Supporting Information

Highly Conductive Graphene-coated Silk Fabricated via a Repeated Coating-Reduction Approach

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Experimental

1.1. Materials

Graphite powder (CP,99.85%), hydrazine monohydrate ($N_2H_4 \cdot H_2O$, ＞98%) and sodium nitrite ($NaNO_2$) (AR, 99.0%) were bought from Aladdin (Shanghai, China). Potassium permanganate ($KMnO_4$) and hydrogen peroxide (AR, 30wt. % in H_2O) were purchased from Kelong (Chengdu, China). Concentrated sulfuric acid (H_2SO_4) was bought from Yubei (Chongqing, China). Bovine serum albumin (BSA)(AR,≥99.0) was bought from GENVIEW （Beijing, China）. The silk fabrics were kindly provided by State Key Laboratory of Silkworm Genome Biology, Southwest University, China. The graphene oxide (GO) used in this work was prepared by a modified Hummers' method[1]. Deionized water (resistance over 18 MΩ cm) was generated by a Millipore Q water purification system.

1.2 Preparation of graphene-coated silk fabrics

Firstly, silk fabrics were cut into 2.5 cm×2 cm pieces and soaked in a 0.5 wt% BSA solution for 10 min at room temperature. BSA was dissolved in DI water and utilized to coat silk fabrics immediately. The BSA-coated silk fabrics were dried in ovens at 30°C for 15 min, followed by three times rinse in distilled water to remove any residual BSA molecules. Then, the prepared BSA-coated silk fabrics were immersed in 2 mg/mL GO solution for 30 min. Upon completion of GO wrapping, the silk fabrics were dried in an oven at 50°C for 15 min. The silk fabrics hung over a hydrazine solution were maintained at room temperature overnight to chemically reduce GO. After that, the graphene-coated

silk fabrics were washed with water for three times. The procedures were repeated to obtain the silk fabrics with thicker graphene coating layers.

1.3 Characterization of the graphene silk fabrics

SEM images of the graphene silk fabrics were obtained using a JSM-6510LV electron microscope (JEOL, Tokyo, Japan) operating at 20 kV. XRD spectra were examined using a Cu Ka-ray with tube conditions of 40 kV and 30 mA ranging from 10° to 80° (XRD-7000, Shimadzu, Japan). Raman spectra were acquired with a Renishaw Raman microscopy using 532 nm laser excitation. The electrical conductivity of the graphene silk was measured using Keithley 2400 Source Meter. The quality of freshly prepared GO nanosheets was verified with atomic force microscopy (Dimension icon, Bruker, USA). The contact angle of the graphene silk fabrics was characterized by Power Each. The surface chemical properties of the graphene silk fabrics were analyzed with FTIR (Nicolet 6700 FTIR, Thermo Electronic Corporation, USA). The elasticity of the silk fabric was measured using a computer-controlled universal testing machine (WDW3050, Changchun, China). Zeta-potentials of BSA molecules and GO nanosheets were obtained using a ZETASIZER Nano ZS90.

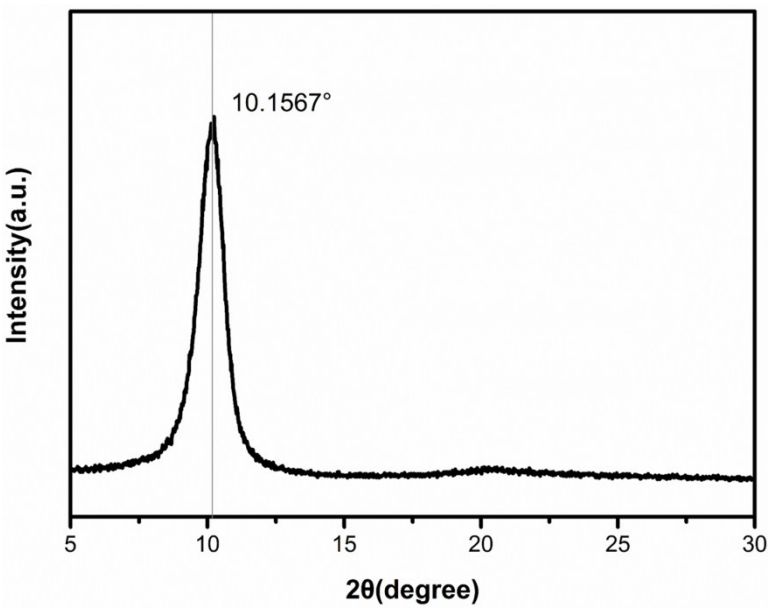

Figure S1. XRD pattern of graphene oxide nanosheets.

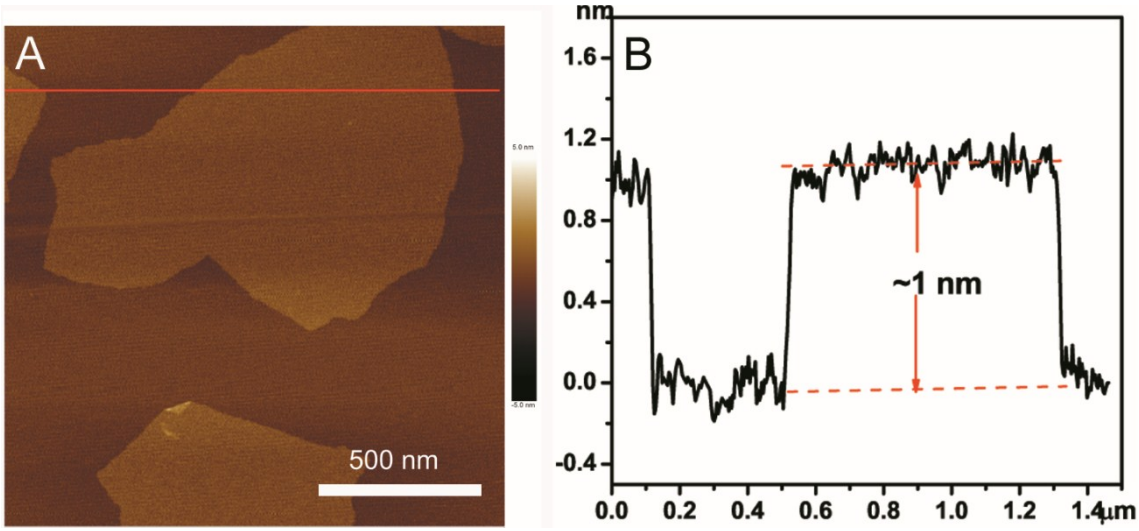

Figure S2. AFM image (A) and the section curve (B) of graphene oxide on a mica substrate.

Figure S3. Pictures of (A) a pristine silk fabric, (B) a GO-coated silk fabric and (C) a graphene-coated silk fabric.

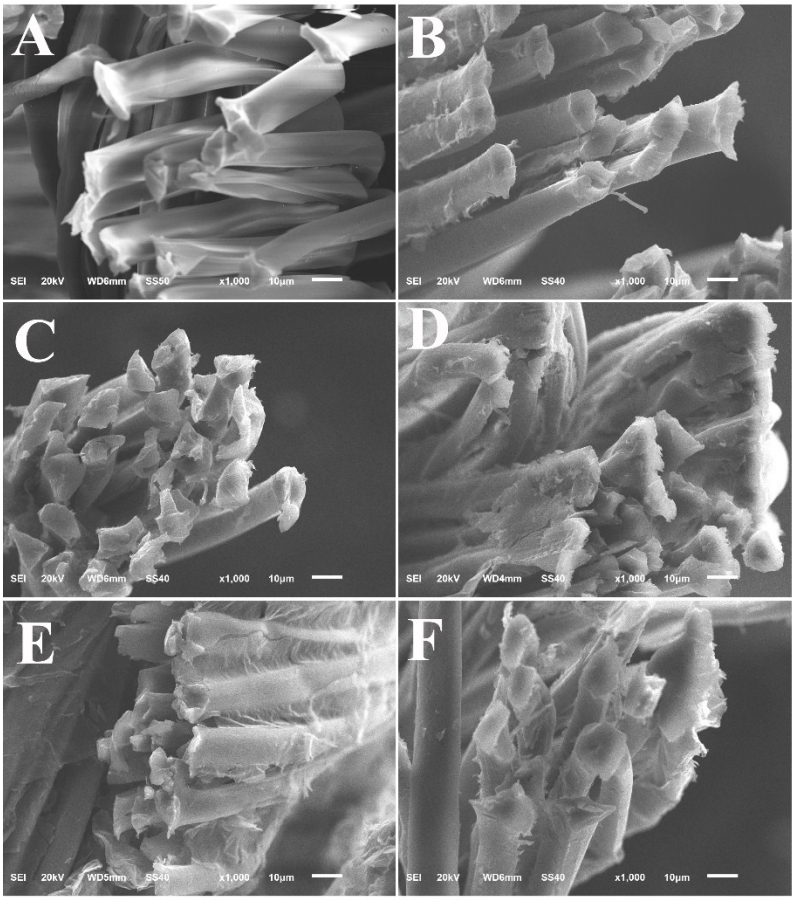

Figure S4. SEM images of the side-view of original silk fabric (A), followed by graphene-coated silk fabrics with 1 (B), 3 (C), 5 (D) and 7 (E), silk fabric after immersion in a GO solution for 3.5 h (F)

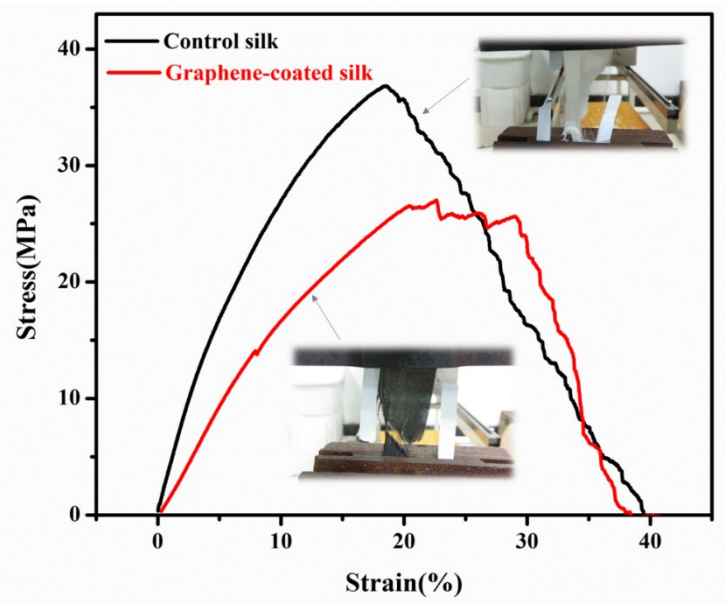

Figure S5. Stress-strain curves of pristine (Black curve) and graphene-coated (Red curve) silk fabrics.

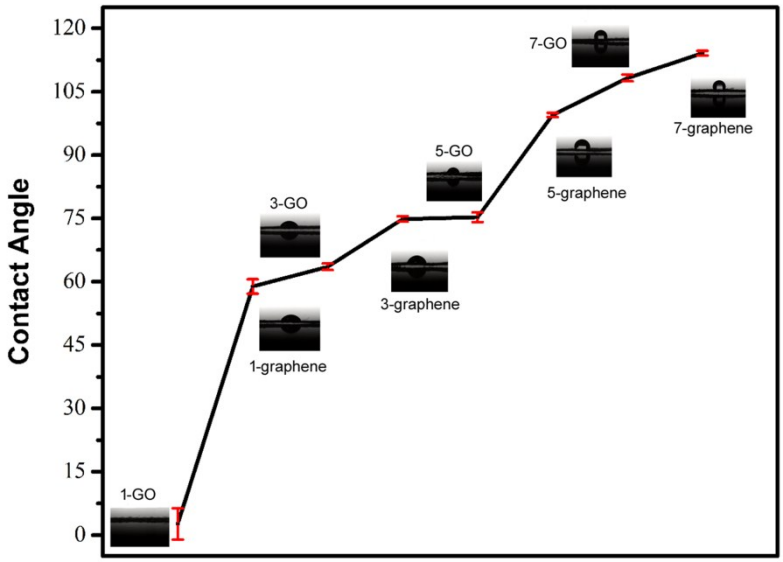

Figure S6. Contact angle of the graphene-coated silk fabrics.

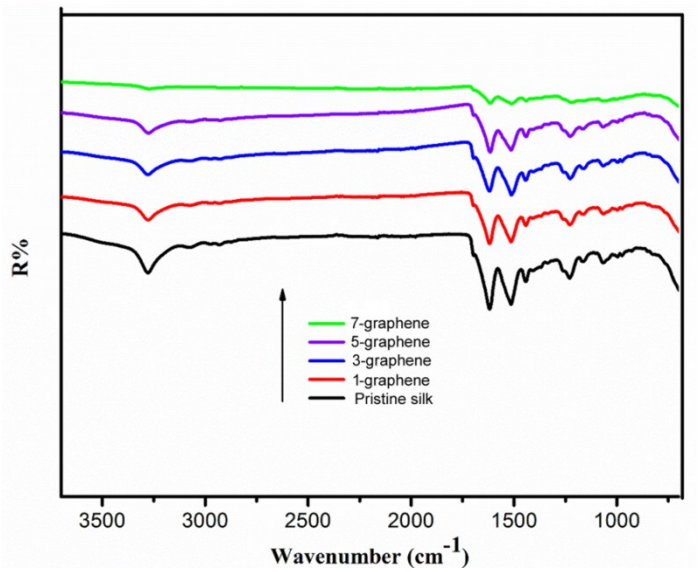

Figure S7. FTIR spectra of pristine silk and graphene-coated silk with different coating times.

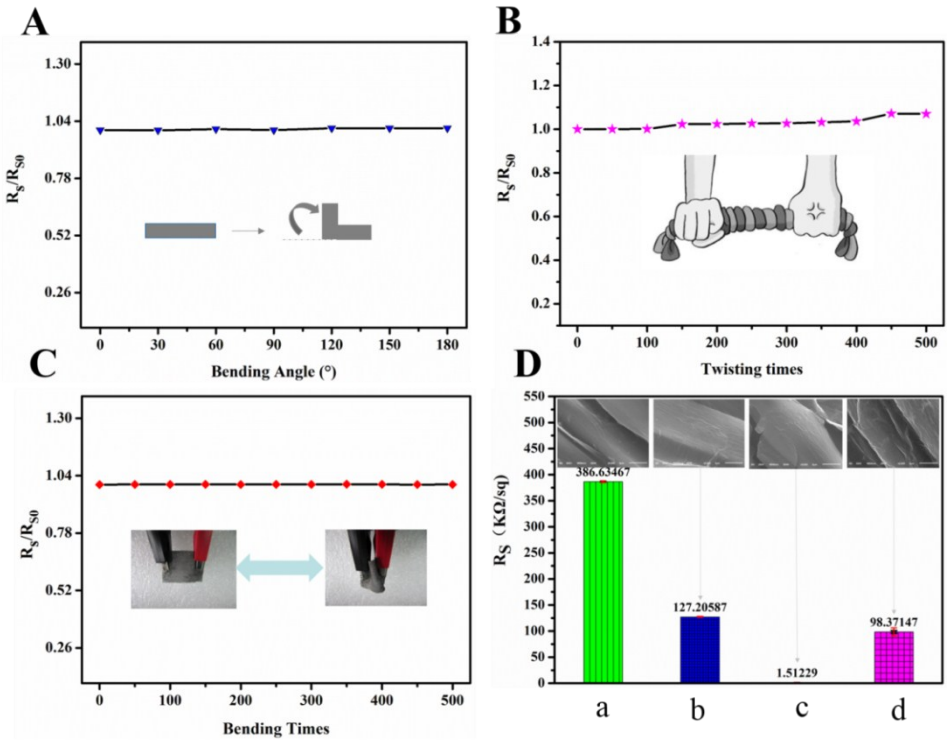

Figure S8. (A) The normalized resistance change according to the bending angle; (B) The normalized resistance change according to the twisting times; (C) The normalized resistance change according to the bending times; (D) Sheet resistants of graphene-coated silk fabrics with 1 (a), 2 (b) and 7 (c) cycles of coating-reduction, respectively. (d) Sheet resistant of a silk fabric after 3.5 h's GO immersion+reduction. Insets are the corresponding SEM images.

Figure S9. The LED connected with a GO-coated silk fabric.

References

1. J. Zhang, Z. Xiong and X. S. Zhao, *Journal of Materials Chemistry*, 2011, **21**, 3634.
2. Y. J. Yun, W. G. Hong, W.-J. Kim, Y. Jun and B. H. Kim, *Advanced materials*, 2013, **25**, 5701-5705.