Supporting Information

Bioinspired Paper-Based Nanocomposites Enabled by Biowax-Mineral Hybrids and Proteins

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Materials and Methods

Materials. Biofiber assemblies (multipurpose copy paper and quantitative filter paper), various drinks, and methylene blue were received from local stores in Harbin, China. Unless otherwise specified, multipurpose copy paper with a basis weight of 70 g/m² was used as the substrate to form functional composites. However, in the case of experimental works pertaining to Figure 2, quantitative filter paper was used to assess the possibility of using biowax to generate self-cleaning superhydrophobicity. Beeswax (B113019) and proteins (gelatins) (G108395 and G108396) were received from Aladdin Biological Technology Co., Ltd., China. Another gelatin sample (a commercial additive for candies, bakery products, etc.) was received from Wanbang Co. Ltd., China. Unless otherwise stated, the gelatin with sample code of G108395 was used as the binding material for biowax or biowax-silica hybrids. Anhydrous ethanol, attapulgite clay, and hydrophilic fumed silica nanoparticles (Aerosil A200 F) were received from Tianli Chemical Co. Ltd., China, Changzhou Dingbang Mineral Products Co. Ltd., China, and Evonik Degussa, Germany, respectively. As described by the manufacturer, the silica nanoparticles are usable as additives for food products.

Preparation of Protein Dispersion. To 97 ml of deionized water, 1 g of gelatin was added, followed by heating to about 100 °C under stirring (700 rpm). The mixture was continuously cooked and mixed at this temperature for 2 h to allow sufficient gelatinization. The resulting gelatin dispersion was cooled down to room temperature prior to use.

Preparation of Functional Composites. In accordance with the proposed concept, biowax-silica hybrid dispersion was sprayed onto protein-deposited biofiber assemblies followed by thermal annealing to generate functional composites. Initially, silica (0.5 g, 1 g, 1.5 g, or 2 g) was mixed
with anhydrous ethanol (50 ml), and the dispersion was stirred at 700 rpm for 30 min (at room temperature). To this dispersion, 5 g of biowax was added, and the mixture was heated to 80 °C under stirring (700 rpm), followed by mixing at this temperature for another 30 min to form biowax-silica hybrid dispersion. Upon coating biofiber assemblies with gelatin dispersion (JFA-II automatic coating machine, China) (liquid “film” thickness: 30 μm) (Video S13), as-formed biowax-silica hybrid dispersion (80 °C) was immediately sprayed onto gelatin-deposited biofiber assemblies with a preheated sprayer (W-71 Sprayer, China), followed by air drying at room temperature. During spraying, sample-nozzle distance was 22 cm, and spray gun was pressurized at 0.7 MPa. Air-dried samples were thermally annealed at 150 °C in an oven for 1 h. For comparison purposes, silica or gelatin was also not used in some sets of experiments for the generation of functional composites. In such cases, the treatment of biofiber assemblies was performed under parallel conditions. Besides biofiber assemblies, other substrates including nonwoven fabric, wood veneer, polycarbonate board, and canvas were used to generate functional composites.

Characterization. SEM images shown in Figure 2 and Figure S1 were collected on a JSM-7500F field emission scanning electron microscope (Japan). Other SEM images were collected on a SU-8010 field emission scanning electron microscope (Japan). AFM images shown in Figure 2 and Figure S2 were collected on a PicoPlus Scanning Probe Microscope (USA). Other AFM images were collected on a NT-MDT NTEGRA Prima scanning probe microscope (Russia). Samples were also characterized on a Thermal Scientific ESCALAB 250XI X-ray photoelectron spectrometer (USA), a Bruker Tensor 27 Fourier Transform Infrared Spectrometer (USA) (32 scans), and a STA 6000-SQ8 simultaneous thermal analyzer (USA). Water contact angles and roll-off angles were obtained with a Dataphysics OCA-20 optical contact angle analyzer (Germany) and a JC2000
optical contact angle measurement analyzer (China), respectively. Brightness and tensile strength were determined with an YQ-Z-48A brightness tester (China) and an IMT-202F tensile strength tester (China), respectively. Prior to strength tests, samples were cut into strips (with a width of 15 mm), and then conditioned at a relative humidity of about 55% for 24 h. After sample conditioning, tensile strength was determined at an elongation rate of 40 mm/min and a test span of 100 mm. Under parallel conditions, all tests pertaining to different paper samples were performed at room temperature. Moreover, interaction of samples with liquids, self-cleaning characteristics, and response to mechanical actions, were observed and assessed.
**Figure S1.** Original unedited SEM images of biofiber assemblies (top) and functional composites (middle, bottom) formed by simply spraying biowax dispersion to fiber assemblies. Quantitative filter paper (biofiber assemblies) was used as the substrate. No binder was used.
Figure S2. Original unedited AFM images of functional composites formed by simply spraying biowax dispersion to fiber assemblies. Quantitative filter paper (biofiber assemblies) was used as the substrate. No binder was used.
Figure S3. (A) Photograph of composites formed by simply spraying biowax dispersion to biofiber assemblies. (B) Photograph of composites by spraying biowax dispersion to polyvinyl alcohol pretreated biofiber assemblies. Multipurpose copy paper was used as the substrate. The use of polyvinyl alcohol (average Mw ~205,000 g/mol) as a binder resulted in pronounced enhancement of surface uniformity.
Figure S4. (A) Original unedited SEM images of biofiber assemblies. (B) Original unedited SEM images of gelatin-deposited biofiber assemblies. (C) Original unedited SEM images of functional composites formed by spraying biowax dispersion to gelatin-deposited biofiber assemblies. (D) Original unedited SEM images of functional composites formed by spraying biowax dispersion to gelatin-deposited biofiber assemblies, followed by thermal annealing. (E) Original unedited AFM images (100 µm²) of functional composites formed by spraying biowax dispersion to gelatin-deposited biofiber assemblies.
Figure S5. (A-D) Original unedited SEM images of functional composites formed by spraying biowax-silica hybrid dispersion (with silica dosages of 0.1, 0.2, 0.3, 0.4 g/g, respectively) to gelatin-deposited biofiber assemblies. (E) Original unedited AFM images (100 µm²) of functional composites formed by spraying biowax-silica hybrid dispersion (with silica dosage of 0.1%) to gelatin-deposited biofiber assemblies. Silica can be packed or enclosed within coatings. (F-I) Original unedited SEM images of consolidated functional composites formed by spraying biowax-silica hybrid dispersion (with silica dosages of 0.1, 0.2, 0.3, and 0.4 g/g, respectively) to gelatin-deposited biofiber assemblies, followed by annealing. (G) Original unedited AFM images (100 µm²) of consolidated functional composites formed by spraying biowax-silica hybrid dispersion (with silica dosage of 0.1 g/g) to gelatin-deposited biofiber assemblies, followed by annealing.
Figure S6. Impact of different gelatins on superhydrophobicity of consolidated functional products. “A” represents consolidated functional composites pertaining to the gelatin with sample code of G108395. “B” presents consolidated functional composites pertaining to the gelatin from Wanbang Co. Ltd. “C” represents consolidated composites pertaining to the gelatin with sample code of G108396. Note that consolidated functional composites were formed by spraying biowax-silica hybrid dispersion (with silica dosage of 0.1 g/g) to gelatin-deposited biofiber assemblies, followed by thermal annealing ((150 °C, 1 h)).
Figure S7. FTIR spectra of consolidated functional composites formed on the basis of different annealing temperatures. Note that composites were formed by spraying biowax-silica hybrid dispersion to gelatin-deposited biofiber assemblies, followed by thermal annealing.
Figure S8. Preliminary results on fruits/vegetables preservation. (A-D) Weight loss pertaining to cherry tomatoes, green grapes, loquats, and mung bean sprouts, respectively, as a function of storage time. UBA represents untreated biofiber assemblies. FC-1 represents functional composites formed by spraying biowax dispersion to gelatin-deposited biofiber assemblies. FC-2 represents functional composites formed by spraying biowax-silica hybrid dispersion (with silica dosage of 0.1 g/g) to gelatin-deposited biofiber assemblies. FC-3 represents functional composites formed by spraying biowax-silica hybrid dispersion (with silica dosage of 0.1 g/g) to gelatin-deposited biofiber assemblies, followed by thermal annealing (150 °C, 1 h). (E-H) Photographs of cherry tomatoes, green grapes, loquats, and mung bean sprouts, respectively, after storage for 5 days. The four sub-photographs in each row pertain to UBA, FC-1, FC-2, and FC-3, respectively.