Buckled Tin Oxide Nanobelt Webs as Highly Stretchable and Transparent Photosensors

Siya Huang, Chuan Fei Guo, Xuan Zhang, Wei Pan,* Xi Luo, Chunsong Zhao, Jianghong Gong, Xiaoyan Li, Zhi Feng Ren,* and Hui Wu*

Stretachable and transparent inorganic semiconductors play a key role for the next generation of wearable optoelectronics. Achieving stretchability in intrinsically rigid inorganic materials is far more challenging than in polymers and metals. Here, we present a low-cost and scalable strategy to engineer inorganic semiconductors into a buckling open-mesh configuration, by which extraordinary stretchability (≈160%) as well as high optical transparency (>86% at 550 nm) can be realized simultaneously in SnO$_2$ nanofiber webs. Moreover, the mechanical stretchability of SnO$_2$ nanowebs can be further improved along with the optical transparency by precisely controlling the nanofiber density. The as-prepared freestanding nanowebs can be laminated onto curved surfaces by conformal contact. It is demonstrated that the fully exposed SnO$_2$ nanowebs can be used as wearable UV photodetectors, showing reliable optoelectronic performance and remarkable tolerance to repeated complex deformations with body movements.

1. Introduction

Wearable electronics, an emerging class of soft electronic systems which can be bent, folded, twisted, and even stretched, have aroused considerable interest in both academic and industrial communities by offering attractive opportunities in a variety of fields, such as intelligent fabrics,$^{[1]}$ artificial skin,$^{[2]}$ epidermal electronics,$^{[3]}$ and bio-integrated devices$^{[4,5]}$. To realize the “wear-and-forget” functionality,$^{[6]}$ the demands of superior mechanical flexibility under both bending and stretching conditions, with reliable performance and good durability, have to be fulfilled. Different from bendability, stretchability is a far more challenging type of mechanics, imposing much larger strains than any other form of deformations. As opposed to metal- and carbon-based stretchable electrodes,$^{[7-10]}$ which have seen great progress so far, little work has been reported on stretchable inorganic semiconductors though they have been serving as the core components of multifunctional opto/electronics. John A. Rogers’s group has initiated some inspiring work on stretchable electronics.$^{[11-13]}$ By introducing buckling geometries, a high level of stretchability up to ≈100% has been achieved in GaAs and Si nanoribbons.$^{[12]}$

To boost the application of soft electronics, facile synthesis techniques, which are not only cost effective but also capable of large-scale processing, need to be put forward. Yan et al.$^{[14]}$ demonstrated a stretchable photodetector with an impressive stretchability of 100% by incorporating inorganic nanowires in an elastomer matrix. Nevertheless, a relatively high nanowire density is required in order to form a percolating nanowire network with fairly good tolerance to
large tensile strains, which results in low optical transmittance or even complete opaqueness. Reduced photoreponse speed with decreased sensitivity is inevitably observed upon straining due to air isolation in the fully embedded structures, which severely impairs the optoelectronic performance of photodetectors. Functional devices that can be laminated onto skin with conformal contact, in a manner that is mechanically invisible to users, would be highly desirable in wearable electronics.\cite{3,15} Polymer-based technology, however, is not an ideal solution to compact integration with complex curvilinear surfaces, and also not compatible with the established inorganic semiconductor industry.

Considering the above principles, we present a universal and scalable strategy to construct highly stretchable and transparent inorganic semiconductors. By engineering a “wavy” and “spring-like” layout with electrospun SnO$_2$ nanowebs, the conventionally rigid inorganic semiconductor demonstrates extraordinary mechanical stretchability with a record strain of 160%. Notably, different from the previously studied embedded structure,\cite{14} the mechanical stretchability of which comes at a price of decreased transparency, our freestanding SnO$_2$ nanoweb exhibits a high specular transmittance of $\approx 86\%$ at 550 nm, and its optical transparency can be even further improved to $\approx 90\%$ upon stretching. The high optical transparency may enable novel applications such as an attachment to windows, which require high transmittance of the visible light.\cite{16} Besides, the closely interwoven nanobelt network is self-supported without the addition of binders, thus ready to be mounted onto any arbitrary curved surface with adequate adhesion by van der Waals forces. This highly stretchable and transparent SnO$_2$ nanoweb demonstrates stable optoelectronic performance (including both photosensitivity and switching speed) while remaining insensitive to strain upon body movements, showing great potential as a wearable UV photodetector.

### 2. Results and Discussion

#### 2.1. Freestanding SnO$_2$ Nanowebs

In this work, an extremely facile and cost-effective technique, electrospinning, is adopted to fabricate inorganic semiconductor nanowebs. As the most efficient method for the synthesis of 1D nanostructures, electrospinning has been commercialized due to its scalability in mass production of uniform fibers.\cite{17,18} The synthesis details of SnO$_2$ nanowebs were described in previous work.\cite{19} As shown in Figure 1a and Figure S1 (Supporting Information), the freestanding SnO$_2$ nanoweb demonstrates great mechanical compliance as a whole. Figure S2 (Supporting Information) and Figure 1b present scanning electron microscopy (SEM) images of as-electrospun nanowebs before and after calcination, respectively, which clearly show that the nanofibers are continuous with a unique ribbon-like geometry. Highly crystallized SnO$_2$ inorganic nanobelts were obtained after heat treatment (Figures S3 and S4, Supporting Information). The electrospun nanofibers are evenly distributed throughout the whole film due to the unique electrospinning process, which employs an electric field to draw fibers and align them in desired patterns. For grounded electrodes made of a flat metal sheet, continuous fibers are deposited over the entire collector surface with a high degree of uniformity, which favors the formation of a self-supported fibermat.

#### 2.2. Tensile Tests

Freestanding SnO$_2$ nanowebs were transferred onto a series of pre-strained polydimethylsiloxane (PDMS) substrates, and their electrical resistance ($R$) was measured under different tensile strains. Samples were fixed on a specially designed stretching machine with two ends secured by clamps. As shown in Figure 2, SnO$_2$ nanowebs with no pre-strain-pre-strains can be stretched to 70%, which is far beyond the requirements for most application cases. Notably, with 100% pre-strains, SnO$_2$ nanowebs can be subjected to tensile strains up to 160% with only a small change in electrical resistance ($R/\rho$) of 3.1. In contrast, the electrical resistance of conventionally sputtered SnO$_2$ thin films increases by 120 times after being stretched to 20% (Figure S5, Supporting Information), which would cause abrupt malfunction during applications. The extraordinary stretchability observed in inorganic semiconductors is of fundamental significance in realizing fully stretchable electronics, both the electrodes and functional parts of which can accommodate large tensile strains. Here, the electrospun SnO$_2$ nanoweb can be reversibly stretched to high strains, demonstrating modest durability in fatigue tests (Figure 3 and Figure S6, Supporting Information). As shown in Figure 3, after 1000 cycles at a tensile strain of 30%, the SnO$_2$ nanoweb still maintains its structural integrity as well as electrical continuity.

#### 2.3. Mechanisms of High Stretchability

The key point that makes a difference between the conventional brittleness of inorganic semiconductors and the
superior stretchability of our SnO$_2$ nanowebs relies on the unique nanostructured open-mesh architecture, which is composed of wavy and spiral buckling geometries. Surprisingly, out-of-plane structural configurations can form simultaneously by transferring SnO$_2$ nanowebs on prestretched PDMS substrates. As shown in Figure 4a, both “spring”- and “wave”-like geometries were observed in SnO$_2$ nanowebs after releasing the pre-strain in PDMS. The behavior of spontaneous formation of such well-defined buckling layouts can be attributed to the extraordinary bendability of the SnO$_2$ nanobelts. From SEM images (Figure 4a and Figure S7 in Supporting Information), we can see that extreme deformations with bending radii smaller than $\approx 200$ nm occur in the kinks and peaks of flexed nanobelts, showing no fractures or cracks. It is found that the top layer of nanobelts, which are free from contact junctions, are likely to form a “spring”-like geometry; while the nanobelts inside the network are more inclined to buckle like waves due to the constraints imposed by intertwined nanobelts in contact. As demonstrated by full three-dimensional (3D) finite-element (FE) simulations (Figure 4b), both spring- and wave-like structures can form via twisting/bending upon releasing 50% pre-strains. The as-formed spring-like structure could elongate up to 100% without fracture. The wavy nanobelt flattens out to a much simpler layout when undergoing a uniaxial tensile strain of 100%, showing a maximum local strain of 1.9%. The FE results indicate that by adjusting the amplitude and wavelength of the geometrical configurations the buckled nanobelts are able to tolerate large reversible strains upon stretching or compressing without imposing substantial strains on the SnO$_2$ itself.

Such a spontaneously formed buckling layout can be attributed to the intrinsic properties of the electrospun nanobelt structures. First, owing to the well-defined ribbon-like geometry, the SnO$_2$ nanobelt has a much smaller bending stiffness $EI$ than that of cylindrical nanowires of a same cross-sectional area, where $E$ is the Young’s modulus and $I$ is the minimum area moment of inertia. For a nanobelt with a rectangular cross section of height $h$ and width $w$, the minimum area moment of inertia $I$ is $hw^3/12$. Here, the electrospun SnO$_2$ nanobelts are of an average width of $\approx 250$ nm and a thickness of $\approx 35$ nm. The minimum $I$ of SnO$_2$ nanobelt is nearly six times smaller than that of a cylindrical nanowire of the same cross-sectional area. Thus, at a certain length, it is much easier for nanobelts to deform into buckling configurations than cylindrical nanowires of the same volume. Secondly, the electrospun continuous SnO$_2$ nanobelt resumes an extremely low percolation density in forming a well-interconnected network. As we know, the length of nanowires and the degree of dispersion uniformity are two key

---

**Figure 2.** $R/R_0$ of SnO$_2$ nanowebs on PDMS with different pre-strains as a function of applied tensile strains. Insets: from left to right are photographs of the sample under tensile strains of 0%, 100%, and 160%, respectively. Scale bar: 1 cm.

**Figure 3.** $R/R_0$ of the SnO$_2$ nanobelt network on 100% pre-strained PDMS as a function of stretching cycles. After 1000 cycles at 30% strain, the SnO$_2$ nanobelt network still retains its electrical continuity.
factors in determining the percolation threshold of networks. According to the random distribution of the conducting stick model,\(^2\) the critical percolation threshold, \(N_c\), is dramatically reduced as the nanowire length \((l)\) increases.\(^3\)

\[
4.236 = \pi \frac{E l^2}{N_c}
\]

Here, our electrospun SnO\(_2\) nanofibers are continuous with lengths over 1 cm, resulting in a percolation density of \(\approx 5.7\) cm\(^{-2}\), which is much lower than that of CNTs \((N_c = 1.43 \times 10^6\) cm\(^{-2}\))\(^4\) and Ag nanowires \((N_c = 7.5 \times 10^6\) cm\(^{-2}\))\(^5\). The extremely low percolation density enables the formation of a well-interconnected nanobelt network with a much larger mesh size. According to Euler’s equation\(^6\)

\[
P_{cr} = \frac{4\pi^2 EI}{l^2}
\]

where \(P_{cr}\) is the buckling load that causes a beam to snap into an unstable equilibrium state and \(l\) is the unsupported length of beam (or mesh size), we could clearly see that long nanowires with a large mesh size are in favor of forming buckling geometries. Thus, under a certain compressive stress, the SnO\(_2\) nanobelt networks are apt to deform into buckling layouts as compared to those consisting of short nanowires, which are normally of 10–20 µm in length. Besides, agglomeration, a common issue existing in the dispersion process of short nanowires, would not be a problem here. The good distribution uniformity of electrospun nanofibers also contributes to the formation of low-dense percolated networks.

As the applied strain exceeds pre-strains, the distortion of nanomesh and formation of delocalized cracks start to take effect. At first, compliant SnO\(_2\) nanobelts align themselves along the direction of the applied tensile stress through localized slipping between overlapped nanobelts. The distortion of the mesh structure can accommodate strains to a certain degree without causing any fracture. As the strain further increases, irreversible damages are eventually caused. However, no fatal fracture occurs as the SnO\(_2\) nanowebs are being stretched to high strain levels, and the samples can keep a well-preserved film integrity until final failure. As shown in Figure 4c, the 50% pre-strained SnO\(_2\) nanoweb shows a closely interwoven web structure with only a few distributed minor cracks after 100% tensile strain. The well-preserved network structure can provide a large number of percolation paths for electron conduction, which ensures the performance reliability of our SnO\(_2\) nanowebs under extreme strain conditions. In contrast, the sputtered SnO\(_2\) thin film ruptures into patches with severe channeling cracks (Figure S8, Supporting Information), which cause a catastrophic failure as the whole conduction path is cut off.

Different from solid thin films, which rupture via localized crack growth under small strains, our SnO\(_2\) nanowebs can survive much larger strains while keeping electrical continuity. This extraordinary stretchability can be ascribed to the distribution of externally applied strains over the entire SnO\(_2\) nanoweb, leading to the formation of delocalized minor cracks instead of localized crack propagation. The strain-delocalization-enabled high stretchability has also

![Figure 4. a) SEM images of pre-strained SnO\(_2\) nanowebs, showing spring- (upper and lower left) and wave-like geometries (lower right). b) Numerical simulation of the deformation of the spring- (upper) and wave-like (lower) nanobelts, demonstrating large reversible stretchability by adjusting the geometrical amplitude and wavelength. c) SEM images of 50% pre-strained SnO\(_2\) nanowebs after being stretched to 100% strain, showing well-preserved network integrity with distributed micro-cracks. Broken nanobelts are detected in the areas of micro-cracks (bottom right).](image-url)
been observed in metallic thin films and nanomesh structures.\[^{24,25}\] On the other hand, the distributed minor cracks endow SnO\textsubscript{2} nanowebs with better mechanical stretchability by enlarging the mesh size.

### 2.4. Optical Transparency

Inorganic semiconductors, which are both mechanically flexible and optically transparent, are highly desired in next-generation soft optoelectronics. However, in order to survive demanding tensile strains of \(\approx 100\%\), most studied nanowire-embedded elastomers completely lose their optical transparency owing to densely overlapped nanostructures.\[^{14}\]

In our case, the thickness of electrospun SnO\textsubscript{2} nanowebs is less than 1 \(\mu\text{m}\), but can accommodate large tensile strains up to 160\%, verifying the possibility of achieving good mechanical stretchability and high optical transparency simultaneously in a single nanomaterial system. To evaluate the optical properties of SnO\textsubscript{2} nanowebs as stretchable electronics, the specular transmittance was measured under a series of tensile strains. As shown in Figure 5a, the 100\% pre-strained SnO\textsubscript{2} nanowebs are highly transparent with a percentage of transmittance \(T\%\) of \(\approx 86\%\) at 550 nm. The transmittance can be further improved to \(\approx 89\%\) at 100\% strain. Much to our interest, a positive correlation is found between the optical transparency and the mechanical stretchability of SnO\textsubscript{2} nanowebs, which breaks the tradeoff dilemma of these two factors in filler-embedded composite structures.

In our experiment, SnO\textsubscript{2} nanowebs with different densities can be prepared simply by controlling the deposition time of electrospinning. S1, S2, and S3 are SnO\textsubscript{2} nanowebs with increased density. The specular transmittance along with their mechanical stretchability on no-pre-strained PDMS was tested. The results reveal that SnO\textsubscript{2} nanowebs with lower nanowire density exhibit higher specular transmittance as well as better stretchability. As shown in Figure 5b, S1 shows the highest specular transmittance of \(\approx 90\%\) as well as the best stretchability with a maximum tensile strain up to 70\%. The superior optical transparency can be attributed to the following two aspects. The first one is the peculiar nanoweb structure with a high open area ratio. The other one is the unique nanoscale ribbon-like geometry of the electrospun SnO\textsubscript{2} nanofibers, which demonstrates small scattering cross-section and little light absorption in the visible regime.\[^{19}\]

### 2.5. Stretchable and Wearable UV Photodetectors

To investigate the optoelectronic properties of SnO\textsubscript{2} nanowebs under stretching conditions, we transferred SnO\textsubscript{2} nanowebs onto 100\% pre-strained PDMS and recorded their time-dependent on/off UV photoresponse under a series of tensile strains at 20 V. As shown in Figure 6, SnO\textsubscript{2} nanowebs exhibit reversible UV photoresponse with only a small decay in the photocurrent as the applied external strain exceeds 50\%. The on/off ratio of photocurrent to dark current does not change much, indicating the performance stability of SnO\textsubscript{2} nanowebs under large stretching deformations.

---

**Figure 5.** a) Specular transmittance spectra of the 100\% pre-strained SnO\textsubscript{2} nanoweb under different tensile strains. Inset shows its transmittance at the wavelength of 550 nm. b) Specular transmittance spectra of SnO\textsubscript{2} nanowebs with different nanobelt densities. S1, S2, and S3 are samples with increased nanobelt density. Inset: \(R/R_0\) of S1, S2, and S3 on no-pre-strained PDMS as a function of applied tensile strains.

**Figure 6.** Time-dependent on/off UV photoresponse of 100\% pre-strained SnO\textsubscript{2} nanoweb under different tensile strains.
The accomplishment of both good mechanical stretchability and high optical transparency makes the SnO₂ nanoweb an ideal candidate for wearable electronics, which are aimed at accommodating complex body movements while pursuing an aesthetically pleasing appearance and a better user experience. To demonstrate the feasibility of SnO₂ nanowebs as wearable devices, UV photodetectors were constructed by laminating freestanding SnO₂ nanowebs onto the knuckle of index fingers. As we know, movements of body joints, such as knuckles, elbows and knees, go through a much more complicated deformation process, involving a combination of bending and stretching. As estimated by \((l - l_0)/l_0\), where \(l\) and \(l_0\) are the length of finger knuckles under bent and straight states, respectively, the nanoweb goes through a tensile strain up to \(\approx 10\%\) upon finger bending. At a fixed voltage of 30 V, the current of photodetectors was monitored during repeated finger movements. As shown in Figure 7a, the SnO₂ nanoweb photodetector exhibits a reversible change in electrical resistance with no obvious decay in electrical conductivity during repeated finger bending cycles, confirming its good mechanical flexibility and durability. The details of the bending test are shown in Movie S1 (Supporting Information).

The UV photoresponse properties of SnO₂ nanowebs were investigated under wearing conditions. Figure 7b shows the typical time-dependent on/off photoconduction curves of SnO₂ nanowebs under the straight and bent states of fingers, respectively. As shown, both photoresponse curves are reversible, indicating the reliability of SnO₂ nanowebs as wearable UV photodetectors. To achieve performance stability, the effect of repeated applied strains on the functionality of inorganic components should be minimized. As for photodetectors, photosensitivity and switching speed are two of the most important performance parameters. As calculated from the on/off ratio of photocurrent to dark current, the UV sensitivity of SnO₂ nanowebs in the straight state is consistent with that in the bent state, showing no strain sensitivity for photocurrent gain. Further analysis confirms that the rise and decay processes upon photoswitching conforms to exponential laws. Thus, the decay time can be defined as the time duration for the current to decrease to \(1/e\) of the steady state photocurrent \((I_0)\), and the rise time is that for current to increase to \((1 - 1/e) I_0\). When the index finger is straight, the decay and rise time of the SnO₂ photodetectors are \(\approx 18\) and \(\approx 12\) s, respectively. Notably, the photoswitching process of SnO₂ nanowebs exhibits the same photoresponse and recovery speed upon finger bending. This is quite different from the fully embedded structures, the switching speed of which would be severely impaired by externally applied strains.[14] The consistency in optoelectronic performance under complex deformations is of great importance for the practical applications of wearable electronics.

3. Conclusion

In summary, a facile strategy is presented to construct highly stretchable and transparent wearable UV photodetectors based on buckled SnO₂ nanowebs. In design of a wavy, spiral open-mesh configuration, the conventionally rigid SnO₂ exhibits extraordinary mechanical stretchability (160% strain). Besides, high optical transparency (86% at 550 nm) is achieved in buckled SnO₂ nanowebs, which can be further improved upon tensile strains. This fully exposed nanoweb structure demonstrates stable and reliable optoelectronic performance as a wearable UV photodetector, showing remarkable tolerance to repeated complex deformations with finger movements. Electrospinning is highly versatile and can be readily extended to a broad range of inorganic materials, which holds great promise in scalable manufacture of wearable multifunctional optoelectronics.

4. Experimental Section

**Sample Preparation:** The freestanding SnO₂ nanowebs were synthesized by electrospinning as described in our previous work.[19] The PDMS substrates were prepared by curing a mixture of
base and curer in a weight ratio of 10:1 in a vacuum oven at 60 °C for 3 h. SnO₂ thin films were fabricated on the as-prepared PDMS substrates by AC magnetron sputtering (LJ-SP103C, LJ-UHV Technology Co., Ltd., Taiwan) at a pressure of 5 mTorr with a power of 150 W for 1 h. The gas flow rates of argon and oxygen are 20 and 5 sccm, respectively.

Characterization: The samples were characterized by field emission scanning electron microscopy (FESEM, JSM-6460LV, JEOL Corp., Japan), transmission electron microscopy (TEM, JEM-2010, JEOL Corp., Japan), and X-ray diffraction (XRD, D/max-2500, Rigaku Corp., Japan). The XRD data are shown in Figure S3 (see the Supporting Information).

Tensile Tests: The PDMS substrates with a thickness of 1 mm were cut into strips. SnO₂ nanobelt network films with a width of 2–3 mm and a length of 5 mm were transferred onto PDMS. Silver nanowires (SLV-NW-90, Blue Nano Inc., USA) are used as purchased and serve as device electrodes with a gap width of 2 mm. The stretchability test was conducted on a self-designed setup with electrical conductivity recorded by a Keithley 2100 multimeter.

Assembly of Photodetectors: A piece of freestanding SnO₂ nanobelt network was transferred onto the forefinger knuckle of a human hand in a rubber glove for finger bending. Electrodes were prepared by silver paste and then connected with silver wires. Time-dependent on/off photoresponse was tested on a Keithley 4200-SCS measurement system. The UV light source was supplied with a low-pressure mercury lamp (Philips TUV 8 W, 254 nm).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The work performed at Tsinghua University was supported by National Basic Research of China (Grant No. 2013CB632702) and NSF of China (Grant No. 51302141), and the work performed at the University of Houston was supported by the US Department of Energy under Contract Number DOE-DE-FG02-13ER46917/DE-SC0010831. The authors thank K. Matsubara, Dr. Y. Rong and Dr. S. Venkatesan for their help in the demonstration of photodetectors.