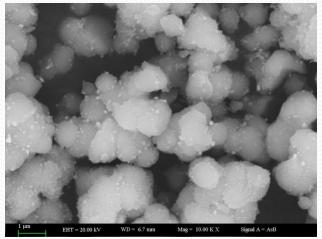
Materials and Method

Cotton gauze



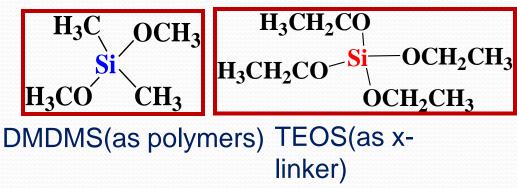
Fabric weight: 60 g/m²

AgBr-TiO2 composite:

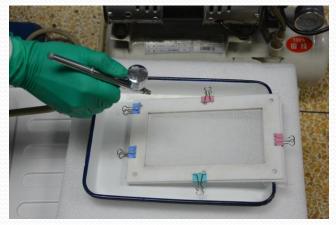


Particle size: 400-600 nm

Silane (anchoring agent):

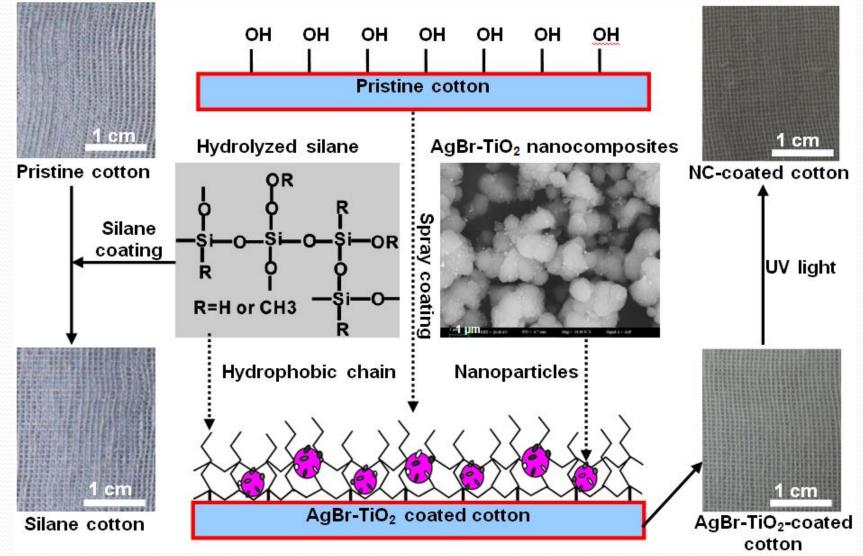


Spray coating:

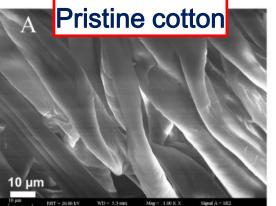


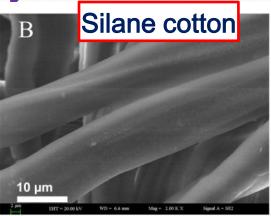
Materials and Method

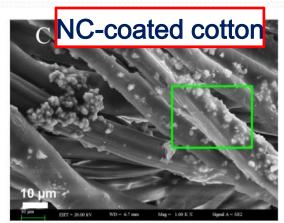
Schematic diagram of the experiments:

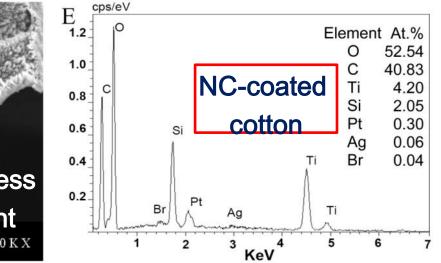


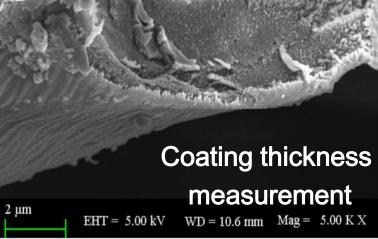
SEM and EDX analysis



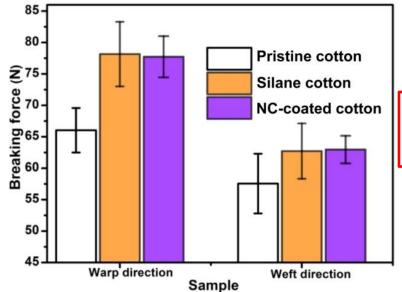


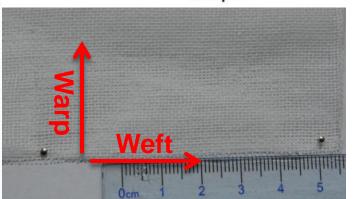






Mechanical and surface wetting properties





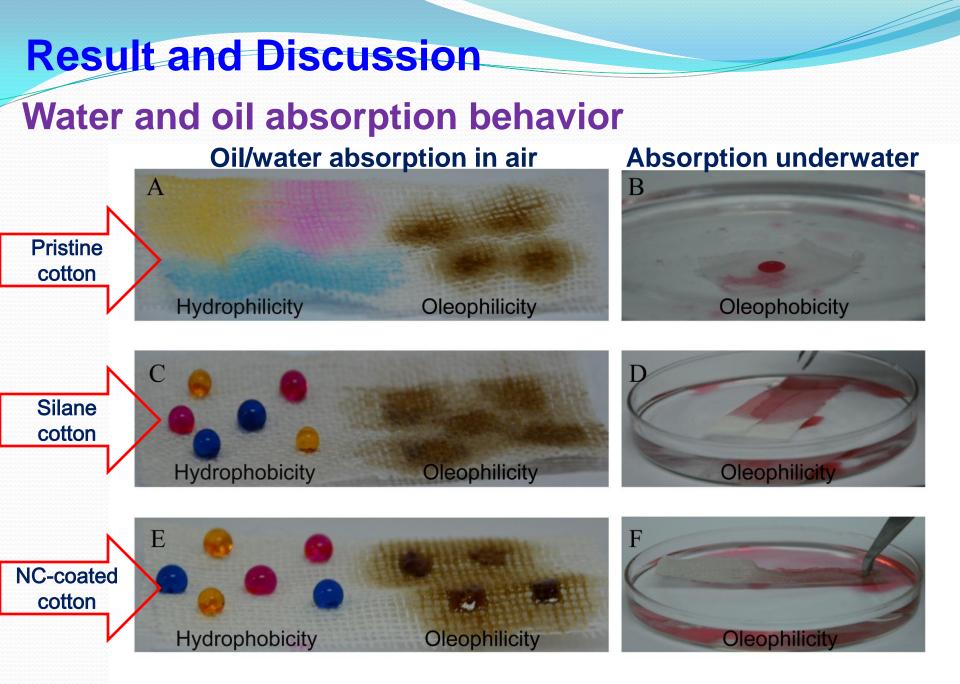
Breaking force enhancement

18% in warp direction (66.0 N to 77.7 N)
 9% in weft direction (57.5 N to 63.0 N)

ıble 1: Contact angle measurement of uncoated and coated cotton.

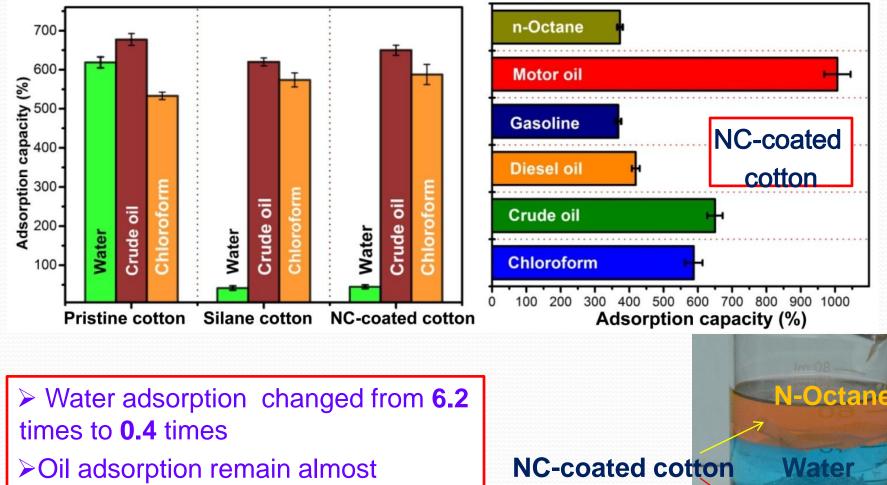
Samula	Contact angle		
Sample	Degree(θ)	Image (10s)	
Pristine cotton	0*	TELE	
Silane cotton	149.1±2.8	Q	
NC-coated cotton	145.8±2.0		

*Apparently zero



unchanged

Oil/water adsorption capacity



Chloroform

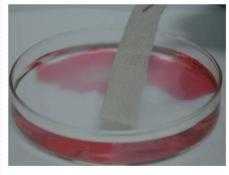
Pristine cotton

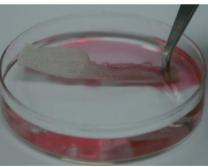
Result and Discussion Selective oil adsorption properties

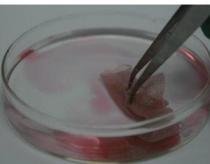
Separation of floating oil/water mixtures

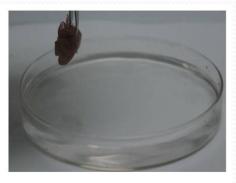


Separation of oily liquids from underwater

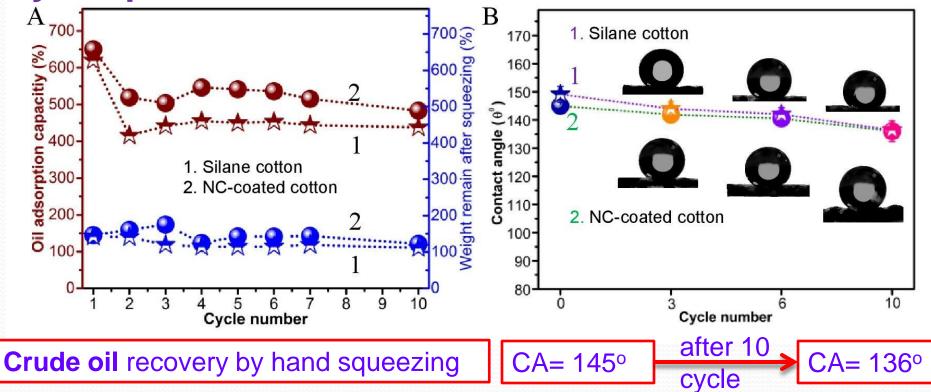








Cyclic performance of material



Crude oil uptake changed 6.5 times to 5.2 times of its original wt. after 1st cycle

Oil remained always about 1.5 times of wt. of original cotton in the structure.

UV-Vis. light absorption and transmission

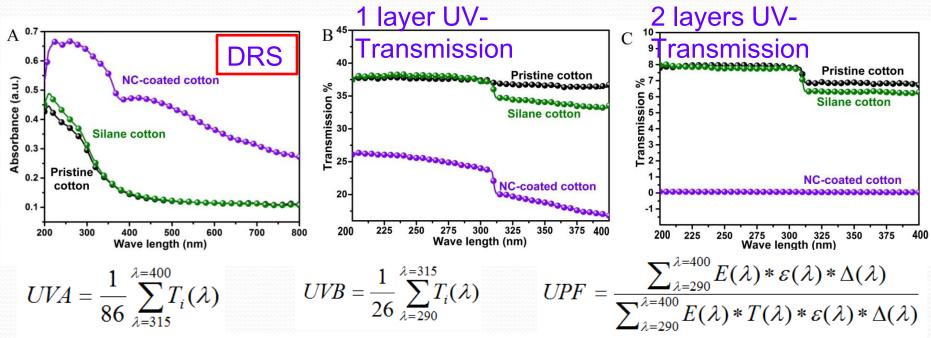


Table 2: UVA, UVB and UPF values of different cotton fabrics.

Sample	UVA	UVB	UPF (1 layer)	UPF (2 layers)
Pristine cotton	36.1	37.3	2.7	13.5
Silane cotton	33.5	36.7	2.8	14.1
NC-coated cotton	18.2	23.0	4.6	41.9

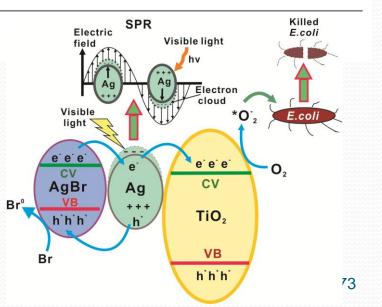
Antibacterial property Table 3: Antimicrobial activity of uncoated and coated cotton fabrics.

Sample	Concentration of bacterial in the initial suspension, M_{θ} (CFU/ml)	Concentration of bacterial after incubation, <i>M_{In}</i> (CFU/ml)	Reduction ratio, R (%)
Pristine cotton	6.20×10^4	1.79×10^{7}	0
Silane cotton	6.20×10^4	1.59×10^{7}	0
NC-coated cotton ¹	6.20×10^4	80	99.87
NC-coated cotton ²	4.30×10^{4}	7.8×10^{3}	81.43

¹ Under the fluorescent light; ² Under the dark condition without light.

Antibacterial Reduction Ratio (%)

$$R = \frac{(M_0 - M_{In})}{M_0} \times 100\%$$



Summary

A facile method to enhance the technical value of cotton fabrics with nanocomposite coating

Multi-functional properties of cotton fabrics with nanocomposites coating

- -- Enhanced mechanical property,
- -- Controllable wettability to water and oil mixture
- -- Highly antibacterial activity against microorganism
- -- Excellent properties for UV blocking and shielding

Cotton fabrics with nanocomposite coating: A promising candidate for medical, personal hygiene and environmental applications

Acknowledgements





RECRUITMENT PROGRAM OF GLOBAL EXPERTS

Program for Outstanding Youth in Xinjiang Province

National Natural Science Foundation of China Western Light Program of CAS

国家自然科学基金委员会

Alliance of Special Fine Chemical Innovation and Industrialization in CAS 75

Thank You

Questions & Comments