Biomass-Derived Multifunctional Conductive Coating with Outstanding Electromagnetic Shielding and Photothermal Conversion for Integrated Wearable Intelligent Textiles and Skin Bioelectronics

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Supplementary Information

Characterization of CMS/PDA/PPy

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrometer (Vertex70, Bruker, Germany) was used to test the functional group changes of the CMS and CMS/PDA/PPy samples at room temperature with a resolution of 4 cm^{-1} in the range of 400 ~ 4000 cm^{-1}.

X-ray diffraction (XRD)

The crystallization behavior of the CMS and CMS/PDA/PPy coatings was tested on a wide-angle X-ray diffractometer (XRD, D8 Advance Bruker, Germany) with Cu-Kα radiation. The scanning angle 2θ ranges from 10 ° to 60 °.

X-ray photoelectron spectroscopy (XPS)

The elemental composition of the CMS and CMS/PDA/PPy samples was analyzed by X-ray photoelectron spectroscopy (KRATOS, Ultra DLD). The vacuum of the analysis chamber is 9.8×10^{-10} Torr, and the excitation source is Al ka ray (hv = 1486.6 eV). The charge correction was performed with the binding energy of C1s = 284.80 eV as the energy standard. The XPS peaks of C1s, O1s and N1s of the samples were processed by Avantage peak difference software combined with Gauss-Lorentz function. The changes of binding energy and group content were obtained.

Thermogravimetric analysis

Thermogravimetric analyzer (TA Instrument Q500) was used to analyze the thermal stability of the CMS and CMS/PDA/PPy coatings. The CMS and CMS/PDA/PPy samples were subjected to TGA analysis at a heating rate of 10 °C/min with a heating range of 40 °C ~ 600 °C.

Surface morphology

The surface morphology of CMS/PDA/PPy samples was observed by scanning electron microscopy (SEM) at resolutions of 1 mm and 100 μm. The test voltage was set to 7 kV.

Application performance of CMS/PDA/PPy in intelligent

electronic textiles

Adhesion properties

The surface adhesion properties of CMS/PDA/PPy coatings were analyzed by covering the coatings on the surface of plastics, rubber, pig skin, glass, copper and other materials, respectively. In order to further explore the adhesion strength of CMS/PDA/PPy coatings , the lap shear test was performed to measure the adhesion properties. The CMS/PDA/PPy coating (2 cm × 2 cm) was coated on the non-woven textile (2 cm × 8 cm). The two layers of non-woven textile were bonded together by the CMS/PDA/PPy coating. The electronic universal testing machine (Yangzhou Xintianhui Electronic Technology Co., Ltd., China) was used to measure the tensile force, and the shear test was completed to obtain the force-displacement curve. Each group of samples was measured three times to take the average.

Printability

The CMS/PDA/PPy coating was fixed on the non-woven textile by screen printing to investigated the printability. CMS/PDA/PPy was poured into the screen-printing template, applied a certain pressure with a scraper, and then move at a constant speed towards the other end of the screen-printing template. The CMS/PDA/PPy coating is squeezed from the mesh of the graphic part to the non-woven textile by the scraper during the movement. The rheological properties of CMS/PDA/PPy coatings were further evaluated by TA Rheometer (DHR-1). The rheological experiments of CMS/PDA/PPy were carried out between parallel plates. The viscosity changes of the coating samples at different shear rates (0.1-100 S^{-1}) were measured at 25 °C to provide reliable data for the analysis and evaluation of their rheological properties.

Mechanical properties

The CMS/PDA/PPy coating was coated on the non-woven textile and cut into a dumbbell shape of 2 mm × 35 mm. The stress-strain curve was obtained using an electronic universal testing machine (Yangzhou Xintianhui Electronic Technology

Co., Ltd., China). The dumbbell-shaped non-woven textile was used as the control group, and the samples in each group were measured three times to obtain the average value. [3]

Antioxidant activity

The non-woven textile coated with CMS/PDA/PPy was cut into a circle with a diameter of 10 × 10 mm. Then, the ultraviolet absorbance at a wavelength of 517 nm was recorded by an ultraviolet-visible spectrophotometer (Lambda25, PerkinElmer, USA). DPPH (3.9 mg) was accurately weighed and dissolved in 50 mL ethanol to prepare DPPH free radical. The coated textile samples were placed into 3.6 mL of free radical solution, and remained them in the test tube for a certain time to ensure full reaction. Finally, the DPPH free radical scavenging rate was calculated according to the UV absorbance at 517 nm in Formula (1):

$$\text{DPPH inhibition (\%)} = \frac{A_0 - A_i}{A_0} \times 100 \quad (1)$$

Where, A_0 is the absorbance of pure DPPH solution at 517 nm; A_i is the absorbance of DPPH solution treated by CMS/PDA/PPy coated non-woven textile at 517 nm.

Conductivity properties

A three-dimensional conductive network was constructed by coating a layer of CMS/PDA/PPy on polypropylene non-woven textile (3 cm × 4 cm) as the substrate of textile devices, so as to study the influence of the concentration and ratio of conductive materials on the conductivity of the coatings. The CMS/PDA/PPy-3 coating was used as the conductor to observe the brightness change of the LED bulb under the action of bending 180 ° and torsion 180 °. The electrical output and real-time resistance were measured using a two-electrode test cell on an electrochemical comprehensive tester (P4000 +, Princeton, USA).

Water contact angle

The effect of CMS/PDA/PPy coating on the hydrophilicity and hydrophobicity of non-woven textiles. The video optical contact angle meter (OCR20, Germany) was

used to test the biomass-based intelligent electronic textile samples assembled by CMS/PDA/PPy coating. The hydrophilicity and hydrophobicity were characterized by judging the water contact angle (WCA). Specific operations: A biomass-based intelligent electronic textile sample was tiled, and a drop of distilled water (5 μL) was deposited on the surface of the sample with a precision syringe. After 3 s, the contact angle on both sides of the droplet was measured using OSA100 software and the average value was calculated. The double-layer non-woven textile was used as the control group, and each group of samples was measured repeatedly for 5 times to obtain the average value.

Water vapor transmission rate

The effect of CMS/PDA/PPy coating samples on the water vapor permeability (WVP) of non-woven textiles was determined by using a water vapor permeability tester (Jinan Languang Mechanical and Electrical Technology Co., Ltd.). Specifically, the assembled biomass-based intelligent electronic textile samples were cut into 7.4 cm in diameter, and the two-layer non-woven textile of 7.4 cm was used as the control group. The average value of WVP of each group of samples was measured three times. The parameters of the test instrument were set to keep the temperature at 38 °C and the relative humidity at 90 %.

Light transmittance

A 3 cm × 4 cm double-layer non-woven textile and a biomass-based intelligent electronic textile sample were put into an ultraviolet-visible-near-infrared spectrophotometer (Cary 5000, Agilent, USA) for testing, and the light transmittance of the biomass-based intelligent electronic textile was evaluated by the test results. Among them, the wavelength range is 200 ~ 800 nm, with air as a control.

Antibacterial properties

The antibacterial properties of CMS/PDA/PPy were evaluated by the inhibition zone method, and the biological Escherichia coli (E.coli) and Staphylococcus aureus (S.aureus) were selected to evaluate the antibacterial properties of CMS/PDA/PPy. The experimental results were expressed as the average diameter of the inhibition

zone, and the unit was mm ± standard deviation (mean ± standard deviation). Firstly, the sterile PBS solution was used to prepare the bacterial suspension with a density of about 107 ~ 108 CFU / mL. Subsequently, the non-woven textile with uniform texture was selected and punched into a circle with a diameter of 10 mm. After sterilization and drying, CMS/PDA/PPy was coated on a circular non-woven textile with a diameter of 10 mm as a test sample. The blank control group was a circular non-woven textile with a diameter of 10 mm. Before the test, it was sterilized under ultraviolet light for 5 min and placed on an ultra-clean bench for later use. 10 mL of agar medium was added to the disposable sterile culture dish, and 100 μL of bacterial suspension was inoculated after it was solidified and formed. The bacterial suspension was evenly coated with L-type disposable coating rod by coating method, and then the sample was placed flat on the culture dish coated with bacteria. Finally, the bacterial culture was cultured at 37 °C for 24 h to observe the size of the inhibition zone, and the antibacterial potency of the drug was determined according to the size of the inhibition zone.

Biocompatibility

The cytotoxicity of the prepared conductive coating (CMS/PDA/PPy-1) freeze-dried sample to Chinese hamster ovary cells (CHL) was detected by CCK-8 assay to determine its biocompatibility. 0.2 g of each sample was put into sterile centrifuge tube and added into complete cell culture medium. After 24 h of extraction at 4 °C, the samples were filtered by 0.22 μm filter membrane and stored at 4 °C. The pH of the sample was adjusted to 7.15-7.35 with 1 M NaOH. Chinese hamster ovary cells (CHL), DMEM culture medium + 10 % fetal bovine serum, 37 °C, 5 % CO_2 environment were selected as cell line culture cells. Before the experiment, the 96-well cell culture plate was plated with a density of 5000 cells / well, and the culture was overnight cultured with the extract solution, 200 μL per well. CHL (5000 cells / well) was seeded in 96-well plates and incubated at 37 °C for 24 h in a 5 % CO_2 atmosphere. The cells were completely adhered and the original cell culture medium was discarded. According to the end point of observation, the fluid was changed every

48 h. Each group had 5 replicates. The viability of CHL cells was detected on the 1st, 3rd and 5th day of culture, and the cells were stained with live and dead fluorescence. On the 1 st, 3 rd and 5 th day of culture, 20 μL CCK-8 was added to each well and cultured at 37 °C for 2 h in a 5 % CO_2 incubator. The absorbance of each well was measured at OD 450 nm using enzyme markers, and cell viability was calculated using Equation (2).

$$\text{Cell Viability}(\%) = \frac{(As - Ab)}{(Ac - Ab)} \times 100 \quad (2)$$

Among them, A_s is the OD value of the pore with cells, CCK-8 solution and drug solution; A_b is the OD value of the hole without cells; A_c is the OD value of the hole with cells, CCK-8 solution and no drug solution.

Calcein-AM / PI live / dead cell double staining was used to further detect the biocompatibility of the biomass-based conductive coating. 100 μL staining solution was added to 200 μL cell suspension, and the mixture was fully mixed. The mixture was then incubated at 37 °C for 15 min. Finally, the image is captured using a laser confocal microscope.

Electromagnetic shielding performance

The network vector analyzer (VNA) was used to test the electromagnetic shielding performance of biomass-based intelligent electronic textile samples. The double-layer non-woven textile (0.90 mm) was used as the control group, and the frequency range of the test instrument parameters was set to 8.2 ~ 12.4 GHz.

Photothermal conversion performance

The near-infrared (NIR) laser with a wavelength of 980 nm was used to irradiate the surface of the bio-based intelligent electronic textile and the real-time temperature was recorded. The photothermal performance was analyzed according to the temperature change. Near-infrared light (980 nm, 1.0 W/cm^2) was irradiated on the surface of the biomass-based intelligent electronic textile, and then the temperature around the irradiation point on the coating surface was recorded by a thermal imager until the temperature stopped rising. The photothermal properties of biomass-based

intelligent electronic textiles were evaluated by temperature-time curves. In addition, the photothermal properties of biomass-based intelligent electronic textiles at different powers (0.8 W/cm^2, 1.0 W/cm^2, 1.2 W/cm^2 and 1.5 W/cm^2) were tested by the same method. Finally, CMS/PDA/PPy-4 was printed on non-woven textiles by screen printing and placed in outdoor sunlight. The infrared thermal images (Ambient temperature : 25 °C) were recorded after 10 s and 60 s, respectively.

Sensing performance

The assembled biomass-based intelligent electronic textiles were attached to different human joints. The electrical output and real-time resistance were measured by an electrochemical comprehensive tester (P4000 +, Princeton, USA) using a two-electrode test cell to study the effects of human physiological signals and other parameters on the electrical conductivity of the composites. The positive and negative electrodes of the wire are fixed at both ends of the prepared biomass-based intelligent electronic textile with copper tape, and the sensing characteristics of the biomass-based intelligent electronic textile under the corresponding conditions are realized by the textile sticking to the human skin movement. These sensors are then used to monitor human joint motion, language system recognition, etc. The bio-based intelligent electronic textile is fixed with medical double-sided adhesive at the bottom of the throat knot, fingers, wrists, elbows, masks and insoles to monitor and collect physiological signals from different parts of the human body.

When testing the temperature sensing performance of the biomass-based intelligent electronic textile, the positive and negative electrodes of the wire are connected to the ends of the biomass-based intelligent electronic textile (3 cm × 4 cm) sealed by the medical PU film with copper tape. It is pasted on the beaker wall of the water beaker with double-sided adhesive, and then the water in the beaker is heated with a heating table. After the resistance signal of the electrochemical workstation is stable, the resistance values at different temperatures are recorded. The temperature coefficient of resistance (TCR) of thermistor can reflect the resistance variation characteristics of thermistor at different temperatures. The temperature coefficient of

resistance is calculated according to Formula (3):

$$TCR = \frac{\partial R}{\partial T \times R} \qquad (3)$$

The temperature coefficient of resistance indicates the change of resistance value when the temperature rises by 1 °C. In practical applications, the average resistance temperature coefficient is usually used:

$$TCR = \frac{(R_2 - R_1)}{(T_2 - T_1) \times R_1} \qquad (4)$$

In addition, according to the thermistor equation with the same set of data:

$$R = R_0 \exp\left\{ B\left(\frac{1}{T} - \frac{1}{T_0}\right) \right\} \qquad (5)$$

The resistance-temperature characteristics of the thermistor are fitted. Among them, R represents the resistance at temperature T (K), R_0 represents the resistance at temperature T_0 (K), and B is the thermistor constant. The greater the B value, the faster the temperature response of the thermistor, which is more suitable for high-sensitivity and high-precision temperature sensors.

During the heating process, the biomass-based intelligent electronic textile (1 cm × 2 cm) was connected to the electrochemical workstation and adhered to the finger pulp of the model. As the water temperature of the water bath beaker rose, the finger pulp of the model was close to the beaker for 10 s at 2 v voltage when the water temperature reached 40 °C, 50 °C, 60 °C, 70 °C and 80 °C. The real-time resistance change was measured, and the temperature warning function of the biomass-based intelligent electronic textile was reflected by the collected electrical signal change.

Table S1 The binding energies and assignments of XPS spectra of CMS and CMS/PDA/PPy-2.

	Assignments	Binding energy of different samples (eV)	
		CMS	CMS/PDA/PPy-2
C1s	C-C, C-H, C-O, C=C	284.9	284.8
C1s	C-O&C-N, C=N, C-O-C	286.4	286.3
C1s	C=O, O=C-O	287.9	288.7
N1s	N-H	—	398.8
N1s	N-C	—	400.1
N1s	N=C	—	401.1
O1s	C-O, C-O-C	531.4	530.1
O1s	C=O, O-C-O, O=C-O	532.8	532.4

Table S2 T5, Tdmax1, Tdmax2, and CY for CMS and CMS/PDA/PPy coatings. (T5 is the first maximum thermal decomposition rate temperature; Tmax1 is the second maximum thermal decomposition rate temperature; Tmax2 is the third maximum thermal decomposition rate temperature; CY is the char yield obtained through TGA.)

	CMS	CMS/PDA/PPy-1	CMS/PDA/PPy-2	CMS/PDA/PPy-3	CMS/PDA/PPy-4
T_5/℃	77.08	71.40	75.90	121.20	88.79
Td_{max1}/℃	299.60	150.48	100.90	224.40	222.07
Td_{max2}/℃	—	175.59	238.29	503.00	318.69
CY/%	28.55	47.33	49.08	11.70	16.23

Table S3 Composition and dosage of raw materials

Sample	CMS/g	H_2O/mL	DA/g	H_2O/mL	Py/mL
CMS/PDA/PPy-1	2.00	90	2.00	10	2.00
CMS/PDA/PPy-2	2.00	90	2.00	10	1.00
CMS/PDA/PPy-3	1.00	60	2.00	10	2.00
CMS/PDA/PPy-4	2.00	90	1.00	5	2.00

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