

博士論文

Discovery and Applications of 2D Materials Trapped at Metastable State during Exfoliation

(酸化チタンナノシート結晶構造緩和およびそれを利用した多孔二
次元材料の開発)

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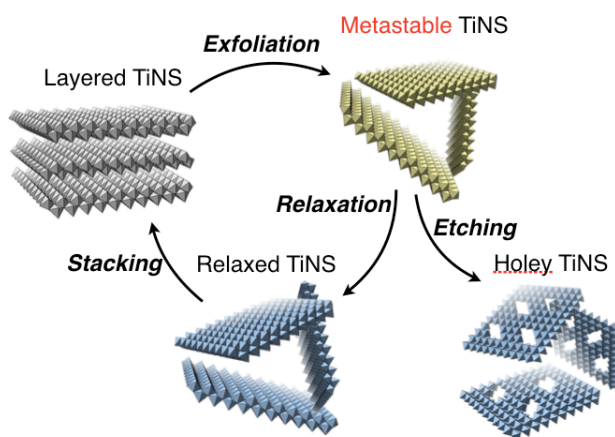
(酸化チタンナノシート結晶構造緩和およびそれを利用した多孔二次元材料の開発)

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Introduction

2D materials, or 2D crystals, are a new class of crystalline substances with a thickness of a few atoms or less that, as a result of their reduced dimensionality, exhibit unique physical and chemical properties that strongly differ from their 3D counterparts.^[1] Currently, most of the investigated 2D materials are derived from the corresponding 3D layered crystals through certain top-down approaches such as mechanical cleavage, liquid exfoliation, ion-intercalation-exfoliation and so on. During exfoliation, the perfect stacking in the out-of-plane direction is completely destroyed, but strong in-plane bonds allow 2D crystals to maintain their ordered structures in the in-plane direction. In this process, numerous new surfaces are created by “slicing” the 3D layered crystals and, in the end, most of the atoms that are originally embedded in the bulk are directly exposed to the environment, which theoretically should be a very unfavorable situation. Accordingly, it is highly possible that surface relaxation takes place during the process of exfoliation, leading to a more thermodynamically favorable structure of 2D nanosheets. This rearrangement is believed to be as fast as other solid surface relaxation phenomena and completed simultaneously in the course of exfoliation operation. Therefore, the exfoliated 2D nanosheets are generally considered to be already at a relatively thermodynamically stable state and their structures are not likely to spontaneously change unless phase transformation is induced by external energy.

In this PhD study, the author happened to notice that, instead of directly going into a thermodynamically stable state, one kind of 2D materials, unilamellar titanate (IV) nanosheets (TiNSs), would be kinetically trapped at metastable state after exfoliation. As schematically illustrated in **Scheme 1**, the metastable TiNSs are structurally unstable and could be easily etched by water, leading to the formation of nano-sized holes on their surfaces. However, if stored in proper condition, these TiNSs gradually but spontaneously relax into a more stable state at room temperature. This relaxation is irreversible and, once relaxed, TiNSs cannot directly return to the metastable state by any other methods unless they are stacked to the original layered conformation again and then subject to re-exfoliation. This observation contradicts the preconception that exfoliated 2D materials will promptly accommodate a thermodynamically stable structure that will not autonomously evolve without external stimuli, and may provide new insights into the structural exploration of 2D materials.



Scheme 1. Schematic illustration of the possible structure evolutions of TiNSs.

Chapter 1. Discovery of metastable 2D materials and related relaxation phenomenon

TiNS investigated in our study has a lepidocrocite-type 2D structure with a composition formula of $\text{Ti}_{0.87}\text{O}_2^{0.52^-}$, and it is a very common and well-studied member of titanium oxide nanosheets family.^[2] TiNSs are obtained through the exfoliation of protonic layered crystallites by quaternary ammonium hydroxide (typically, tetramethylammonium hydroxide, or TMA^+OH^-), and they are usually stored and used in the form of nanosheets dispersion in water. TiNSs are presumed to be structurally stable in water just like other polymorphs of titania for a long time. However, during our study, the author happened to notice that the just-exfoliated TiNSs (denoted as **Fresh TiNSs**) were not as stable as expected: after removing the excessive TMA^+OH^- in the TiNSs dispersion, simple dilution by deionized water could lead to the dissolution of TiNSs, forming many nano-sized holes on their surfaces. Still confused by this result, the author was surprised again when he found that after storing these **Fresh TiNSs** at room temperature for several months, they became much more stable that few hole-formation due to dissolution could be observed when subject to the same diluted condition. In order to differentiate these stable TiNSs from **Fresh TiNSs**, they were named as **Aged TiNSs** and the transformation from **Fresh TiNSs** to **Aged TiNSs** was called aging process.

The author posits, as shown in Fig 1A, that just after exfoliated from parent layered titanates, the **Fresh TiNSs** will be kinetically trapped at a metastable state owing to the coverage of TMA^+ cations on their surface. Although **Fresh TiNS** possesses energetically unfavorable structure and tends to relax, the spatially close presence of positively charged TMA^+ due to strong electrostatic interactions would prevent the transformation of TiNS structure. Nevertheless, this prevention is not perfect since TMA^+ could be detached

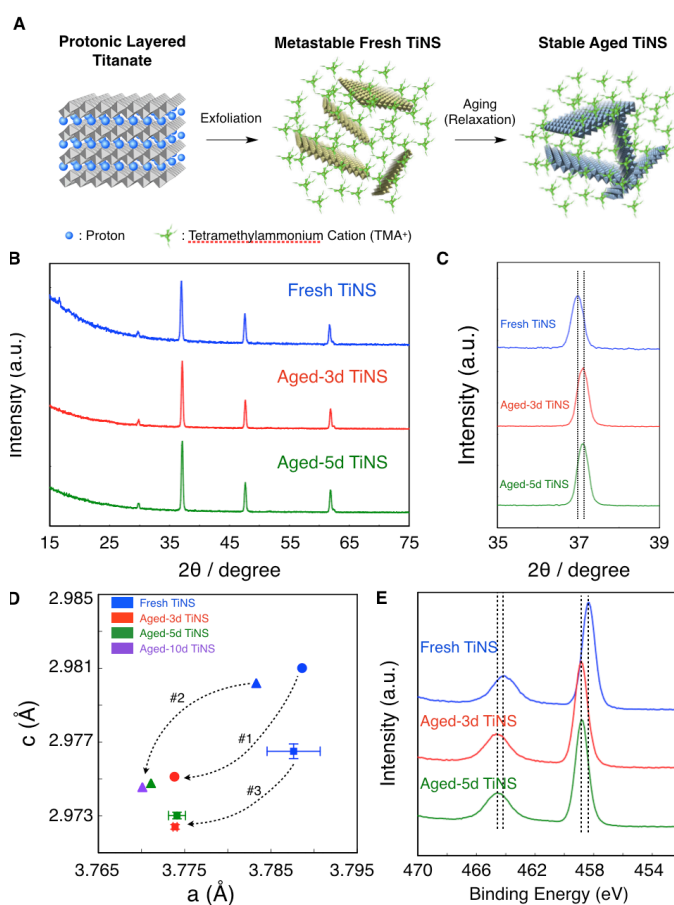


Figure 1. Characterization of structure evolution between metastable TiNS and relaxed TiNS. (A) A schematic representation of kinetic trapping of metastable Fresh TiNS by TMA^+ cations and the subsequent relaxation into more stable Aged TiNS. (B, C) Full In-plane XRD patterns (B) and expanded patterns around 37° (C) of Fresh TiNS, Aged-3d TiNS and Aged-5d TiNS. (D) Summary of calculated lattice parameters along a and c directions. Aging state is indicated by colors and batch difference by shapes of data points. (E) XPS spectra of Fresh TiNS, Aged-3d TiNS and Aged-5d TiNS.

Table 1. Ti 2p Binding Energy and Energy Separation for Fresh TiNS, Aged-3d TiNS and Aged-5d TiNS. ^a

Sample	2p _{3/2} (eV)	2p _{1/2} (eV)	$\Delta 2p$ (eV)
Fresh TiNS	458.33	464.11	5.78
Aged TiNS 3d	458.84	464.66	5.82
Aged TiNS 5d	458.80	464.53	5.73
Anatase ^{ref}	458.72	464.40	5.68

a. Values of anatase are listed for comparison.

from TiNS surface temporarily because of thermal agitation. Therefore, **Fresh TiNS** is able to gradually relax into more stable **Aged TiNS**. This conjecture is in good agreement with the fact that raising temperature could increase aging speed since higher temperature means stronger thermal agitation. Also, in order to prove if TMA^+ is really crucial for trapping metastable state, the author investigated the impact of TMA^+ on the aging speed. The results suggested that aging speed is negatively correlated with TMA^+ concentration, which is in well accordance with the speculation that TMA^+ acts as “preventer” on relaxation.

Next, the author explored the structure of **Fresh TiNS** and **Aged TiNS** in detail to see if there is really any structure difference between them. Since natural aging at room temperature is very slow, TiNSs aged at elevated temperature were used for most of experiments. Typically, **Fresh TiNS** were aged at 80 °C in a oven, and the resultant **Aged-TiNSs** were denoted as **Aged-X TiNS** where X represents the aging time, often in the unit of d. Selected area electron diffraction (SAED) was first used by TEM but no difference was observed between **Fresh TiNS** and **Aged TiNS**, indicating that their structures are basically similar to each other. Then, for better resolution, synchrotron in-plane XRD measurement was applied. Fig. 1B depicts the in-plane XRD patterns for **Fresh TiNS** and **Aged TiNS** that were aged for 3 d and 5 d. All three samples exhibited four sharp diffraction peaks at around 29.7°, 37°, 47.5°, 61.7°, which are assigned to 11, 20, 02 and 22 faces, respectively. At first glance, there appeared to be a negligible difference in the patterns. Nevertheless, a distinct change between **Fresh TiNS** and two **Aged TiNSs** could be observed if the patterns in the position of reflection peaks were expanded. For example, Fig. 1C portrays the expanded patterns in the position of the 20 face appeared around 37°. A clear shift towards higher angles was observed after 3 days aging, but no further change could be noticed afterwards when aging time was extended to 5 days. Based on XRD data, lattice parameters a and c along the in-plane directions were calculated and plotted in Fig. 1D (#3). To enhance reliability, lattice parameters of TiNSs that were prepared and measured at different times were also included. The absolute values of **Fresh TiNSs** were not exactly the same for different groups. This may be attributed to batch difference of TiNS itself or system error during XRD experiments. However, there is an evident gap between **Fresh TiNS** and **Aged TiNSs** in lattice parameters on both axes regardless of the groups. Always, about 0.3–0.4% shrinkage along a axis and 0.1–0.2% shrinkage along c axis could be observed.

The X-ray photoelectron spectroscopy analysis provided another clue to verify this structural change from a different viewpoint. The wide-scan XPS spectra of **Fresh TiNS**, **Aged-3d TiNS** and **Aged-5d TiNS** show the Ti, O, and C and N peaks, of which the C and N are due to the TMA^+ and surface contamination. Some interesting spectral modifications were observed in the Ti 2p region, as shown in Fig. 1E. The peak

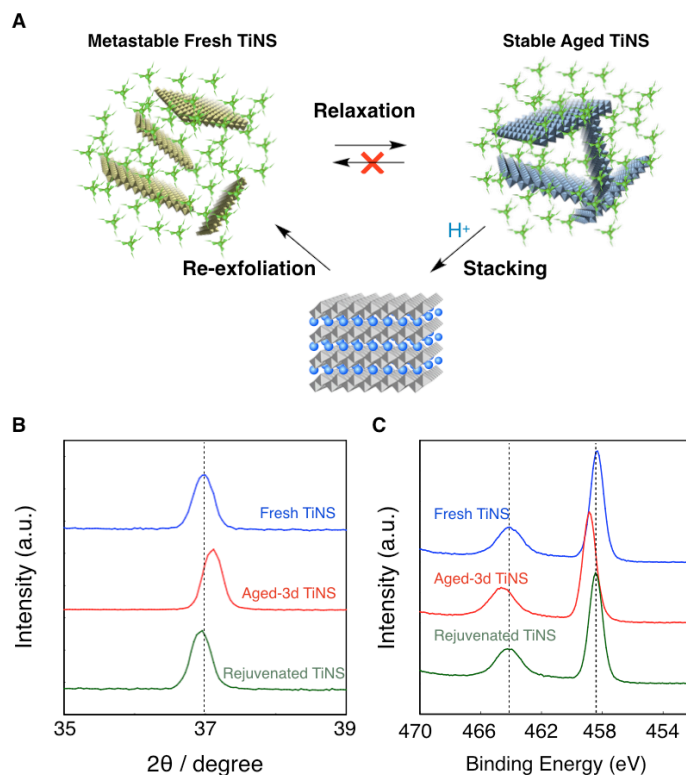


Figure 2. Rejuvenation from relaxed TiNS to metastable TiNS. (A) A schematic representation of the rejuvenation from relaxed Aged TiNS to metastable Fresh TiNS through stacking by protons and re-exfoliation. (B) Expanded in-plane XRD patterns of Fresh TiNS, Aged TiNS and Rejuvenated TiNS. (C) Ti 2p XPS spectra of Fresh TiNS, Aged TiNS and Rejuvenated TiNS.

parameters obtained are listed in Table 1 for comparison. As shown in Fig. 1E, the Ti 2p XPS spectrum of **Fresh TiNS** exhibits symmetrical profiles, indicating clearly a single oxidation state of the Ti atom. There were two Ti 2p components with binding energy 458.33 eV for Ti 2p_{3/2} and 464.11 eV for Ti 2p_{1/2} (Table 1). It is worthy to note that the values of Ti 2p peaks of **Fresh TiNS** are lower than those observed for anatase single crystals, a well-known stable polymorph of titanium (IV) oxide, indicating a less favorable environment for Ti atoms in **Fresh TiNS**. After aging for 3 days, the Ti 2p peaks of the resulting **Aged-3d TiNS** were found to shift to the high binding energy direction: the Ti 2p_{3/2} peak shifted from 458.33 to 458.84 eV and Ti 2p_{1/2} peak increased from 464.11 to 464.66 eV. These values are very close to those for anatase, suggesting similar Ti atoms environment.^[3] Because the possibility of Ti⁵⁺ atoms being present in the TiNS is very small, the binding energy shift to the high binding energy side may indicate that the interaction between the Ti atoms and the coordinated oxygens changes from weak for **Fresh TiNS** to strong for **Aged-3d TiNS**. No significant change of Ti 2p peaks could be observed between **Aged-3d TiNS** and **Aged-5d TiNS**, implying the change of structure was completed within 3 days.

In fact, as a result of environment change, 2D materials are believed to possess slightly different structures before and after exfoliation. Due to the mitigation of electrostatic repulsion between titanium ions in the negatively charged nanosheet and its counteraction, TiNS is expected to exhibit certain expansion in sheet thickness direction upon exfoliation.^[4] Unfortunately, in-plane XRD cannot give any information for the structural change in out-of-plane direction. The author strongly surmises that the current observation of lattice shrinkage in in-plane directions are simply a concurrent arrangement of a much more prominent expansion in out-of-plane direction. In order to get information in the thickness direction, X-ray absorption fine structure (XAFS) analysis is under way to detect a full image of chemical state and local atomic structure of TiNS. However with all these being said, both in-plane XRD and XPS results manifested enough evidence that structure transformation undoubtedly takes place during aging process. Concerning the facts that aging spontaneously proceeds and more stable TiNS is obtained, it is concluded that the present hypotheses about the existence of metastable **Fresh TiNS** and its subsequent relaxation to more stable **Aged TiNS** are sufficiently plausible.

Another convincing verification of our hypothesis came from the rejuvenation experiments. Since it is impossible for relaxed **Aged TiNS** to spontaneously go back to the metastable state, aging is definitely an irreversible process. The rejuvenation from relaxed state to metastable seems unlikely as long as TiNS stays in isolated condition. Hence, the author wondered what would happen if these isolated TiNS were restacked with each other again. Therefore, the author intentionally restacked the **Aged TiNSs** by adding an excessive amount of HCl, and re-exfoliated the aggregates by TMA⁺OH⁻ again. The restacked and then re-exfoliated TiNS is called **Rejuvenated TiNS**. In-plane XRD (Fig. 2B) and XPS (Fig. 2C) results revealed that **Rejuvenated TiNS** possessed a very similar structure as **Fresh TiNS**. Also, **Rejuvenated TiNS** showed the same kind of structural instability as Fresh TiNS: after removing the excessive TMA⁺, dissolution of **Rejuvenated TiNS** easily occurred in water. All these evidences indicated that, through stacking and re-exfoliation, the structure of stable relaxed TiNS was successfully transformed back to a metastable state. The success of rejuvenation has both very important scientific and practical meanings. In practical, it could be considered as a tool to prepare **Fresh TiNS**. More importantly, the fact that reversible switch between metastable and stable structures could be accomplished through stacking and exfoliation clearly show that the trapping of metastable TiNS takes place during exfoliation, right between two stable state (stable stacked state and stable isolated state).

Chapter 2. Scalable and controllable fabrication of 2D holey materials

Fabrication of 2D holey materials has been an appealing endeavor in materials science over the past few years motivated by the exceptional holey structure in combination with the intrinsic properties of 2D morphologies.^[5] Many synthetic strategies have been made to fabricate 2D holey nanomaterials such as local oxidation, defects degradation by utilizing electron beam, photo, and oxygen plasma-etching approaches. However, the co-realization of scalability and controllability remains difficult. To date, it is still a large scientific and technological challenge for creating tunable holes in 2D nanostructures through scalable and controllable methods. However, taking advantage of the metastable nature of **Fresh TiNS** and its relaxation into **Aged TiNS**, scalable and controllable fabrication of **Holey TiNSs** could be accomplished.

As mentioned earlier, **Fresh TiNSs** are structurally unstable. They could be easily etched by water if TMA^+ cations in the TiNS dispersion are extensively removed, leading to the formation of **Holey TiNSs** (Fig. 3A). Once TMA^+ cations are removed from TiNS surface, protons ionized from water will compensate for the missing TMA^+ , leading to the proton-promoted dissolution of TiNS. The removal of TMA^+ could be realized by repeated wash (centrifugation and redispersion with pure water), extensive dilution or mixing with ion-exchange resins. The pore-forming process was relatively slow, but could be accelerated upon UV irradiation, perhaps because UV can assist the removal of TMA^+ . **Holey TiNS** was proved to maintain a similar structure as **Fresh TiNS** by SAED as well as diffraction mapping, and the holes exhibited quasi-square shape with longer axis aligning to a axis of TiNS lattice. So far, dissolution of crystalline titania polymorphs in pure water at room temperature has yet to be reported. It was deduce that the unique dissolution phenomenon here is owing to the single-layer structure of TiNS and, most importantly, to the metastable structure of **Fresh TiNSs**. Also, it shall be highlighted here that the whole hole-forming procedure is very simple and environmentally friendly. Thus, the author considers it as a promising method to scalably fabricate 2D holey materials.

The hole-forming process of **Holey TiNSs** is not only scalable, but also exhibits independent controllability over pore size and density. As a typical example of the hole-forming reaction, washed **Fresh TiNS** dispersion was diluted from 0.4 wt% to 0.004 wt% by pure water and incubated in the presence of UV irradiation. As observed by TEM a large amount of nano-size holes could be visualized on TiNS after only 1h reaction and the average size of holes continuously increased with increasing reaction time before reaching maximum at 24 h (Fig. 3D). This trend can be more obviously observed in Fig. 3C, in which the average value and polydispersity index (PDI) of hole diameters with respect to the reaction time are

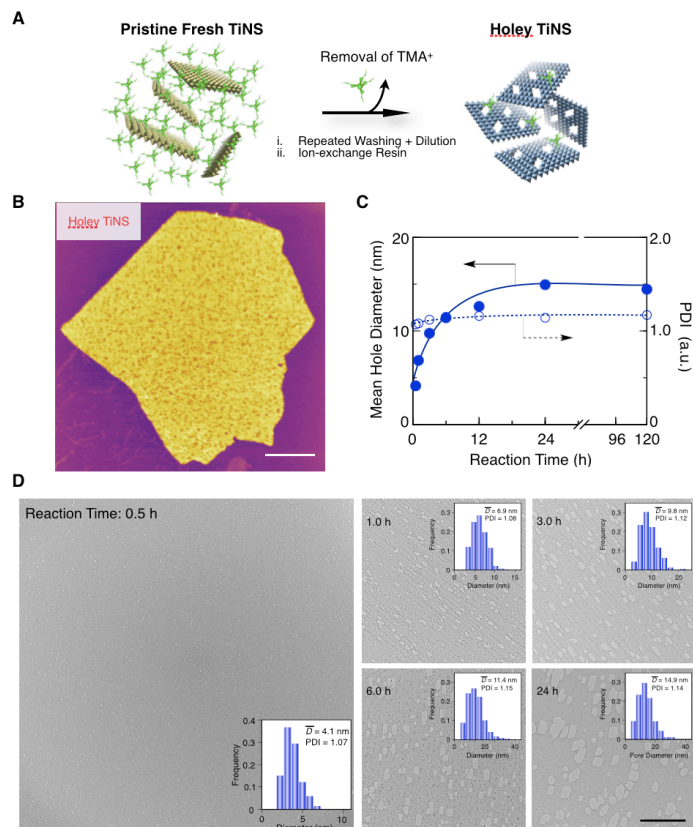


Figure 3. Fabrication and hole size control of 2D holey materials. (A) A schematic representation of fabrication of Holey TiNS from metastable Fresh TiNS simply by removal of TMA^+ cations. (B) A typical AFM image of Holey TiNS. Scale bar is 1 μm . (C) Variations of mean diameters and PDI of holes on increasing reaction time. (D) Typical TEM images and size distribution of hole sizes for Holey TiNS obtained by 0.5, 1, 3, 6 and 24 h reaction time. Scale bar is 100 nm.

summarized. Therefore, it is possible to control the hole size by just controlling the reaction time. Usually, 2D nanosheets with very small holes (say, less than 5 nm) are more attractive because they could be utilized for separation of various molecules or ions.^[6] The author noticed that in our system, just by reducing the reaction time, it is easy to obtain such kind of **Holey TiNSs**. As shown in Fig. 3D (left), 30 min reaction would lead to the formation of numerous small holes, which distribute uniformly throughout the surface of TiNS. These holes possess a small average diameter of 4.08 nm and a narrow PDI of 1.07. This kind of narrow size distribution is rarely seen for solution-state methods and for sure beneficial.

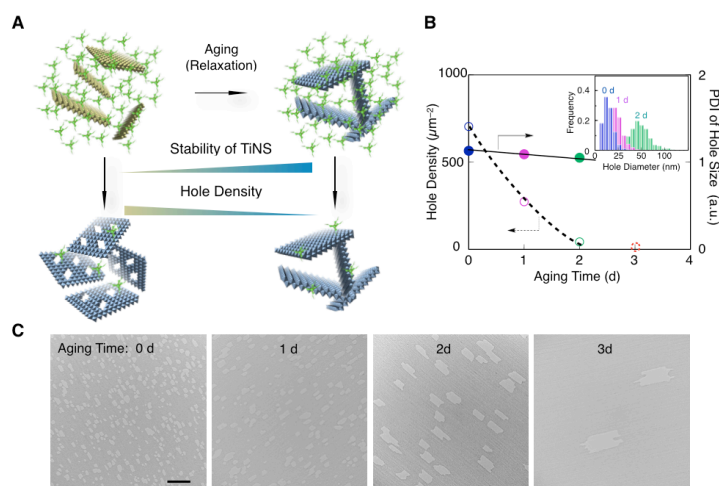


Figure 4. Hole density control of 2D holey materials. (A) A schematic representation of controlling hole density by taking advantage of increasing stability during aging. (B) Variations of hole density and PDI of hole sizes on increasing aging time. (C) Typical TEM images hole sizes for Holey TiNS obtained by 0, 1, 2 and 3 d aging time. Scale bar is 100 nm.

Compared with size control, accurate hole density (the number of holes in a defined unit area) control appears to be a more challenging task for scalable synthesis of 2D holey materials. Conventional chemical etching approaches often try to control the pore number by tuning the reaction time and the amount of etchants. This kind of control is rather rough and hole density is always related to hole size. So far, independent control of hole density is rarely demonstrated. However, it was found that the hole density of **Holey TiNS** could be readily tuned by utilizing TiNSs at different aging state. This hole density control is very simple but effective, and shows a totally different hole density–hole size relationship compared to previous examples. As illustrated in Fig. 4A, TiNSs will become more and more stable during aging process, resulting in the gradual decline of their reactivity with water, which in turn lead to the decrease of pore density when subject to hole-formation conditions. As a representative example for density control, four sets of typical 0.4 wt% **Fresh TiNS** dispersions were prepared and then incubated at 80 °C for 0 d, 1 d, 2 d, and 3 d, respectively. These TiNS dispersions were then deionized and subject to dissolution reaction for 24 h to make **Holey TiNSs**. The obtained **Holey TiNSs** possessed different hole density depending on the aging time. As shown in the typical TEM images of **Holey TiNSs** in Fig. 4C, in which each image covers a same area of 736.69 nm × 736.69 nm, it can be easily observed that hole density dramatically decreases with the gradual increase of aging time. Statistical analysis revealed that **Fresh TiNS** (or **Aged-0d TiNS**) exhibited the highest average hole density of about 704 μm⁻², while **Aged-2d TiNS** possesses a very low average pore density of 43 μm⁻². Furthermore, holes are scarcely found on **Aged-3d TiNS**, indicating these TiNSs were completely aged. All these results clearly demonstrate that hole density could be effectively controlled in a wide range simply by tuning the aging time of TiNS.

Chapter 3. Photo-Switchable Magneto Orientation of Aged TiNS

The discovery of metastable TiNS would bring seminal effects on a wide range of studies in 2D materials science, urging us to change our preconception on the structural flexibility of 2D material. It can be predicted that, apart from stability, some other properties may also depend on the aging state of TiNS. Indeed, our preliminary studies revealed that not only the dissolvability to water but also various other properties, such as surface potential and photocatalytic activity, are significantly different between **Fresh TiNS** and **Aged TiNS**. Also, it is found that **Aged TiNS**, a kind of diamagnetic metal oxide nanosheets, could be transformed into paramagnetic material when the Ti^{4+} ions were reduced into Ti^{3+} state under UV irradiation in the absence of molecular oxygen. The change of magnetic property gave rise to the switch of magnetic alignment modes (Fig. 5): from the orthogonal alignment to the magnetic flux when it was diamagnetic to the parallel alignment when it became paramagnetic. This switch was totally reversible since Ti^{3+} ions can be oxidized back to Ti^{4+} upon exposure to oxygen in air. In addition, these photo-reduced nanosheets have potential to

be used as radical and electron transfer agents due to the unique feature of Ti^{3+} ions. This observation exhibits the possibility of combining two different kinds of external stimuli with respective advantages, which may significantly enlarge the fields of stimuli-responsive systems.

Summary

The author discovered that TiNS would be kinetically trapped at metastable state after exfoliation. The metastable TiNSs are structurally unstable and could be easily etched by water. This feature could be used to the scalable and controllable fabrication of 2D holey materials. However, if stored in proper condition, these TiNSs will spontaneously relax into a more stable state at room temperature. Metastable and relaxed TiNS exhibit very different properties although the structural difference is very small. The present observation contradicts the preconception that exfoliated 2D materials will promptly accommodate a thermodynamically stable structure that will not autonomously evolve without external stimuli, and may provide new insights into the structural exploration of 2D materials.

References

- [1] *Chem. Soc. Rev.*, **2017**, 46, 4387. [2] *Chem. Mater.*, **1998**, 10, 4123. [3] *J. Appl. Phys.*, **1994**, 75, 2945. [4] *J. Phys. Chem. B*, **2004**, 108, 13088. [5] *Nanoscale*, **2014**, 6, 1922. [6] *Nature*, **2016**, 536, 197

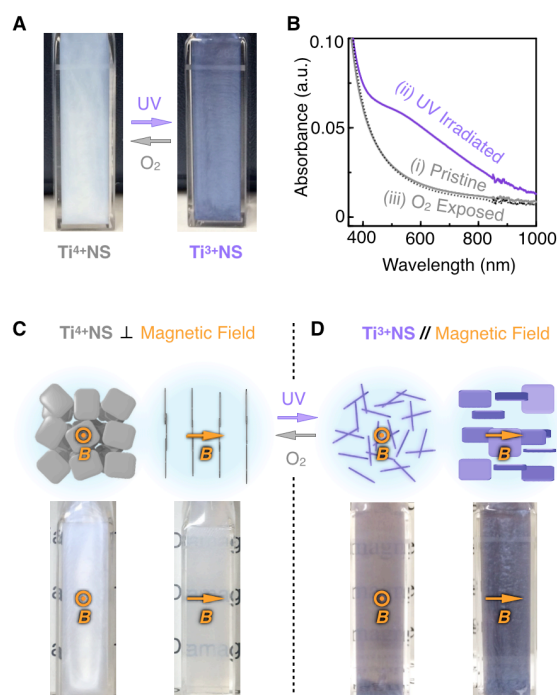


Figure 5. (A) Pictures of the pristine (left) and UV-irradiated (right) dispersions containing 0.4 wt% nanosheet. (B) UV/Vis absorption spectra of (i) pristine, (ii) UV-irradiated, and (iii) O₂-exposed dispersions. (C, D) Aqueous dispersions of Ti⁴⁺NS (A) and Ti³⁺NS (B) held in 10 mm × 10 mm cuvettes. The cuvettes were placed in a 9-T magnetic field at 25 °C, and the pictures were taken from the direction parallel (left) and orthogonal (right) to the applied magnetic field.