# Guiding growth orientation of two-dimension Au nanocrystals with marine chitin nanofibrils for ultrasensitive and ultrafast sensing hybrids

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# **Experimental Section**

# Materials

Raw chitin powders were supplied by Yuhuan Chitin Co. Ltd (Zhejiang, China) and purified according to the literature.<sup>1</sup> Silver conductive paste (EN-06B8) was purchased from Yingxun electronics Co. Ltd (Guangzhou, China). Thermoplastic elastomer SEBS was provided by Jiayun Baling Petrochemical Co. Ltd (Hunan, China). Tetrachloroauric acid (HAuCl<sub>4</sub>, 48% Au basis) was purchased from Sigma. All the other reagents (HCl, NaOH, HAc, etc.) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification.

#### **Exfoliation of Chitin Nanofibrils**

Purified chitin powders (5 g) were deacetylated in 33 wt% NaOH (125 mL) containing 0.15 g NaBH<sub>4</sub> by vigorously stirring at 90 °C for 2 h. Then, the partially deacetylated chitin, with a degree of deacetylation of approximately 9.6% measured by potentiometric titration, was washed with deionized water and further dispersed in acetic acid aqueous solution (pH 3.5). Mechanical agitation (1300 rpm, 7 days) and ultrasonication (400 W, 30 min) were used to exfoliate deacetylated chitin slurry into different dispersed state, i.e. partial exfoliation and complete exfoliation, to obtain corresponding aggregated chitin nanofibrils bundles (CNF-bundles) and homo-dispersed chitin nanofibrils (CNF), respectively. Finally, the chitin nanofibrils were dialyzed with regenerated cellulose tubes against distilled water for 1 week.

#### Synthesis of Au Nanocrystals

Au nanocrystals with different morphologies were produced through a wet chemical method. Chloroauric acid was added and used as a precursor and chitin nanofibrils served as reductant, capping agent and soft template. Typically, 164  $\mu$ L HAuCl<sub>4</sub> (24.4 mM) was added in 10 mL solutions of chitin nanofibrils with predetermined concentrations, followed by incubating at 90 °C for 6 h. In the case of CNF-bundles, synthesis of Au nanoribbons and nanokites was carried out at pH 3.5 in aqueous solution of CNF-bundles at 0.01 wt% and 0.04 wt%, respectively. In the case of CNFs, Au nanosheets were naturally reduced by CNFs ( $c_{CNF}$ =0.09 wt%) at pH 2.

## **Preparation of Flexible Hybrid Circuit**

Gold nanosheets was washed by precipitation for three times to remove the dissociative CNF, and the gold content in the obtained gold/CNF composite was determined to be 89 wt% by TGA measurement. Then, hybrid circuit was prepared by sequentially filtering the suspensions of purified gold nanosheets (conductive layer) and chitin nanofibrils (robust substrate) with the assistance of a filtering mask. In order to construct the humidity sensor, the as-prepared circuit was cut into rectangular strips and then was connected to copper wires at both of the two ends with silver paste. Finally, the circuit was immobilized on the glass slide by double faced adhesive tape before test.

#### **Preparation of Conductive Tissue Paper**

Tissue paper was used as filtering membranes to filtrate the suspensions of Au nanoribbons. After repeated filtration, the changing colour of tissue paper from white to brown suggested successfully adsorption of Au nanoribbons on surfaces of cellulose fibres. For pressure sensing, both the sides of rectangular tissue paper were connected with flexible copper wires

through silver paste, and a piece of nickel foam was attached to the bottom-side of tissue paper. The resultant tissue paper was then immobilized on a glass side for pressure-sensing.

### Characterizations

The deacetylation degree of chitin nanofibrils were determined by potentiometric titration. Firstly, the pH value of quantitative chitin nanofibrils suspensions was adjusted to approximately 2.0 by dropwise adding aqueous HCl solution. Subsequently, the mixture solution was titrated with 0.1 M NaOH, with the standard substance  $KH_5C_8O_4$  used for calibration. The DD value was calculated as follows:

#### DD= $((V_2 - V_1) \times c \times 0.016)/(0.0994 \times W)$

where *c* is the accurate concentration of aqueous NaOH solution (mol L<sup>-1</sup>), V<sub>1</sub> is the volume of aqueous NaOH solution (mL) at the first titration jump, V<sub>2</sub> is the volume of aqueous NaOH solution at the second titration jump, W is the sample weight (g), 0.016 is the molar mass weight of NH<sub>2</sub> (kg mol<sup>-1</sup>), and 0.0994 is the theoretical NH<sub>2</sub> percentage in chitosan. Optical images were obtained using an optical microscope with a single reflex camera (Zeiss Axioskop 2 mot). Transmission electron microscopy (TEM) measurements were performed on a Hitachi TEM (H-7650) instrument operating at a voltage of 100 kV. The samples were prepared by dropping the solutions on carbon-coated Cu grids followed by airdrying. AFM measurements were performed on Agilent 5400 in an intermittent mode at a scan rate of 1 Hz using silicon nitride cantilevers (Bruker). Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 operated at 10 kV.

UV-Vis spectroscopy was performed on a DU800 UV-Vis spectrophotometer. The solutions were diluted and scanned in 1-cmpathlength quarts cuvettes at 480 nm/min. FTIR spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrometer. The specimens were prepared by the KBr-disk method. X-ray diffraction (XRD) measurements were conducted on a XRD diffractometer (Bruker D8 ADVANCE). The patterns with Cu K $\alpha$  radiation ( $\lambda$ = 0.15406 nm) at 40 kV and 30 mA were recorded in the region of 2 $\theta$  from 5 to 80° with a step speed of 5 °/min. Thermogravimetric analysis (TGA) was carried out on an Ulvac TGD 9600 apparatus. The sample was placed in a platinum pan and heated from 25 to 1000 °C at a rate of 10 °C/ min under an air atmosphere. The loading of tensile strain was performed with a universal tensile-compressive tester.

The conductivity of composite film was determined by using RTS-8 4-Point Probes Resistivity Measurement System. The resistance of the humidity sensor and pressure sensor was recorded by a digital multimeter (MS8265). The current differences and the I-V characteristics for the sensors were recorded by a modular electrochemical workstation (CHI 660E)

 Table S1 Comparison of sensitivity and response time of flexible hybrid circuit with different humidity sensors.

Sensor materials	Minimum detection	Maximum detection	Resistance change	Response	Recovery	
Sensor materials	(%)	(%)	ratio	time (s)	time (s)	References
VS <sub>2</sub>	90	100	0.243	30–40	12–50	2
SnO <sub>2</sub> Nanowire	30	48	0.113	120-170	20-60	3
TiO <sub>2</sub> /SBA	83.5	98	0.724	14	19	4
Ag/SBA	60	80	1.275	100	125	5
Ag-SnO <sub>2</sub> /	32.5	53.5	1.5615	5	8	6
SBA						
WO <sub>3</sub> /SBA	33	54	1.02	18	25	7
Mn/SBA	51	61	0.86	110	170	8
LiCl/HPPMs	35	55	0.6	2	32	9
LiCl-doped TiO <sub>2</sub>	32	54	0.855	2	6.5	10
GO-PSS	60	80	0.0665	44	43.3	11
GO-based	20	90	0.4143	105	48	12
Graphene oxide	45	65	0.5	0.03	0.03	13
GO	93.5	97.5	0.35	156	80	14
GO/silicon	88	98	0.1163	46	32	15
GO	80	90	0.2	10.5	41	16
Carbon nanosheets	60	80	0.0616	120	260	17
Supramolecular	41	46	0.48	0.008	0.024	18
nanofiber						
Black phosphorus	12	32	0.128	101	26	19
Gold/Amyloid Fibrils	90	100	5	/	/	20
Au nanosheet	57	64	1019	0.07~0.16	0.60~ 5.24	This work

Resistance change ratio was defined as  $(R_{\rm RH}/R_{\rm RH-x})/x$ ; The response time/recovery time was defined as the time to go from base-line to valley of the  $I_t/I_0$ -*t* curves and *vice versa*; HPPMs, hierarchically porous polymeric microspheres; PSS, Poly(Sodium 4-Styrenesulfonate); SBA, Santa Barbara Amorphous.

 Table S2. Comparison of sheet-resistance of conductive fabric with different conductive composites.

	Sheet resistance	Volume fraction of		
Composite materials	(kΩ/sq.) conductive fillers (vol%)		Keferences	
Amyloidfibrils/graphene	21.4	7.21	21	
Amyloidfibrils/gold nanoplatelet	2.4*10 <sup>-5</sup>	32.4	20	
Gelatin/graphene	141.8	0.56	22	
Cellulose/GO	1.3*10-4	91.92	23	
CNC/RGO	0.98	5.99	24	
CNC/RGO	6*10-3	26.11	25	
Cellulose/CNT	6.6	2.02	26	
Bacterial cellulose/graphene	709.2	3.24	27	
Bacterial cellulose/graphene	0.01	10.24	28	
PMMA/graphene	53191	0.8	29	
CNC/CNT	2.08	0.67	30	
PU/CNT foam	96.7	0.47	31	
PEDOT–PSS/CNT aerogel	0.31	0.13	32	
PDMS/CNT	0.02	1	33	
Epoxy/CNT	11.0	0.29	34	
Methylcellulose/AgNW	52.2	0.11	35	
PC/AgNW	1.5	0.12	36	
PLA/Carbon black	1.64	1.1	37	
PS/PMMA/Modified RGO	1274	0.61	38	
PS/PMMA/RGO	108003	1	38	
Natural rubber/Carbon black	591	2.49	39	
Natural rubber/Carbon black	1519.8	0.1	40	
Tissue paper/gold nanoribbons	0.22	0.09	This work	

Table S3 Comparison of sensitivity and response time of conductive tissue paper with other

Composite materials	Minimum	Maximum	Sensitivity	Response	Recovery	References
	detection	detection	(kPa <sup>-1</sup> )	time (s)	time (s)	
P(VDF-TrFE)	0.1 Pa	12 Pa	0.41 V•Pa <sup>-1</sup>	0.05	0.055	41
nanofiber						
Graphene-	9 Pa	10 kPa	0.26 kPa <sup>-1</sup>	-	-	42
Polyurethane Sponge						
Polypyrrole	1 Pa	11 kPa	133 kPa <sup>-1</sup>	~0.05	~0.05	43
hollow-sphere						
R-GO foam	163 Pa	49 kPa	15.2 kPa <sup>-1</sup>	~1	~2.5	44
CNTs/PDMS	0.2 Pa	59 kPa	15.1 kPa <sup>-1</sup>	~0.04	~0.04	45
interlocked microdome						
R-GO micropyramid	1.5 Pa	1.4 kPa	5.5 kPa <sup>-1</sup>	0.0002	-	46
SWCNTs/PDMS	0.6 Pa	1.2 kPa	1.8 kPa <sup>-1</sup>	< 0.01	<0.01	47
microstructure						
PSR nanowire	0.5 kPa	15 kPa	11.5 μS•	< 0.1	< 0.1	48
(NW)-FET			kP <sup>-1</sup>			
Coplanar-gate	5 kPa	40 kPa	0.12 kPa <sup>-1</sup>	< 0.5	< 0.5	49
graphene-FET						
			60.97-78.23			
ZnO Nanoplatelet	0.02 MPa	3.64 MPa	meV•MPa <sup>-</sup>	0.005	0.005	50
			1			
Anodic aluminum	300 Pa	1.5 kPa	6.92 kPa <sup>-1</sup>	~ 0.3 s	~ 0.5 s	51
oxide membrane						
Tissue paper/gold	0.2 kPa	24.5 kPa	0.13~0.97	~ 0.006	~ 0.008	This work
nanoribbons			kPa <sup>-1</sup>			



**Fig. S1**. TEM images of CNF-bundles (A) and CNFs (B). CNF-bundles and CNFs showed different exfoliated states.



**Fig. S2**. Potentiometric titration curves (A) and zeta potential (B) of CNF-bundles and CNF. C) FT-IR spectra of native chitin powders, CNF-bundles, CNFs. CNFs after reducing HAuCl4 were also listed. Different exfoliation did not alter greatly the deacetylation degrees and zeta-potential of chitin nanofibrils.



**Fig. S3**. A) Potentiometric titration curves of CNF-bundles with various deacetylation times. B) Digital photographs of as-prepared CNF-bundles and CNFs suspensions. C) Digital photographs of CNF-bundles and CNF suspensions after storing for 24 h. The suspension of CNFs showed higher stability. High deacetylation tended to increase colloidal stability of CNFs and CNF-bundles.



**Fig. S4**. Size distribution histograms of CNFs (A, B) and CNF-bundles (D, F) counted from TEM images. C) Corresponding size distribution of CNFs obtained by DLS measurement.



Fig. S5. SEM images of Au nanosheets (A), Au nanokites (B) and Au nanoribbons (C). Insets show visual observation of corresponding suspensions of Au nanocrystals. D-F) Optical microscopy images of Au nanosheets produced under indicated concentrations of CNFs at pH~2 and  $c_{HAuCl_4}$ =0.4 mM.



**Fig. S6**. XRD patterns (A) and electron diffraction patterns (B) of Au nanocrystals with different geometries. The strong (111) X-ray diffraction peaks suggested their predominant exposing {111} crystallographic surfaces.



**Fig. S7**. A) Digital photographs of the suspensions of pristine chitin powders before (left) and after (right) reacting with HAuCl<sub>4</sub>. B) SEM image showed that only a few of irregular Au particles formed on the surface of pristine chitin after reaction. In brief, there lacked a clear template effect of pristine chitin to guide growth of Au nanocrystals.



**Fig. S8**. A) Time-resolved UV–vis spectra of chloroauric ions reduced by CNFs ( $c_{HAuCl4}=0.4$  mM,  $c_{CNF}=0.08$  wt%, pH=2). B) Typical TEM image of Au nanoparticles after reaction for 10 min. C) SEM image shows that the surface of Au nanosheets was capped by high density of CNFs.



**Fig. S9**. A) Time-resolved UV–vis spectra of chloroauric ions reduced by CNF-bundles  $(c_{HAuCl4}=0.4 \text{ mM}, c_{CNF-bundles}=0.01 \text{ wt\%}, \text{pH}=3.5)$ . B) Typical TEM image of Au nanoparticles after reaction for 10 min. C) Variation of UV–vis absorbance at 290 nm of chloroauric ions in the present of CNF-bundles with various concentrations ( $c_{HAuCl4}=0.4 \text{ mM}$ , pH=3.5). D) TEM images of wider Au ribbons obtained in the presence of 0.02 wt% CNF-bundles. E) TEM images of abundant Au nanokites.



**Fig. S10**. A-B) UV-vis spectra and TEM images of Au nanoparticles formed under higher pH values ( $c_{\text{HAuCl4}}=0.4 \text{ mM}$ ,  $c_{\text{CNF}}=0.08 \text{ wt\%}$ ). C) TEM images of Au nanoparticles obtained in the presence of 0.09 wt% CNF-bundles.

The reduction rate of HAuCl<sub>4</sub> is a key factor that determines the final shape of gold nanocrystals. Typically, HAuCl<sub>4</sub> is first reduced to form small seeds composed of gold metal atoms. When the pH value or degree of deacetylation is high, the chitin nanofibrils possessed relatively strong reducing ability, leading to a fast reduction rate (Figure S9). As a result, sufficient Au atoms are produced and can be added to the surface of gold seeds for continuous growth. Under this condition, the growth of gold followed a "thermodynamically controlled" pathway. Thus, spherical-like gold nanoparticles with minimum surface energy are formed. With a decrease of pH value and degree of deacetylation, the reduction rate declines, resulting in a low concentration of as-reduced gold atoms. In this case, the atoms tend to aggregate into small clusters, which further agglomerate into nanoparticles. The stacking faults (or twin planes) introduced by slow reduction guide the formation of plate-like seeds. This is known as a "kinetically controlled" pathway.



**Fig. S11**. A-B) SEM images showed the formation of large Au nanoparticles in the presence of chitin nanofibrils with relative higher degree of deacetylation (DD=17.6%). C) SEM images show that Au nanoribbons and nanokites could also form by reducing chitin nanofibrils (DD=17.6%) concentration. D) Zeta potential of CNF-bundles and CNFs for different deacetylation time.



**Fig. S12**. High-resolution SEM images of Au nanosheets after washing for 0 (A), 1 (B), 2 (C), 3 (D), 6 (E) and 8 (F) times.



**Fig. S13**. A) Schematic pathway followed to design Au nanosheets/CNFs electronic circuit. B) Tensile stress-strain curves of hybrid circuit. C) High-resolution cross-section SEM image shows abundant CNFs adhering to Au surface.



**Fig. S14**. A) Current-voltage (I-V) behaviours measured under different RH values, which show an obvious slope decreasing with an increase of RH. B) Resistance change of sensor tested at 58% RH and 64% RH for 10 cycles. C) Current response of humidity sensor to the humid air generated by blowing from mouth, revealing high-speed responsiveness of the humidity sensor.



**Fig. S15**. A-C) Surface SEM images of hybrid film composed of CNF-bundles and Au nanoribbons with different Au contents. D) TGA of hybrid film shown in A and C. E) Non-linear relationship between in-plane conductivity *versus* weight fraction of Au in the hybrid films composed of Au nanoribbons and CNF-bundles, demonstrating an unprecedented low percolation threshold.



**Fig. S16**. A) SEM images of tissue paper and conductive tissue paper, which show a porous structure and rough surface. B) Schematic pathway followed to modify tissue paper with Au nanoribbons suspension. The conductive performance of tissue paper could be easily tuned from uniform conductor to Janus-faced conductor, according to the adsorbed content of Au nanoribbons. C-E) Enlarged SEM images of native and Janus-faced conductive tissue papers. F) Corresponding EDS spectra of tissue papers.



Fig. S17. Stability of conductive tissue paper under bending (A), twisting (B), washing (C) and heating (D).



**Fig. S18**. A) Resistance *v.s.* pressure for pressure sensor. B) Relative change in resistance of the pressure sensor versus the applied pressure.  $R_{min}$  was the resistance of sensor under 24.5 kPa. C) Current response of pressure sensor under finger touch (~ 2.0 kPa), revealing high-speed responsiveness of pressure sensor. D-E) Response (D) and recovery (E) time of pressure sensor.



**Fig. S19**. A) Photograph of a typical circuit composed of two types of sensor. Schemes and performance characteristics of the 'AND' (B) and 'OR' (C) logic gates. Photographs to show the flexible (D) and adhesion (E) of the logic circuit.

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