

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

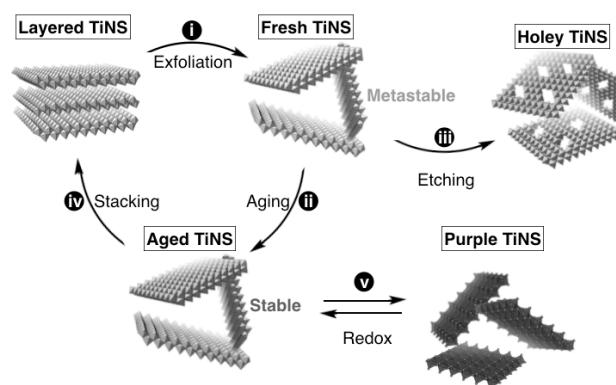
(酸化チタンナノシート結晶構造緩和およびそれを利用した多孔二次元材料の開発)

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## 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.<sup>[1]</sup> 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.



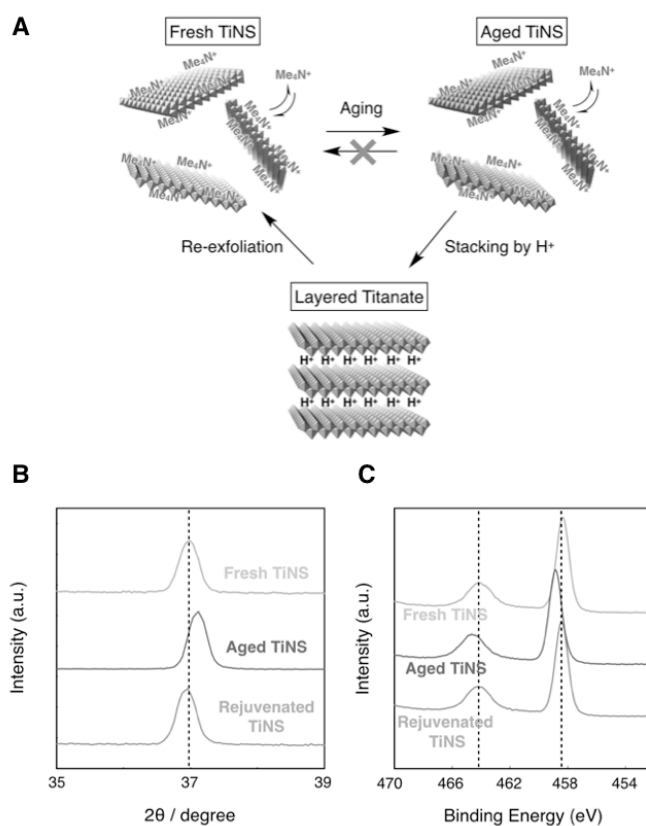
**Scheme 1.** Schematic illustration of the possible structure evolutions of TiNSs.

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

TiNSs investigated in our study are obtained through the exfoliation of protonic layered crystallites by quaternary ammonium hydroxide (typically, tetramethylammonium hydroxide, or TMA<sup>+</sup>OH<sup>-</sup>). 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  $\text{TMA}^+\text{OH}^-$  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  $\text{TMA}^+$  cations on their surface. Although **Fresh TiNS** possesses energetically unfavorable structure and tends to relax, the spatially close presence of positively charged  $\text{TMA}^+$  due to strong electrostatic interactions would prevent the transformation of TiNS structure. Nevertheless, this prevention is not perfect since  $\text{TMA}^+$  could be detached 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  $\text{TMA}^+$  is really crucial for trapping metastable state, the author investigated the impact of  $\text{TMA}^+$  on the aging speed. The results suggested that aging speed is negatively correlated with  $\text{TMA}^+$  concentration, which is in well accordance with the speculation that  $\text{TMA}^+$  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 an oven. Fig. 1B depicts the in-plane XRD patterns for **Fresh TiNS** and **Aged TiNS** that were aged for 3 days. A distinct change between **Fresh TiNS** and two **Aged TiNSs** could be observed if the patterns in the position of reflection peaks were expanded. To enhance reliability, prepared and measured at different times were characterized. 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. As shown in Fig. 1C, 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<sub>3/2</sub> and 464.11 eV for Ti 2p<sub>1/2</sub>. After aging for 3 days, the Ti 2p peaks of the resulting **Aged TiNS** were found to shift to the high binding energy direction: the Ti 2p<sub>3/2</sub> peak shifted from 458.33 to 458.84 eV and Ti 2p<sub>1/2</sub> peak increased from 464.11 to 464.66 eV. 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 TiNS**.



**Figure 1.** Characterization of structure evolution between metastable TiNS and relaxed TiNS. (A) A schematic representation of aging phenomenon and rejuvenation process. (B) Expanded patterns around 37° of Fresh TiNS, Aged TiNS and Rejuvenated TiNS. (C) XPS spectra of Fresh TiNS, Aged TiNS and Rejuvenated TiNS.

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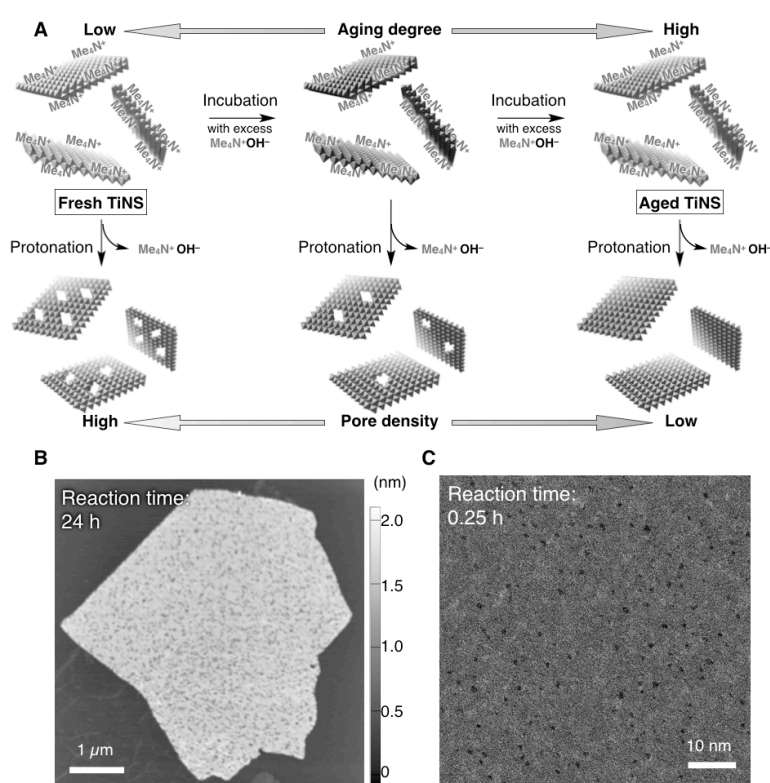
Another convincing verification of our hypothesis came from the rejuvenation experiments. The author intentionally restacked the **Aged TiNSs** by adding an excessive amount of HCl, and re-exfoliated the aggregates by  $\text{TMA}^+\text{OH}^-$  again. The restacked and then re-exfoliated TiNS is called **Rejuvenated TiNS**. In-plane XRD (Fig. 1B) and XPS (Fig. 1C) 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  $\text{TMA}^+$ , 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.

## 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. 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  $\text{TMA}^+$  cations in the TiNS dispersion are extensively removed, leading to the formation of **Holey TiNSs** (Fig. 2A). Once  $\text{TMA}^+$  cations are removed from TiNS surface, protons ionized from water will compensate for the missing  $\text{TMA}^+$ , leading to the proton-promoted dissolution of TiNS. The removal of  $\text{TMA}^+$  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  $\text{TMA}^+$ . **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. 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. 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. 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. 2C, 15 min



**Figure 2.** Fabrication of Holey TiNS. (A) A schematic representation of fabrication of Holey TiNS from metastable Fresh TiNS simply by removal of  $\text{TMA}^+$  cations. (B) A typical AFM image of Holey TiNS. (C) HAADF-STEM image of Holey TiNS with subnanometer holes.

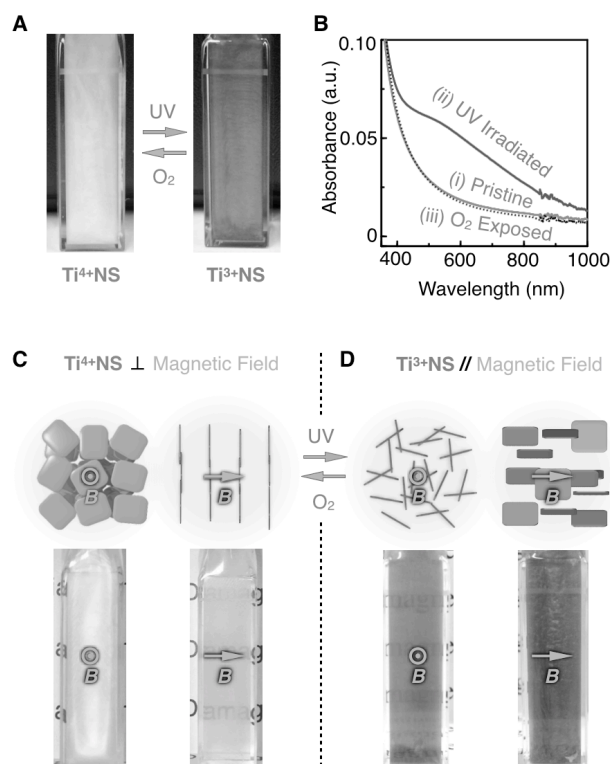
reaction would lead to the formation of numerous subnanometer holes. So far, independent control of hole density is rarely demonstrated. However, it was found that the hole density of **Holey TiNS** could be readily tuned by utilizing TiNSs at different aging state. As illustrated in Fig. 2A, TiNSs will 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. 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. 3): 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.



**Figure 3.** (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) O<sub>2</sub>-exposed dispersions. (C, D) Aqueous dispersions of Ti<sup>4+</sup>NS (A) and Ti<sup>3+</sup>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.