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Soft Exfoliation of 2D SnO with size-dependent optical properties

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Two-dimensional material, tin monoxide, liquid phase exfoliation, metal oxides, p-type, quantum confinement.

Abstract

Two-dimensional (2D) materials have recently gained unprecedented attention as potential candidates for next-generation (opto)electronic devices due to their fascinating optical and electrical properties. Tin monoxide, SnO, is an important *p*-type semiconductor with applications across photocatalysis (water splitting) and electronics (transistors). However, despite its potential in several important technological applications, SnO remains underexplored in its 2D form. Here we present a soft exfoliation strategy to produce 2D SnO nanosheets with tunable optical and electrical properties. Our approach involves the initial synthesis of layered SnO microspheres, which are readily exfoliated through a low-power sonication step to form high quality SnO nanosheets. We demonstrate that the properties of 2D SnO are strongly dependent on its dimensions. As verified through optical absorption and photoluminescence studies, a strong size-dependent quantum confinement effect in 2D SnO leads to substantial variation in its optical and electrical properties. This results in a remarkable (>1 eV) band gap widening in atomically thin SnO. Through photoconductivity measurements, we further validate a strong correlation between the quantum-confined properties of 2D SnO and the selective photoresponse of atomically thin sheets in the high energy UV light. Such tunable semiconducting properties of 2D SnO could be exploited for a variety of applications including photocatalysis, photovoltaics and optoelectronics in general.

Introduction

Two-dimensional (2D) materials have recently emerged as a novel class of compounds with unique electrical, optical and mechanical properties.¹ They constitute a paradigm shift in the way we conceive and design nanomaterial-based devices, and they are predicted to revolutionize current electronic device technologies.² Following the pioneering work on both mechanically exfoliated³ and liquid-phase exfoliated graphene,⁴ many 2D materials have been synthesized, including transition metal dichalcogenides (TMDC, such as MoS₂, MoSe₂, WS₂, WSe₂, NbS₂),^{5,6} metal oxides and hydroxides (such as MoO₃, MnO, WO₃, Ni(OH)₂ and many ternary and quaternary compounds),^{7,8} metal nitrides and carbides (such as hexagonal BN and the family of compounds known as MXenes),⁹ elemental compounds (including phosphorene, antimonene and silicene),^{10,11} and cesium lead halide perovskites.¹²

Although these classes of compounds all have their distinctive properties and applications, metal oxides are particularly interesting because they are environmentally stable, relatively easy to fabricate, and typically comprised of non-toxic, naturally occurring elements, which make them even more interesting for potential large scale production. Two-dimensional metal oxides have also been proven successful as active materials in many applications including energy storage,⁷ transistors,¹³ photodetectors,¹⁴ photovoltaics,¹⁵ water splitting,¹⁶ plasmonics¹⁷ and sensing.¹⁸

SnO is an important *p*-type semiconductor, with very interesting optoelectronic properties, including a small indirect band gap of ~0.7 eV, a much larger direct band gap of ~2.7 eV, and high hole mobility.^{19,20} SnO is also a rare example of an oxide semiconductor in which ambipolar conductivity can be obtained, as it simultaneously offer reasonably large electron affinity (3.7 eV – suitable for n-doping) and reasonably small ionization potential (4.4 eV – suitable for p-doping). Due to these properties, SnO has been used to fabricate high

mobility *p*-type^{19,21} and ambipolar²² thin film transistors, efficient photocatalysts for water splitting,²³ anodes for lithium ion batteries,²⁴ and, just recently, improved anodes for sodium ion batteries.²⁵ Moreover, bulk SnO has a tetragonal crystalline structure which is layered along the (00*z*) crystallographic direction. The layered nature of the crystalline lattice makes SnO highly promising as a 2D material.²⁶ However, despite its scientific and technological importance, SnO has hardly been reported in a 2D form. Only a few studies have shown the fabrication of 2D nanosheets of SnO using either time-consuming hydrothermal and intercalation treatments,^{21,25} or using expensive and lengthy vacuum-based methods such as pulsed laser deposition.²³ Liquid phase exfoliation methods are promising thanks to their inherent simplicity, and as such have been employed for the synthesis of many 2D materials, although they usually require lengthy and energy-intensive ultrasonication steps.^{27,28} In this study we present the “soft” liquid-phase exfoliation of layered SnO microspheres to produce 2D SnO nanosheets with tunable optical and electronic properties. By developing a strategy to synthesize highly layered SnO microspheres, we were able to obtain SnO nanosheets in just a few minutes through the simple exfoliation of these microspheres in ethanol using a standard low-power (40 W) bench-top ultrasonic bath. Our method produces highly crystalline, atomically thin and free-standing SnO nanosheets with lateral dimensions typically between 0.5 and 5 μm . We demonstrate that large, thick sheets of 2D SnO show bulk-like optical and electronic properties, whereas small, thin 2D SnO displays optical properties consistent with a highly quantum-confined material. We envisage that the ability to tune the properties of 2D SnO nanosheets according to their thickness will have important technological implications for the fabrication of highly efficient optoelectronic devices.

Results and Discussion

Our approach to synthesize 2D SnO nanosheets uses a “soft” liquid phase exfoliation strategy, which is both reproducible and facile. Firstly, we developed and optimized a robust method for preparing layered SnO microspheres through the thermal decomposition of a tin oxide hydroxide intermediate at moderate temperatures (see Materials and Methods). Briefly, a tin precursor (tin(II) 2-ethylhexanoate) is first reacted with triethylamine at room temperature (see FTIR in Supporting Information, Figure S1). This mixture is then injected into water, causing the instantaneous precipitation of tin oxide hydroxide ($\text{Sn}_6\text{O}_4(\text{OH})_4$) as a white powder. Subsequent heating of this powder in an ambient environment at 180 °C causes its thermal decomposition into SnO in the form of a black powder (Figure 1), as confirmed by thermogravimetric analysis (TGA) and x-ray diffraction (XRD). TGA shows ~4.2% weight loss which corresponds to the full dehydration and decomposition of the initial oxide hydroxide to SnO (Supporting Information, Figure S2). XRD also shows full conversion of $\text{Sn}_6\text{O}_4(\text{OH})_4$ (ICDD No. 84-2157) to SnO (ICDD No. 85-0423) after annealing at 180 °C (Figure 1). All diffraction peaks detected in the annealed sample can be ascribed to tetragonal SnO, and no residual impurities coming from the initial oxide hydroxide phase could be detected. Scanning electron microscopy (SEM) images of the as-synthesized tin oxide hydroxide and of the annealed SnO show a clear change in morphology from featureless powders to porous layered microspheres with diameters in the range of 5-20 μm (Figure 1b-e and Supporting Information, Figure S3). We note that a similar morphology of layered SnO microspheres was recently obtained through a biomimetic approach.²⁹ SEM analysis of our SnO microspheres indeed confirms their lamellar structure, which is conducive to the formation of thin SnO nanosheets upon subsequent exfoliation.

Figure 1. a) XRD patterns of $\text{Sn}_6\text{O}_4(\text{OH})_4$ powders (bottom, green line), layered SnO microspheres (center, blue line) and exfoliated 2D SnO (top, red line). The main diffraction peaks of $\text{Sn}_6\text{O}_4(\text{OH})_4$ and SnO are assigned according to the reference ICDD card No. 84-2157 and No. 85-0423, respectively. The insets show pictures of the prepared materials. b-e) SEM analyses and corresponding EDX maps of the SnO powders showing the distinctive layered microsphere morphology. f) SEM of a single SnO nanosheet obtained after exfoliation. g) XPS characterization of the Sn 3d and O 1s core levels for exfoliated SnO nanosheets.

The as-prepared SnO microspheres are then dispersed in common solvents (including ethanol and N,N-Dimethylformamide, DMF), and through a simple sonication treatment for a short period of time (1-5 minutes) in a standard bench-top ultrasonic bath a yellow colloidal suspension of exfoliated nanosheets is produced (Figure 1a). This facile exfoliation is in stark contrast with other commonly employed liquid-phase exfoliation techniques currently used to synthesize 2D materials, which involve lengthy (several hours) and powerful (hundreds of Watts) ultrasonication treatments.²⁸ The ability of our method to easily exfoliate SnO nanosheets is ascribed to the distinctive lamellar morphology of the synthesized SnO microspheres. XRD analysis of the exfoliated sample deposited on glass substrate shows pure SnO phase, with a preferential orientation along the (00z) direction, as evidenced by the increase in relative intensity of the (001) and (002) diffraction peaks, and the strong reduction in the intensity of the (110) and (220) peaks (Figure 1a and Supporting Information, Figure

S4). This suggests that the exfoliated nanosheets lay flat on the substrate exposing their (00z) surfaces parallel to the substrate. Calculation of the texture coefficient and of the alignment factor (see Supporting Information, Table S1) shows that the extent of orientation is greater than 55% in the exfoliated sample.³⁰ Conversely, the as-synthesized SnO microspheres, although layered, are randomly oriented during XRD measurements, as expected.

To further analyze the morphology of the exfoliated SnO, we carried out SEM analyses of drop-casted samples of the nanosheet suspensions (Figure 1f and Supporting Information, Figure S5). SnO nanosheets can be clearly seen, with lateral dimension predominantly in the 0.5-1 μm range, consistent with the average lateral size of the platelets composing the initial SnO microspheres (Figure 1e). However, both larger (2-5 μm) and smaller (<500 nm) nanosheets are also observed (as also evident later from TEM images). It should be noted that the smaller nanosheets may result from the fracture and/or further exfoliation of the SnO platelets during sonication. The different electron contrast of the nanosheets in the electron microscopy images is indicative of their different thicknesses.

As discussed earlier, XRD analysis of the exfoliated material showed the absence of additional species other than SnO (as for example, metallic Sn or SnO₂). To ensure that no surface oxidation/reduction of SnO occurred during the exfoliation process, the chemical nature of the surface of exfoliated SnO was probed using X-ray photoelectron spectroscopy (XPS, Figure 1g). The core level spectrum of Sn 3d shows the characteristic Sn 3d_{5/2} and Sn 3d_{3/2} splitting components (spin-orbit splitting of 8.5 eV) with sharp peaks observed at binding energies of 486.1 and 494.6 eV, which correspond to Sn²⁺ in pure tetragonal SnO.³¹ Additionally, the O 1s spectrum shows two components with the lower energy feature corresponding to oxygen atoms within the crystalline lattice, while the higher energy

component corresponds to surface oxygen atoms, including hydroxyl groups and adsorbed organics.^{32,33} All these values are in good agreement with literature data for crystalline SnO.^{31,34}

Transmission electron microscopy (TEM) was also used to characterize the morphology and crystallinity of the exfoliated SnO. In agreement with SEM, nanosheets with lateral dimension ranging between hundreds of nanometers and few micrometers are readily observed (Figure 2). In addition, both thick (with high electron contrast) and thin nanosheets (with low electron contrast) can be detected. High resolution TEM images of a single flake (Figure 2d-f) show highly ordered atomic structures, as also evidenced from the extremely regular fast Fourier transform (FFT) and selected area electron diffraction (SAED) patterns. All spots observed in these patterns could be readily assigned to the [001] zone axis of tetragonal SnO, showing predominant distances between lattice planes of 2.71 Å and 1.91 Å, which can be indexed to the (110) and (200) planes respectively. Collectively, these results confirm the highly crystalline nature of the exfoliated SnO, and corroborate the XRD results showing that the nanosheets, which lay flat on the TEM grid, primarily expose the (00z) family of lattice planes.

Figure 2. TEM analyses of exfoliated SnO nanosheets in low resolution (a-c) and high resolution (e-g). Panel (d) shows the “ball and stick” model of the SnO crystalline structure. The insets in (e) show the fast Fourier transform (FFT) of the highlighted yellow circles. The inset in (f) shows the selected area electron diffraction (SAED) pattern. Panel (g) is the enlarged view of the yellow square in panel (e), and the inset shows the peak profile along the dotted blue line.

To gain further insights into the quality of exfoliated SnO, we used Raman spectroscopy (Figure 3). SnO typically has two main Raman peaks, albeit weak, at 113 and 211 cm^{-1} , corresponding to the B_{1g} and A_{1g} vibrational modes, respectively (see also Supporting Information, Figure S6).³⁵ These peaks are readily observed in both the as-synthesized SnO (layered microspheres) and in the exfoliated nanosheets. The absence of any additional peaks that may arise from impurities or decomposition products establishes that the soft exfoliation strategy proposed in this study does not influence the intrinsic material properties of SnO.

However, Raman analysis of a number of individual SnO microspheres and exfoliated flakes revealed a change in the relative intensity of the B_{1g} and A_{1g} peaks between microspheres and nanosheets (Supporting Information, Figure S7). Specifically, the A_{1g}/B_{1g} ratio is greater than 1 in thin nanosheets (typically in the range of 1.5-2.4, even if sometimes the B_{1g} peak is almost suppressed), while it is smaller than 1 in microspheres (typically between 0.6 and 0.9). This distinctive behavior of few-layered SnO with respect to bulk has also been observed recently for vacuum-deposited SnO.²¹ This evidence may indicate that the relative intensities of these two Raman modes could be used to distinguish SnO nanosheets from bulk SnO. However, we note that Raman modes of highly anisotropic structures, and especially 2D materials, have been shown to be sensitive to light polarization and crystal orientation, and therefore the thickness of the nanosheets might not be the only factor affecting the ratio between A_{1g} and B_{1g} peaks.³⁶ In addition, we observed a progressive decomposition of SnO (both microspheres and exfoliated nanosheets) when conducting the Raman measurements with laser powers above 5 mW at 532 nm. This was evidenced by the progressive weakening of the two SnO modes identified earlier and by the concurrent appearance of additional Raman signatures in the 100-180 cm^{-1} range (Supporting Information, Figure S8). This finding highlights the importance of tuning the acquisition parameters to ensure that the pristine material properties are preserved, and to avoid misleading results. A two-dimensional Raman map of a SnO flake shows good match with its optical image (Figure 3b and c), confirming that the Raman signal is indeed arising from the SnO.

Atomic force microscopy (AFM) was also used to characterize the SnO nanosheets. Figure 3d shows an AFM image of a single flake with a lateral size of approximately 0.5 μm and a height of 4.5-5 nm, as confirmed by a line scan (Figure 3e). Considering that the theoretically expected thickness of a SnO monolayer is 0.484 nm, we can deduce that the flake is composed of ~ 10 layers of SnO.²⁶ However, thinner and smaller flakes can also be observed,

with height below 2 nm, which correspond to ~ 4 layers of SnO. These thin flakes could potentially show distinctive properties due to quantum confinement, as already reported for other 2D materials including phosphorene³⁷ and MoS₂.³⁸ Thicker (30-40 nm) SnO platelets are also observed (Figure 3f,g), possibly resulting from incomplete exfoliation of the layered microspheres. To prove that the AFM images are indicative of SnO, and therefore to exclude the presence of contaminants that could affect the surface morphology of the samples, we performed Raman and AFM analyses on the same spot (Figure S9 in the Supporting Information). We detected SnO Raman signals in correspondence of the nanosheets observed in the AFM, confirming that the structures observed in the AFM images are indeed SnO nanosheets.

Figure 3. a) Raman spectra of a single SnO flake. b) Raman map and c) corresponding optical microscope image of a typical SnO flake. d) AFM image of thin SnO nanosheets. e) Height profile scan along the green and blue dashed lines in (d). f) AFM image of a thick SnO nanosheet. g) Height profile scan along the green and blue dashed lines in (f)

In order to further investigate the properties of 2D SnO according to its dimensionality, we separated different populations of nanosheets by applying controlled centrifugation conditions (see the Methods section) as reported previously for other 2D materials.^{39,40} While it is typically difficult to precisely separate 2D materials according to their dimensions (thickness and lateral size) using centrifugation-based methods, these methods do allow a series of samples of progressively reduced dimensions to be isolated when increasing the centrifugation speed. All the samples obtained at different centrifugation speeds were initially analyzed using TEM (Supporting Information, Figure S10). As expected, SnO nanosheets isolated at low centrifugation speeds are typically larger and thicker, as evident from their high electron contrast in the TEM images. However, very thin nanosheets (with low electron contrast) are also observed in these samples. By increasing the centrifugal force, larger and thicker, *i.e.* heavier flakes are progressively eliminated from the solutions until only very thin and small nanosheets remain. These are sometimes very hard to distinguish because they tend to wrinkle and wrap around each other, and their electron contrast is very similar to the underlying carbon coating of the TEM grid, which is an indication of their near-atomic thicknesses. AFM measurements on SnO flakes revealed that in general, the flakes obtained at low centrifugation speeds (1000-2000 rpm) were highly polydisperse, with thickness up to ~40 nm, while those obtained at high speeds (12000 rpm) were predominantly within the 2-5 nm range of thicknesses, which corresponds to 4-10 atomic monolayers (additional AFM images in Supporting Information, Figure S11).

After confirming the reduction in size of SnO with increasing the centrifugal force applied to the sample, we assessed the optical properties of 2D SnO as a function of the centrifugation speeds (Figure 4 and Supporting Information, Figure S12). At low speeds, solutions are yellow in color and slightly scattering, corroborating the presence of large and/or thick flakes within the suspension. By increasing the centrifugation speed, the solutions

become progressively less scattering and less colored. The prominent yellow color of the exfoliated SnO can be ascribed to its bulk direct band gap with an associated energy of ~2.8 eV, as confirmed by the Tauc plots presented in the Supporting Information in Figure S13.

The black color of the as-synthesized powders (SnO microspheres) is due to the low indirect band gap of SnO (~0.7 eV),^{19,20} which is predominant for bulk, micrometer-sized materials, and becomes negligible for dilute nano-sized materials.

By measuring the absorbance of SnO samples both in standard configuration and within an integrating sphere (see Methods), and by analyzing the tin concentration in each individual solution using atomic emission spectroscopy (Table S2), we obtained absorption, extinction, and scattering plots as a function of wavelength. Briefly, the extinction spectra are obtained from standard transmittance (T) data using the well-known Lambert-beer law in the form of $T=10^{-\epsilon Cl}$, where ϵ is the molar extinction coefficient, C is the molar concentration of SnO, and l is the cuvette path length. However, the extinction data encompasses the contribution from both absorption (α) and scattering (σ), according to the relationship $\epsilon(\lambda) = \alpha(\lambda) + \sigma(\lambda)$, where λ denotes the wavelength dependence of these functions.^{40,41} By inserting the SnO samples within an integrating sphere we also measured the pure absorptive component of the samples. The scattering contribution is then evaluated by simply subtracting the absorption from the extinction. As expected, the scattering component decreases with increasing the centrifugation speed, due to the progressive removal of larger sheets from the suspensions. The direct band gap component of SnO is observed at ~2.8 eV in the samples centrifuged up to 6000 rpm, but it cannot be detected when applying higher centrifugation speeds. Interestingly, another sharp absorption edge can be identified at higher energies (~4.1 eV) in all samples, which seems rather independent from centrifugation speed. This distinctive UV absorption, which is

supported by recent density functional theory (DFT) calculations, is ascribed to band gap widening in quantum confined, atomically thin SnO sheets.⁴²

Figure 4. a) Digital photograph of the SnO suspensions centrifuged at different speeds (1000 rpm to 12000 rpm, left to right). b) Absorption, extinction and scattering plots for the sample centrifuged at 2000 rpm. c) Absorption, d) extinction and e) scattering plots as a function of centrifugation speed. f,g) Linear-logarithmic plots of absorption, extinction and scattering coefficient at two fixed wavelengths as a function of centrifugation speed.

The optical absorption characteristics as a function of centrifugation conditions are further validated by photoluminescence (PL) measurements (Figure 5 and Figure S14). All

samples show two main emission peaks, one centered at 313 nm (3.97 eV, peak 1) and another one centered at 407 nm (3.05 eV, peak 2). The first peak can be ascribed to the band edge emission of quantum confined sheets, corresponding to the sharp absorption observed at 4.1 eV, while the second peak, which is much broader, is possibly due to surface defects and trap state emissions that are commonly observed in many semiconducting nanomaterials.^{43,44,45} Similar PL spectra of nanostructured SnO showing two separate contributions – a sharp UV peak and a broad peak in the blue range – have also been observed recently.⁴⁶ Interestingly, at low centrifugation speeds the broad emission peak in the visible region shows an additional low energy contribution centered in the 425-450 nm range (2.75-2.9 eV, peak 3), which is ascribed to the bulk direct band gap discussed earlier. We note that the evaluation of the band gap using both the absorption edge and the PL peak is an approximation of the actual band gap value. Specifically, while the Tauc analysis is fairly accurate for band-to-band transitions in bulk semiconductors, it fails to precisely identify excitonic transitions in highly quantum confined materials, due to size-dependent variation in exciton binding energies and dielectric screening. Conversely, PL spectra are representative of the recombination of the excitons, but they are also affected by other parameters such as non radiative relaxations and trap states. However, when applied to our SnO samples both techniques identify a high energy component (4-4.1 eV), ascribed to highly quantum confined SnO, and a lower energy component (2.75-2.9 eV), which is consistent with literature values for the direct band gap transition in bulk SnO.

Overall, these optical measurements support (i) the presence of highly quantum confined SnO thin sheets in all samples, and (ii) the additional presence of thicker nanosheets and platelets in samples separated at low centrifugation speeds, which are responsible for the lower energy absorption/emission components, and for the scattering contribution.

Figure 5. a) Photoluminescence (PL) spectra of SnO suspensions at different centrifugation speeds. b-h) Deconvolution of PL spectra into three separate contributions fitted with Gaussian functions. Plot of the peak maxima (i) and the relative peak intensities (j) of these three contributions as a function of the centrifugation speed.

Given the observed variations in optical properties according to centrifugation speed, we further explored the energy levels of SnO through the use of photoelectron spectroscopy in air (PESA, Supporting Information, Figure S15). This technique enables to measure the ionization potential of materials, and to evaluate the work function and the energy level associated with the valence band maximum (for metallic and semiconducting samples, respectively).⁴⁷ The layered SnO microspheres have a valence band maximum of 4.4 eV, in line with both theoretical⁴² and experimental²⁰ reported values for SnO. The exfoliated SnO samples show a very similar valence band maximum at 4.4-4.5 eV. Notably, at higher centrifugation speeds the top of the valence band is seen to shift towards deeper values, especially in the samples centrifuged at 8000 rpm or above, although the signal-to-noise ratio in these samples is rather low due to the small amounts of material probed. Optical absorption measurements show that these samples do not contain thick flakes that would have otherwise been responsible for optical absorptions in the visible range, but they all possess a wide band gap associated with quantum confined sheets. In light of this, we can conclude that thick

exfoliated flakes show bulk-like properties (direct band gap energy and valence band maximum similar to micron-sized SnO), while highly quantum confined sheets show a wider band gap and a deeper valence band maximum, which is consistent with recent theoretical predictions for atomically thin SnO nanosheets.⁴² These thin SnO nanosheets are responsible for the distinctive optical and electronic properties observed in the samples separated at high centrifugation speeds.

To assess the potential applicability of 2D SnO as a semiconducting material for optoelectronics, and to further demonstrate the different properties of bulk-like and quantum confined nanosheets, we evaluated the electrical response of the SnO flakes under photo-excitation. Two sets of SnO nanosheets were separated at either 1000 rpm or 12000 rpm and were deposited between two pre-patterned Au electrodes as described in the Methods section. As presented earlier, samples separated at high centrifugation speeds are composed only of quantum confined nanosheets which can absorb only UV light with wavelengths shorter than ~ 300 nm (estimated band gap >4 eV). Conversely, exfoliated SnO nanosheets separated at low centrifugation speeds also show a prominent absorption at ~ 2.8 eV, corresponding to the bulk direct band gap. These nanosheets can absorb light in the blue region, with wavelengths up to ~ 450 nm. Therefore, the photoresponse of the “thick” flakes is expected to be radically different compared to that of the thin, quantum confined nanosheets. Figure 6 shows the absorption spectra of the two families of SnO nanosheets, together with the emission spectra of the UV (peak at 280 nm) and blue (peak at 455 nm) LEDs that we used to probe the optoelectronic responses of SnO devices. Thicker nanosheets separated at 1000 rpm can absorb light emitted by both LEDs, while quantum confined SnO obtained at high centrifugation speeds can only absorb the high energy UV radiation. It was observed that the current through the device comprising the thick flakes increased during exposure to both light sources (Figure 6b), while in the case of the quantum confined nanosheets, the current increased only on exposure to UV

light and no discernible response was seen under blue light excitation (Figure 6d). Moreover, the photocurrent measured when a thick flake is exposed to UV light is higher compared to that measured when the same flake is exposed to blue light ($\sim 60\%$ increase compared to the baseline value under UV, with respect to $\sim 30\%$ increase under blue light). This is in agreement with the lower energy associated with visible light compared to UV light, and the lower absorption cross section of SnO at visible wavelengths (see Figure 6a). These results correlate well with the optical properties presented earlier and highlight the distinctive change in the intrinsic characteristics of 2D SnO when it reaches the quantum confinement regime.

Figure 6. a,c) Absorption spectra for SnO nanosheets obtained after centrifugation at 1000 rpm (a) and 12000 rpm (c). The emission spectra for the UV (280 nm) and blue (455 nm) LEDs used for the photoconductivity measurements are shown as well. b,d) Current output at an applied voltage of 2 V for SnO nanosheets obtained after centrifugation at 1000 rpm (b) and 12000 rpm (d) during exposure to UV and blue LEDs. Three on/off cycles are presented except for the 12000 rpm (thin) nanosheets exposed to blue light, because no photoresponse was detected.

Conclusion

In conclusion, we have presented a new “soft” exfoliation strategy to successfully exfoliate SnO nanosheets composed of <10 atomic monolayers. This strategy relies on producing highly layered SnO microspheres using tin (II) 2-ethyl hexanoate and triethylamine. This morphology enables the fast and easy exfoliation of SnO nanosheets through simple sonication at low powers and in common solvents such as ethanol. Highly crystalline nanosheets with lateral size ranging between hundreds of nanometers and few micrometers, and thickness as low as 2 nanometers are readily achieved. Controlled centrifugation is then applied to separate different populations of nanosheets, which possess size-tunable optical and electronic properties, including widening of the band gap, indicating a strong quantum confinement effect in 2D SnO. Photoconductivity measurements demonstrate a strong correlation between the quantum-confined properties of thin SnO nanosheets and their selective photoelectrical response in the high energy UV light, therefore indicating the potential of few monolayer thick SnO for optoelectronic applications under specific UV light conditions. These results highlight the importance of carefully designing the starting materials that can then be easily exfoliated to produce their 2D counterparts. The strategy proposed here constitutes a step forward to developing reliable and scalable methods for the production of 2D materials, which can then be used for the fabrication of next-generation (opto)electronic devices.

Methods

Materials

Tin (II) 2-ethyl hexanoate (SnHex, 92.5-100%), triethylamine (TEA, >99%) and N,N-dimethylformamide (DMF, anhydrous 99.8%) were supplied by Sigma Aldrich. Ethanol (>99.5%), acetone (>99%), and diethyl ether (>99.5%) were purchased from Chem-Supply.

SnO Synthesis

In a standard reaction, SnHex (5 mL) and TEA (2 mL) are mixed at room temperature and vigorously stirred for 2 minutes triggering a mild exothermic reaction. Separately, a vial containing 9 mL of deionized (Milli-Q) water is preheated in a water bath at 40 °C and the SnHex-TEA mixture is rapidly injected into the water under stirring causing the instantaneous precipitation of tin oxide hydroxide ($\text{Sn}_6\text{O}_4(\text{OH})_4$) in the form of a white powder. After 15 minutes the flask is removed from the water bath, letting the solid phase sediment at the bottom of the vial. The liquid supernatant is then removed, and the flask is placed in a preheated oven at 180 °C for 60 minutes causing the conversion of $\text{Sn}_6\text{O}_4(\text{OH})_4$ to SnO microspheres in the form of a black powder. The resulting powder is then suspended in a mixture of acetone and ethanol and centrifuged at 4000 rpm for 5 minutes to remove the unreacted precursors and excess organics. This procedure is repeated 3 times, and then an additional wash cycle is done with diethyl ether. The obtained SnO powders are dried overnight in vacuum and stored in the dark.

Exfoliation of SnO powders is conducted by suspending 160 mg of the synthesized powders in 40 mL ethanol and by sonicating the suspension in a benchtop ultrasonic bath (Unisonics FXP4M with operating power of 40 W) for 5 minutes. Within a few seconds, the suspension becomes yellow and slightly scattering, confirming the successful exfoliation of SnO. The suspension is then centrifuged at 500 rpm for 5 minutes to remove any unexfoliated powder, and the supernatant is split into seven tubes and centrifuged at different speeds (1000, 2000, 4000, 6000, 8000, 10000 or 12000 rpm for 5 minutes). Of each tube, only the supernatant is kept and the pellet is discarded. The obtained samples are then stored in the dark for future use.

Characterization techniques

Unless specified differently, all characterizations were performed on samples deposited on silicon substrates by simply drop-casting the SnO nanosheet solutions and letting the solvent evaporate naturally. X-ray diffraction (XRD) patterns were collected on samples deposited on

glass substrates using a Bruker D4 Endeavor diffractometer equipped with a Cu-K α radiation source and operated at 40 kV and 35 mA. Thermogravimetric analysis (TGA) of powder samples was conducted on a Perkin Elmer Pyris 1 instrument at a heating rate of 5 °C/min. Scanning electron microscopy (SEM) images were acquired on a FEI Nova 200 NanoSEM operated at 10 kV and 30 pA. Transmission electron microscopy (TEM) images were acquired on a Jeol 1010 microscope operated at 100 kV. High resolution (HR) TEM images were acquired on a Jeol 2100F microscope operated at 80 kV. For TEM analyses, samples were prepared by depositing a drop of the nanosheet solutions on a holey carbon-coated copper grid. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific K-Alpha instrument using an Al K α x-ray source (1486.7 eV). Samples were deposited on Au-coated Si substrates and the core level XPS spectra of the target elements (Sn 3d and O 1s) were obtained and corrected for charging effect. All spectra were corrected using Shirley background correction and resolved using standard Gaussian-Lorentzian functions. Raman spectra were acquired on a Horiba LabRAM HR Evolution Raman spectrometer using a 532 nm laser and power ranging between 0.5 and 50 mW (1-100% of the total laser power) using either pure Si or Si/SiO₂ (300 nm of thermally grown oxide) as substrates. Atomic Force Microscopy (AFM) images were collected using a Bruker Dimension Icon instrument in tapping mode. The chemical composition of the samples centrifuged at different speeds was analyzed with atomic emission spectroscopy (AES) using an Agilent 4200 MP-AES instrument after digesting the solution in concentrated hydrochloric acid. Optical absorption spectra of nanosheet suspensions in the UV-Vis-NIR range were conducted on a Perkin Elmer Lambda 1050 spectrophotometer equipped with an integrating sphere. The extinction spectra of SnO suspensions were acquired in standard configuration, while the absorption component of the extinction was obtained by inserting the cuvettes with the SnO suspensions within the integrating sphere, allowing for the simultaneous collection of both transmitted and scattered

radiation. The scattering component was then obtained by subtracting the absorption from the extinction. Photoluminescence (PL) spectra were obtained on a Perkin Elmer LS50 fluorimeter using an excitation wavelength of 280 nm. Photoelectron spectroscopy in air (PESA) was conducted on a Riken Keiki AC-2 spectrometer using 50 nW radiation on samples deposited on glass substrates. The electrical measurements were conducted on SnO nanosheets drop-casted onto pre-patterned electrodes. The patterns were created on Si substrates covered with 100 nm SiO₂: a photoresist layer was deposited by spin coating and dried at 100 °C, exposed to UV light through a mask using a mask aligner system (MA6, SUSS MicroTech) which defined the patterns, and subsequently developed. The Cr/Au metal electrodes (10/100 nm) were then deposited on the developed patterns using electron beam evaporation. Finally, the lift-off in acetone was carried out to reveal the required metallic contact pads for micro-probes and electrical measurement. The electrical measurements were conducted under ambient air and at room temperature using a Keithley 4200SCS semiconductor parameter analyser. The optical stimulation is provided by using commercial high power light-emitting diodes (LED, Thorlabs, Inc.). The illumination power was calibrated at 2.5 mW/cm² using a commercial UV-enhanced silicon photodetector (Newport Corporation).

Author Contributions

MS and EDG contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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