Multiscale deformations lead to high toughness and circularly polarized emission in helical nacre-like fibres

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Nacre-like composites have been investigated typically in the form of coatings or freestanding sheets. They demonstrated remarkable mechanical properties and are used as ultrastrong materials but macroscale fibres with nacre-like organization can improve mechanical properties even further. The fiber form or nacre can, simplify manufacturing and offer new functional properties unknown yet for other forms of biomimetic materials. Here we demonstrate that nacre-like fibres can be produced by shear-induced self-assembly of nanoplatelets. The synergy between two structural motifs—nanoscale brick-and-mortar stacking of platelets and microscale twisting of the fibres—gives rise to high stretchability (>400%) and gravimetric toughness (640 J g⁻¹). These unique mechanical properties originate from the multiscale deformation regime involving solid-state self-organization processes that lead to efficient energy dissipation. Incorporating luminescent CdTe nanowires into these fibres imparts the new property of mechanically tunable circularly polarized luminescence. The nacre-like fibres open a novel technological space for optomechanics of biomimetic composites, while their continuous spinning methodology makes scalable production realistic.
Realization of materials with high toughness combined with other properties is one of the key challenges for both load-bearing and functional materials. This materials science challenge can often be addressed using biomimetic design taking naturally occurring composites that have been optimized over long evolutionary periods as inspiration. The ‘brick–and–mortar’ layered design of nacre, with alternating layers of inorganic platelets and biopolymers, inspired biomimetic research for several decades. The materials architecture with alternating layers of hard inorganic components and soft organic polymers effectively arrests the propagation of cracks. The process has been replicated using a large variety of inorganic components, including clay, Al2O3 (refs 1,8) and layered double hydroxides, combined with various organic polymers including poly(vinyl alcohol) (PVA), polyelectrolytes and chitosan. The layered biomimetic nanomaterials are much tougher than their inorganic and organic components alone, and often reveal exceptionally high strength and stiffness. Further improvement of toughness in biomimetic nanocomposites is restricted, however, by the low strains of composite materials, especially when the volume fraction of the stiff inorganic phase is high. The layered biomimetic nanomaterials are much tougher than materials’ strains.

The combination of two structural motifs at different scales, specifically nanoscale and microscale in this case, is designed to simultaneously increase both the stretchability and toughness of a composite. Indeed, a stretchable graphene film combined with ripples and yarns exhibited improved tensile strain of 30% (ref. 12) and 76% (ref. 13), respectively. This inspired our search for methods to create nacre-like composites with multiscale structural motifs and evaluate their mechanical properties, which we expected to be quite unique as well as technologically valuable. Here we demonstrate that it is possible to transform flat nacre films into fibres that combine layered nanoscale and spiral microscale structural motifs. The resulting fibres can sustain longitudinal strains as high as 414%. This is 10–1,000 times higher than typical biomimetically designed layered composites and other fibre-like nanocomposites. The nacre-like fibres display an unusually high gravimetric toughness of ~640 J g−1, which significantly exceeds those of natural nacre (~1 J g−1)9, dragline silk (165 J g−1)14, graphene (171 J m−3)13, Kevlar (KM2) (78 J g−1)14 and some of the best examples of composed single-wall carbon nanotube (SWNT) fibres (570–970 J g−1)15–17. Such unusual mechanical properties are attributed to multiscale deformation combining both the sliding of nanoscale platelets and unravelling of microscale spiral curls. Moreover, the described process of fibre spinning and strain-induced particle self-organization enables continuous scalable production of this material. Furthermore, the helical patterns of the multiscale deformations causes circularly polarized luminescence (CPL) to be emitted at ~575 nm when cadmium telluride (CdTe) nanowires are incorporated into PVA/CaCO3 fibres. The high stretchability of the fibres allows the wide-range modulation of the luminescence dissymmetry ratio (gD) and the same is expected for many other optically active materials and different wavelengths. This novel optomechanical property of the fibres highlights the emergence of novel possibilities for engineering chiral nanomaterials that may be useful for remote monitoring of materials’ strains.

Results
Preparation of CaCO3 and graphene nanoplatelets. To prepare the nacre-like fibres we used two types of inorganic ‘building blocks’: one is platelets of CaCO3 (vaterite) synthesized from calcium chloride and ethylene glycol by a hydrothermal method, and the other is graphene-based nanosheets (G) made by electrochemical exfoliation of highly oriented pyrolytic graphite. The vaterite platelets had diameters and thicknesses of 4–20 μm and 100–500 nm (Supplementary Fig. 1), respectively; these dimensions are very similar to the microplatelets of the aragonite inorganic phase in seashell nacre. G nanosheets displayed diameters and thicknesses of 5–45 μm and 1–5 nm, respectively (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects, (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like fibres because of their low density of defects. Calcium carbonate and ethylene glycol by a hydrothermal method, and the other is graphene-based nanosheets (G) made by electrochemical exfoliation of highly oriented pyrolytic graphite. The vaterite platelets had diameters and thicknesses of 4–20 μm and 100–500 nm (Supplementary Fig. 1), respectively; these dimensions are very similar to the microplatelets of the aragonite inorganic phase in seashell nacre. G nanosheets displayed diameters and thicknesses of 5–45 μm and 1–5 nm, respectively (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects, (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects, (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects, (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects, (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects. Calcium carbonate and ethylene glycol by a hydrothermal method, and the other is graphene-based nanosheets (G) made by electrochemical exfoliation of highly oriented pyrolytic graphite. The vaterite platelets had diameters and thicknesses of 4–20 μm and 100–500 nm (Supplementary Fig. 1), respectively; these dimensions are very similar to the microplatelets of the aragonite inorganic phase in seashell nacre. G nanosheets displayed diameters and thicknesses of 5–45 μm and 1–5 nm, respectively (Supplementary Fig. 2a–c). CaCO3 and G were chosen a pair of building blocks for the nacre-like composites because of their low density of defects.钙碳酸盐和乙二醇水合物通过水热法制备，而G则是由高度定向的石墨烯氧化物制备的。钙碳酸盐的直径和厚度为4–20 μm和100–500 nm（ Supplementary Fig. 1），而G的直径和厚度为5–45 μm和1–5 nm（ Supplementary Fig. 2a–c）。CaCO3和G被选择为一组构建块，因为它们的低密度缺陷。钙碳酸盐和乙二醇水合物通过水热法制备，而G则是由高度定向的石墨烯氧化物制备的。钙碳酸盐的直径和厚度为4–20 μm和100–500 nm（ Supplementary Fig. 1），而G的直径和厚度为5–45 μm和1–5 nm，而G被选择为一组构建块，因为它们的低密度缺陷。
Morphology evolution during twist spinning. To better understand the mechanical performance of the products, we investigated how the microscale morphology evolved after drawing them out of the coagulation bath. After extrusion of the PVA/G composite from a 400 μm diameter nozzle, a belt-like fibre (Fig. 2a), ~225 μm in diameter, was formed; its nanoscale organization was characterized by disordered packing of the nanosheets (Fig. 2g). After twisting, the fibres became thinner (diameters ~120 μm) and nearly circular in cross-section (Fig. 2e,f). Additional twisting further decreased the fibre diameters to ~110 μm, and resulted in the formation of uniform, spring-like coils (Fig. 2c).

A similar progression of fibre shapes can be seen for the PVA/CaCO₃ composite (Supplementary Fig. 5). Unlike the PVA/CaCO₃ composite, the surface of belt-like fibres from G sheets had a non-uniform orientation of platelets (Fig. 2d). After the twist spinning, the fibres showed helical corrugations along the fibre axis with periodicity of 250–600 nm (Fig. 2e,f). The torque applied during spinning of the wet fibre resulted in considerable improvement of platelet alignment (Fig. 2j–l). Enhanced alignment of the platelets was also confirmed using synchrotron small-angle X-ray scattering (S-SAXS). 2D scattering patterns accompanied with the profile of scattering intensity ($I \times q^2$) as a function of scattering vector ($q = 4\pi\sin\theta/\lambda$) and profile of scattering intensity ($I$) as a function of azimuthal angle ($\phi$) are given in Fig. 2m–o and Supplementary Fig. 6, respectively. Since PVA scatters X-rays weakly, the diffraction peaks originated from the G. The elliptical S-SAXS pattern and absence of sharp scattering peak (Fig. 2m and Supplementary Fig. 6d) obtained for belt-like fibres before twisting indicated poor alignment of nanosheets. The nearly perfect nacre-like layering in the transversal direction of the fibre indicated by the sharp scattering peak (Fig. 2n) was observed after twisting. This was accompanied by sharp peaks at 154° and 329°, as shown in Supplementary Fig. 6d, which highlighted the strong alignment of platelets in the twisting fibre. Further twisting led to the formation of a coiled fibre and its longitudinal direction alignment (Supplementary Fig. 6c) resulted in an absence of a sharp peak in the 2D scattering pattern (Fig. 2o). The monotonous intensity drop without noticeable intensity peak (Supplementary Fig. 6e) is characteristic of the uniform dispersion of G in the PVA matrix for all of the samples, which is both essential and non-trivial for composites with high content of G. For both of the PVA/G and PVA/CaCO₃ composites, the nanoscale structure of the fibres was analogous to the nacre-like materials previously reported, with the exception of additional circular bending of the inorganic phase that becomes progressively more pronounced with increased coiling (Fig. 2j–l).

Mechanical properties of nacre-like fibres. Mechanical properties of the fibres were assessed using the stress–strain test (Fig. 3a). The tensile strength was 270 ± 30 MPa, which was comparable to other nacre-like materials made from clay, graphene or graphene oxide (GO). Herein, the tensile stress was calculated from the normalization of the applied force with a cross-section of microfibre after fracture. More importantly, elongation to fracture, that is, maximum tensile strain ($\varepsilon$), was as high as 330 ± 60%; this compares favourably to tensile strains of natural nacre ($\varepsilon = 2\%$), dragline silk ($\varepsilon = 31–47\%$), graphene composites ($\varepsilon = 1.6–76\%$) and SWNT composite fibres ($\varepsilon = 104–430\%$). The area under the stress-strain curve was used to calculate toughness, which was determined to be 460.3 ± 42 MJ m⁻³ and 168.1 ± 18.2 MJ m⁻³ for G (Fig. 3a) and vaterite fibres (Supplementary Fig. 7), respectively. In contrast, for an equivalent PVA fraction of 66 wt%, belt-like and circular fibres dissipated only 46.3 ± 5.4 MJ m⁻³ and 118.2 ± 9.7 MJ m⁻³, respectively, before fracture. Because the density of our fibres is ~0.84 g cm⁻³, the weight-specific toughness of the material was calculated to be 548 ± 50 J g⁻¹. For comparison, tensile strength, $\varepsilon$, and toughness for ‘flat’ graphene paper obtained by vacuum assisted filtration (VAF) without polymer were reported to be 41.7 ± 4 MPa, 1.34 ± 0.07% and 0.23 ± 0.03 J g⁻¹; the same values for PVA/graphene nanocomposites prepared via layer-by-layer assembly were 143.1 ± 1.12 MPa, 0.051 ± 0.013% and 6.1 MJ m⁻³, respectively. We also prepared a PVA/G composite using the VAF method with 66 wt% PVA (Supplementary Fig. 8). It showed tensile strength, $\varepsilon$, and toughness of 65.8 ± 12 MPa, 95.5 ± 8% and 48.6 ± 6 J g⁻¹, respectively. The maximum strain sustained by the nacre-like PVA/G fibre is ~246 times higher than that of the neat G film or
approximately 3.5-4 times higher than that of nacre-like flat PVA/G composite film (VAF) with the same G loading. The toughness of spring-like PVA/G fibre is 2,380 and 11 times higher than that of the G paper and 'flat' 66% PVA/G composite film made by VAF, respectively. Similarly, outstanding mechanical properties were also obtained for PVA/CaCO₃ fibres (Supplementary Fig. 7a), which showed a strain of 200.6 ± 14%, and toughness of 107.1 ± 11.6 J g⁻¹, with a fibre density of 1.57 g cm⁻³.

A cyclic stretching test with ε = 20% was used to investigate the strain-hardening processes of the nacre-like fibres (Supplementary Fig. 9a). For the first to 50th cycles, the PVA/G fibres exhibited considerable plastic deformation typical of many biological and synthetic materials. After the 50th cycle, the deformation became mostly elastic (Fig. 4). The tensile stress for ε = 20% saturates at ~39 MPa for the 80th cycle (Fig. 4 and Supplementary Fig. 9b), which is about 1.18 times its initial value. Strain hardening was accompanied by tighter packing of the nanosheets and an increase of their curvature (Supplementary Fig. 9c–f). After being pre-stretched, the fibre still showed the visible hysteresis between the loading and unloading curve with energy dissipation of 0.13 J g⁻¹ (Supplementary Fig. 10), indicating viscoelastic behaviour of the nacre-like fibre. Notably, the spring constant (Supplementary Fig. 11) after strain hardening was 76.8 ± 1.8 N m⁻¹, twice as much as conventional steel-based tension springs and carbon nanocoils.

It is informative to compare the mechanical properties and toughness of the obtained nacre-like fibres with other well-known materials, such as dragline silk (165 J g⁻¹) and Kevlar(KM2) (78 J g⁻¹), as well as additional human-made fibres exemplified by various carbon nanotube- and graphene-based composites (Supplementary Table 1). Note that while nacre is known for its toughness of ~1 J g⁻¹, the twisted PVA/CaCO₃ composite fibres are over ~107 times tougher.

It is also instructive to compare the mechanical properties of the prepared twisted fibres with those made from neat PVA using the same apparatus. The maximum strain and toughness of neat PVA fibre without G are 102.6 ± 14% and 13.6 ± 3.8 J g⁻¹,
respectively. This fact is remarkable because parent polymeric materials typically exhibit higher stretchability than their resulting composites. Both vaterite and $G$ composites display greater strains than their parent polymers. The fibre’s mechanical properties for different mass fractions of PVA peak at about 65% PVA (Supplementary Fig. 12).

The fibres can be made by a continuous mode, forming rolls of nacre-like fibrous material (Fig. 5) with identical morphology over the entire fibre, exemplified by a 4 cm long fibre, displaying uniform diameter and pitch over its entire length (Supplementary Fig. 11b).

**Circularly polarized emission of helical fibres.** Luminescent helical fibres were prepared by incorporating CdTe nanowires into PVA/CaCO$_3$ composites during the spinning process (Methods section). The content of CdTe nanowires was about 0.9 wt%, as measured by thermogravimetric analysis (Supplementary Fig. 15), and the fibres retained their original morphology and stretchability. Both left- and right-handed helical fibres can be produced through controlling the spinning direction (Fig. 6b inset). Strong CPL of these fibres was observed under the illumination of non-polarized light. Shifting the excitation wavelength by 20 nm (from 358 to 338 nm) did not change the peak maxima of the corresponding photoluminescence spectra (Supplementary Fig. 16), which demonstrated that Raman scattering was not a major contributor to these chiroptical properties and confirmed the photoluminescence origin of the observed spectra when the fibres are irradiated with CPL light.
Consecutive measurements of the same fibres yielded identical \( g_{\text{lum}} \) spectra (Supplementary Fig. 17), confirming that these fibres are relatively optically robust when irradiated.

The luminescence dissymmetry ratio \( (g_{\text{lum}}) \) was calculated as

\[
g_{\text{lum}} = \frac{\Delta I}{\frac{1}{2}I} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)}
\]

where \( I_L \) and \( I_R \) represent left- and right-handed CPL, respectively. Fibres of opposite handedness (Fig. 6a) exhibit almost mirror-imaged \( g_{\text{lum}} \) spectra along the \( x \) axis with peak maxima of similar intensities: \( 3.7 \times 10^{-3} \) (580 nm) for the right-handed fibres and \( 4.0 \times 10^{-3} \) (572 nm) for the left-handed fibres (Fig. 6b). The value of \( g_{\text{lum}} \) is comparable to that observed for other semiconductor materials such as cysteine-capped CdSe nanoparticles \( (3 \times 10^{-3} \text{ and } 4 \times 10^{-3}) \) and CdS nanoparticles templated in a protein nanocage \( (4.4 \times 10^{-3}) \), though our macroscale twisting process is considerably simpler.

CPL activity is associated with the helicity of the fibres. An effective validation of this mechanism would be modulation of CPL activity by fibre helicity changes induced by a mechanical deformation operation such as stretching. Indeed, the \( g_{\text{lum}} \) spectra of luminescent spring fibres show a strong dependence of CPL attenuation on the fibre elongation (Fig. 6c,d and Supplementary Fig. 18). As the fibres are stretched from their original length to 1.5 and 2 times their original length, the \( g_{\text{lum}} \) at peak maxima is decreased from \( 3.7 \times 10^{-3} \) to \( 2.8 \times 10^{-3} \) and finally to \( 1.3 \times 10^{-3} \) (Fig. 6c,d). This mechanical manipulation of CPL emission is efficient in a broad illumination wavelength range of 400–900 nm (Fig. 6d), showing that smaller \( g_{\text{lum}} \) values can be obtained from the increasingly stretched fibres.

**Discussion**

Previous versions of coiled fibres obtained by spinning and scrolling carbon nanotubes and GO films dissipated energy predominantly via macroscale deformation of the coils and displayed toughness of 28.7 J g\(^{-1}\) and 17 J m\(^{-3}\), respectively\(^{13,35}\). Other deformation modalities involving, for instance, nanoscale deformations, might be expected but were not investigated. This may be partially related to less pronounced structural changes than those observed in Figs 2 and 3, and the related inability to use SAXS to visualize the structural evolution under strain.

The unusually high toughness for nacre-like fibres in Figs 1 and 2 is attributed to multiscale deformation of the fibres on strain that involves both sliding/reorganization of the nanoscale sheets and microscale deformation of the coils. Indeed, opening of the coils and decreasing coil density can be seen as the strain increases from 0 to 60\%, 170\% and 245\% (Fig. 3b). Various degrees of coil opening along the length of the fibre (Fig. 3c–f) suggests somewhat unequal strain along the fibre during stretching.

The combination of nanoscale and microscale deformations allows the material to experience strong intermolecular interactions between the nanosheets and the polymers, while uniformly distributing the stress along the length of the fibre. While the former mechanism is possible for ‘flat’ nacre-like composites, the latter, or uniform stress distribution, is not. Minor defects result in stress concentration in the small volumes of the material and consequent failure. Other processes to achieve high elongation and thereby toughness include using elastic polymers or

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**Figure 4** | Tensile testing. Tensile stress and spring constant (\( k \)) of PVA/G fibre at \( \epsilon = 20\% \) as a function of the cycle number during cyclic tensile testing.

**Figure 5** | Characterization of a coil of PVA/G and PVA/CaCo\(_3\) fibre. (a) Photograph of PVA/G fibre wound on a reel, (b) Top view: a coil of spring-like PVA/G fibre, (c) SEM image of coiled spring-like PVA/G fibre marked in box in b, (d) Photograph of PVA/CaCo\(_3\) fibre wound on a reel, (e) A coil of spring-like PVA/CaCo\(_3\) on a roll, (f) SEM image of a coil of PVA/CaCo\(_3\) fibre. Scale bars in b and e are 4 mm, c and f are 0.5 mm, respectively.
composites\textsuperscript{17,36}, taking advantage of the intrinsic elasticity of polymers\textsuperscript{36} or interconnected networks and chemical bonds of constituents\textsuperscript{17}. While yielding high-performance materials, the mechanism of energy dissipation in these fibres is different from that described for fibres with G, CaCO\textsubscript{3} and CdTe.

Distribution of stress over the extended volume of the material in helical fibres can be seen from the conical shape of the fracture surface (Fig. 3g). The cracks apparently do not propagate perpendicularly to the surface but do so parallel to the length of the fibre, which dissipates more energy. In contrast, the fracture surface in the belt-like fibre (Fig. 3h) is perpendicular to the fibre axis. Consequently, tensile strength, stretchability and fracture surface in the belt-like fibre (Fig. 3h) is perpendicular to perpendicularly to the surface but do so parallel to the length surface (Fig. 3g). The cracks apparently do not propagate in helical fibres can be seen from the conical shape of the fracture surface (Fig. 3g).

The same multiscale deformations result in a novel chiroptical functionality: CPL. Circular asymmetry of emission is possible but difficult to obtain for optically active compounds including quantum dots\textsuperscript{33}, nanofibres\textsuperscript{37}, liquid crystals\textsuperscript{38} and molecular luminophores\textsuperscript{39}. In our case, CPL is not only strong in intensity but also difficult to obtain for optically active compounds. While strain-induced particle self-organization can be realized for a variety of nano-scale components\textsuperscript{43,44}, the method of fibre preparation can be generalized to other inorganic nanomaterials for mechanically tunable CPL-active composites and enables a novel technologically significant method to manipulate the chiroptical activity of materials that can be utilized among other applications for the stand-off assessment of mechanical strains.

**Methods**

**Electrochemical exfoliation of graphene-based nanosheets.** Highly oriented pyrolytic graphite (HOPG, 1 \times 1 \times 0.3\,\text{cm}) was employed as the electrode and source of graphene for electrochemical exfoliation. The anode was a block of HOPG, gripped and inserted into the electrolyte. A Pt plate served as the grounded electrode, and was placed parallel to the HOPG with a separation of about 4\,\text{cm}. The electrolyte was prepared by applying DC bias on the HOPG electrode (from \(-10\)\,\text{V} to \(+10\,\text{V}\)). When the HOPG was completely exfoliated, G nanosheets were collected by vacuum filtration and rinsed at least three times with deionized water.

Characterization of low defect graphene-based nanosheets. Supplementary Figure 2a shows an scanning electron microscopy (SEM) image of G made by electrochemical exfoliation of HOPG on a SiO\textsubscript{2}/Si substrate. The sheet sizes range from 5 to 45\,\text{nm}. Supplementary Figure 2b shows a typical atomic force microscopy image of low defect graphene-based nanosheets.
Synthesis of CaCO3 nanoplatelets. The CaCO3 nanoplatelets were prepared as follows: 2 g of CaCl2 and 2 g of urea were added into 6.0 ml of deionized water and reacted at 50 °C for 4 h. After the reaction, the autoclave was cooled, and the suspension was centrifuged at 6,000 r.p.m. for 5 min. The centrifugation and redispersion cycles were repeated twice with deionized water and ethanol, respectively. The precipitate was oven dried at 60 °C for 12 h.

Synthesis of TGA–CdTe NPs. Cd(ClO4)2·6H2O (0.985 g) and thioglycolic acid (TGA, 0.392 ml) were dissolved in 125 ml of deionized water, followed by adjusting the pH to 11.2 with 1 M NaOH. This solution was placed in a three-neck round-bottom flask and stirred with N2 for 30 min. H2Te gas (generated by reacting 0.13 g Al2Te3 with 25 ml of 0.5M H2SO4) was slowly passed through the solution. The solution was then allowed to reflux under N2 for 100 °C for 120 min to obtain the TGA–CdTe NPs (Supplementary Fig. 13).

Preparation of TGA–CdTe nanowires. 15 ml of TGA–CdTe NP solution was mixed with 22.5 ml of methanol, yielding red precipitation in the solution. After centrifuging at 1,500 r.p.m. for 3 min, the supernatant was removed and the precipitate was re-dispersed in deionized water and pH adjusted to 9 by the addition of 0.1 M HCl solution. The solution was aged in the dark at room temperature and nanowires (Supplementary Fig. 14) were formed after 6 days of aging.

Preparation of nacre-like PVA/G composite fibres. For preparation of PVA/G composite fibres, dried and powdered G was re-dispersed in deionized water by gentle sonication; the concentration was 10 mg ml⁻¹. PVA aqueous solution with a mass fraction of 5% was prepared from dissolved PVA (molecular weight ~205,000, hydrolysis <89%, Aladin) in deionized water. For preparing 66 wt% PVA/G mixture, 2.7 ml 5 wt% PVA aqueous solution was added to 7.3 ml G suspension (10 mg ml⁻¹) and stirred at 600 r.p.m. for 12 h. Then the mixture was concentrated by heating until a final mixture volume of 7 ml. Other ratios of PVA in the mixture were prepared by adding different volumes of 3 wt% PVA solution. For the wet-spinning process, first the concentrate was loaded into a 50 ml plastic syringe with a spinning nozzle (diameters = 100, 200 and 400 μm), and injected into a container with 300 ml coagulation bath (for example, ethanol with 5 wt% NaOH, acetone, Na2SO4) by a syringe pump at speed of 0.05–3 ml min⁻¹. After coagulation, the fibres were thoroughly washed with water and ethanol under a stated ratio of 1:9, followed by re-attachment to the sample holder for subsequent CPL measurements.

Preparation of PVA/CaCO3 composite fibres. The spinning process is the same as that of PVA/G detailed in Fig. 1. In brief, 0.4 g dried CdTe nanocapsules were added into 3.5 ml of ethanol and 5.0 ml of deionized water and stirred for 20 min. Then, 8 g of 5 wt% of aqueous solutions of PVA and 5 ml as-prepared CdTe nanowire solution was added into the above solution and stirred for 24 h. The solution was centrifuged at 3,000 r.p.m. for 3 min. The sediment was re-dispersed in a little deionized water, and stirred vigorously (the content of CdTe was about 0.2–0.4 mg ml⁻¹). Then the mixture was injected into 5 wt% of ethanol solution of sodium hydroxide (the total volume was 200 ml) and a fibre was formed. To curl the fibre, it was kept for 15 min in a coagulation bath. The wet fibre was dried at 60 °C for 1 h under vacuum. Twist-spinning process was similar to that for the PVA/G spring fibre.

Preparation of PVA/CaCO3/CdTe composite fibres. The spinning process is the same as that of PVA/CaCO3 fibre detailed in Fig. 1. In brief, 0.4 g dried CaCO3 nanocapsules were added into 3.5 ml of ethanol and 5.0 ml of deionized water and stirred for 20 min. Then, 8 g of 5 wt% of aqueous solutions of PVA and 5 ml as-prepared CdTe nanowire solution was added into the above solution and stirred for 24 h. The solution was centrifuged at 3,000 r.p.m. for 3 min. The sediment was re-dispersed in a little deionized water, and stirred vigorously (the content of CdTe is about 0.9 wt% thermogravimetric analysis curve in Supplementary Fig. 15). Then the mixture was injected into pure ethanol solution and a fibre was formed. To curl the fibre, it was kept for 15 min in a coagulation bath. Twist-spinning process was similar to that in the PVA/G spring fibre.

Characterization. SEM images were obtained using a Hitachi SU–8000 with accelerating voltage of 15 kV. AFM images were acquired in the tapping mode with a commercial multimode Nanoscope IIIa (Veeco Co., Ltd.). Raman spectra were collected using a LabRAM XploRA laser Raman spectroscope (HORIBA Jobin Yvon Co., Ltd.) using a 532-nm laser with incident power of ~1 mW. The high-resolution TEM was used in SEM, AFM and Raman characterizations. TEM images were obtained by VAF.

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Author contributions

P.A.H. and N.A.K. supervised the project. J.Z. carried out fibre fabrication, characterization and testing. W.F. carried out the synthesis and characterization of CdTe NPs and NWs. W.F. and H.A.C. performed the CPL experiments. B.Y. carried out fibre testing and characterization. W.F. and H.A.C. performed the S–SAXS characterization. F. G. Bian, Dr X. H. Li, and Dr F. Tian in the SSRF (BL16B1 experimental station) for S–SAXS characterization. We thank Dr J. Q. Yang for the analysis of S–SAXS data.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

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