Multiwalled boron nitride nanotubes with a strong nonlinear chiroptical response

Chiral crystals are sought after for their ability to tune the polarization of light. Now, multiwalled boron nitride nanotubes (BNNTs) are shown to be promising chiral crystals with coherently stacked structures, wherein the component tubes display mono-chirality, homo-handedness and unipolarity. This unique architecture endows BNNTs with strong optical nonlinearity and a chiral geometry-dependent chiroptical response.

The mission

Nonlinear optical crystals, capable of optical frequency conversion, are pivotal in both classical and quantum optics[1]. When these crystals are chiral, they respond differently to left-circularly polarized and right-circularly polarized light (known as circular dichroism), enabling the modulation of the polarization of nonlinear parametric light[2]. Such modulation is highly desirable for many advanced applications, including optical encryption and security, nonlinear holographic imaging and quantum information processing. However, traditional nonlinear optical crystals typically lack chirality for circular dichroism owing to spatial translational symmetry, and assemblies of chiral molecules often result in suboptimal frequency conversion efficiency. Despite considerable efforts[3], the quest for intrinsically chiral materials with high stability, pronounced optical nonlinearity and a large chiroptical response remains unfulfilled.

The solution

One-dimensional (1D) nanotubes are robust crystals with tunable chiral geometries, defined by their chirality, handedness and polarity[4] (Fig. 1a,b). However, the component tubes within a multiwalled nanotube typically exhibit arbitrary chiral geometries. Thus, the phase of the nonlinear optical response from the component tubes is random, which decreases the total intensity of the response.

Boron nitride nanotubes (BNNTs) are promising 1D chiral nonlinear optical materials, and theoretical simulations suggest that they could have strong optical nonlinearity[5]. We grew multiwalled BNNTs using a chemical vapour deposition method and investigated their structure-dependent nonlinear optical responses. Through transmission electron microscopy (TEM) imaging of the as-grown multiwalled BNNTs, we found that the individual BNNTs exhibit a preference for coherently stacked configurations, in which the component tubes display nearly mono-chirality, homo-handedness and unipolarity.

The unique structure of the BNNTs could facilitate the constructive enhancement of the optical nonlinearity of each coaxial tube, resulting in a giant response that increases quadratically with the total thickness of the BNNT walls. Indeed, a single BNNT with a modest diameter of 350 nm achieved second-harmonic generation (SHG) — the most fundamental nonlinear optical response — with an SHG intensity about 100,000 times stronger than that of a BN monolayer and a high conversion efficiency of 0.01%. A single BNNT thus produced a panchromatic SHG output at the microwatt power level. This level of output is sufficiently intense to be perceptible, unaided, to the human eye. The operation range of the BNNTs is quite broad, encompassing wavelengths from the ultraviolet to the near-infrared region.

Moreover, we anticipated that the uniform chiral geometry of the component tubes within a single BNNT could contribute to a large circular dichroism effect. We therefore measured the circular dichroism of SHG in 10 BNNTs with different chiral angles. We found that the circular dichroism was continuously tunable from −0.7 to 0.7 with respect to the chiral angle (Fig. 1c), which agrees well with the results of our physical model and simulations. Overall, the combination of high optical nonlinearity and the robust chiral structure suggest that BNNTs are promising candidates for chiral nonlinear optical crystals.

Future directions

Engineering of interfacial stacking has yielded considerable achievements in two-dimensional layered materials[6]. Our findings challenge the prevailing notion of random stacking configurations in 1D nanotubes. The observation of BNNTs with coherently stacked structures suggests the potential for exploring stacking configurations in 1D nanotubes, which could give rise to effects such as sliding ferroelectricity, chiral shift currents, nonreciprocal superconductivity and bulk photovoltaic effects.

For practical applications, the controlled growth of samples is of paramount importance. However, the growth method we used does not provide control over the chirality, handedness and polarity of BNNTs. Moreover, the diameter of BNNTs needs to be further increased to enhance the nonlinear optical response, which would be of benefit to a multitude of applications.

The unique optical properties and high stability of BNNTs, as well as their good integrability with silicon-based devices, should offer exciting opportunities in the design of optoelectronic and nanophotonic devices. Our next aim is to hybridize the BNNTs with a nanocavity or metasurface for the realization of on-chip light sources and modulators.

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EXPERT OPINION

"The authors synthesized multi-walled boron nitride nanotubes (BNNTs) and discovered an exciting structure in which the composite coaxial tubes are coherently stacked. This leads to large second-harmonic generation (SHG) yield and circular dichroism (CD) of the SHG signal. The combination of large SHG and CD is not commonly seen and these BNNTs could enable effective control of light polarization in nonlinear processes, promising for a number of applications." **Shengxi Huang, Rice University, Houston, TX, USA.**

FIGURE

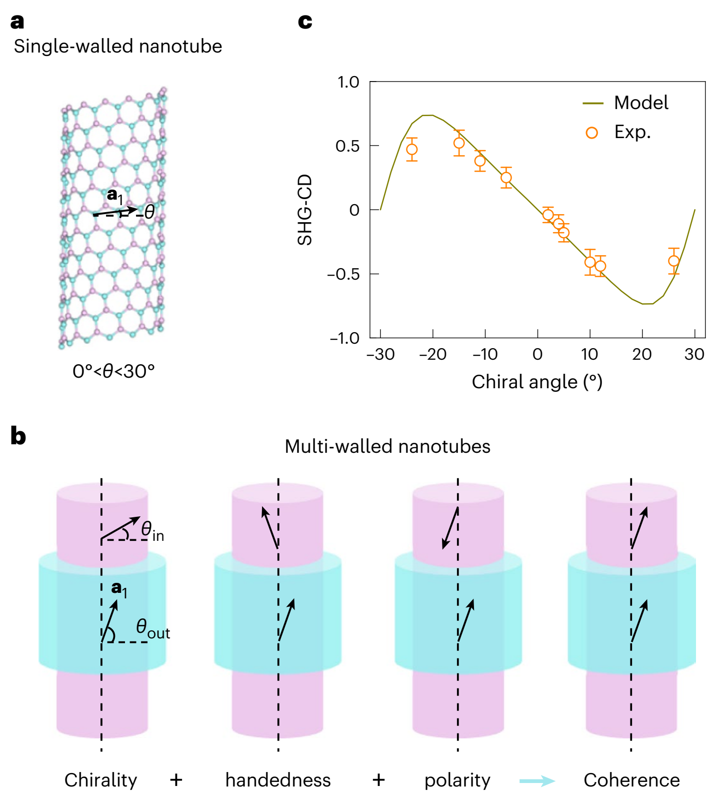

Fig. 1 | Coherently stacked BNNTs for strong and tunable nonlinear optical circular dichroism. **a**, A single-walled BNNT, where the chiral angle, θ, is defined as the angle between vector $\mathbf{a}_1$ and its radial direction. **b**, Stacking configuration of the component tubes within multiwalled BNNTs, where θ_{in} and θ_{out} correspond to the chiral angles of the inner tube and outer tube, respectively. Coherent stacking implies that the component tubes have uniform chirality, handedness and polarity. **c**, Chiral angle-dependent circular dichroism of second-harmonic generation (SHG-CD) in BNNTs. The experimental data agree well with our physical model. Error bars represent standard deviations from multiple measurements. © 2024, Ma, C. et al.

BEHIND THE PAPER

In general, it is thought that the stacking order is typically random within multiwalled 1D nanotubes, such as carbon nanotubes and transition metal dichalcogenide nanotubes. However, we occasionally observed an exceptionally large nonlinear optical response in as-grown BNNTs that was visible to the naked eye. This suggested that the stacking order must be highly coherent. Detailed structural characterization confirmed our hypothesis. The robust and unique architecture of BNNTs, especially the chiral structure, motivated us to develop BNNTs as functional nonlinear optical crystals. As we had anticipated, the performance is commendable: a single BNNT can provide an application-level chiroptical response. Overall, it was exciting to find this 1D platform for exploring novel physics and applications through interfacial stacking engineering. **K.L.**

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FROM THE EDITOR

"The paper is relevant because it introduces stacking engineering in nanotubes (here, multiwalled BN) for the generation of controlled chiroptical response at the nanoscale. The fact that the response is strong (with a second-harmonic generation efficiency of ~0.01%) could lead to further explorations with immediate implications for miniaturized chiroptoelectronic devices." **Alberto Moscatelli, Chief Editor, *Nature Nanotechnology*.**