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## Unstable Single-Layered Colloidal TiS<sub>2</sub> Nanodisks\*\*

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Layer-structured materials are an important class of solid materials,<sup>[1]</sup> and are especially useful as electrode materials.<sup>[2]</sup> Usually, multilayered materials are formed by the weak interaction between the layers, which serves to stabilize the structure.<sup>[3]</sup> The intercalation or doping into the interlamellar space of these materials enables materials scientists to tailor their physical properties.<sup>[4]</sup>

It has been suggested that the number of layers is closely related to the physical properties,<sup>[5]</sup> thus allowing the electrical properties to be tuned by adjusting the number of layers. With the help of the accumulated synthetic knowledge, there has been special interest in monolayered materials.<sup>[6]</sup> Although the preparation of single-layered materials including graphene<sup>[6a]</sup> is quite challenging, many studies have been conducted in an attempt to find an efficient synthetic route. There are two main ways to prepare single-layered materials; layer separation from multilayered materials or the direct synthesis of monolayered materials. In the former case, the relatively weak interaction between the layers that stabilizes the structure must be overcome. Thus, the physical separation of the layers or, more recently, the chemical functionalization of the layers, has been actively explored.<sup>[7]</sup> In the latter case, although it is not common, there are rare reports on the direct synthesis of a monolayered structure under specialized conditions.<sup>[8]</sup>

Titanium disulfide (Figure 1) is known to form the layered structural motif<sup>[9]</sup> (Figure 2b), in which each layer is stacked via relatively weak van der Waals interactions with its

neighboring layers. In each layer, the titanium atoms are located in the same planes, while the sulfur atoms are located on top of and below the titanium planes. Thus, the side view of one layer consists of three planes composed of S, Ti, and S, respectively. The titanium atoms co-ordinate with the six neighboring sulfur atoms to form an octahedral geometry and the sulfur atoms are connected to the three neighboring titanium atoms, as shown in Figure 2b.

Multilayered (80–100 layers) fullerene-like titanium sulfide materials have been prepared using titanium chloride and H<sub>2</sub>S gas by the vapor-deposition method at 650–800 °C.<sup>[10]</sup> Also, multilayered (around 10 layers) titanium sulfide nanotubes have been prepared at relatively low temperature (450 °C).<sup>[11]</sup> The lithium- or magnesium-doped titanium sulfide showed promising electrical properties for the development of new electrode materials.<sup>[12]</sup> Titanium sulfide nanotubes have been employed as hydrogen-storage materials.<sup>[13]</sup>

It has been suggested that the physical properties of titanium sulfide are dependent on the number of layers.<sup>[14]</sup> The orbital overlap of the atoms on the surface of each layer can have a significant influence on the resultant bandgap structure and this effect will be more significant as the number of layers decreases. Thus, it was theoretically anticipated that single-layered titanium sulfide would have semiconducting properties, while the bulk material would be semimetallic.<sup>[15]</sup> Recent attempts have been made to prepare single-layered titanium sulfide in order to study its physical and electrical properties.<sup>[16]</sup> However, except for one paper<sup>[16]</sup> on this subject, as far as we are aware, there have been no reports on the monolayered structure of these materials. In this Communication, we report the preparation of monolayered colloidal titanium sulfide nanodisks and discuss their instability and dynamic structural changes at room temperature.

For the preparation of the single-layered nanodisks, titanium chloride was dissolved in well-dried oleylamine under argon at room temperature. In this step, when the titanium chloride was injected into the oleylamine, orange-colored precipitates were formed immediately. After the precipitates were treated with sonication for an hour at room temperature, the solution turned an orange color. It should be noted that to be free from contamination by titanium oxide, water should be strictly excluded in the preparation of the precursor solution. Sulfur was dissolved in oleylamine at 110 °C under argon and this solution was cooled to room temperature. The titanium precursor solution was injected into the sulfur solution at room temperature, whereupon the color of the solution turned blue-black. The temperature of the reaction mixture was increased rapidly from room temperature to 110 °C and then increased slowly to 215 °C at a rate of 4 °C min<sup>-1</sup>. The reaction mixture was stirred overnight (12 h) at this temperature. After cooling to room temperature, the reaction mixture was poured into excess methanol and centrifuged to retrieve the nanomaterials. The precipitates were black in color. The materials were redispersed in methylene chloride solution for analysis.

As shown in Figure 1, transmission electron microscopy (TEM) analysis showed the assembly of very thin plates. The thickness of each disk was 0.6 nm, which corresponds to the

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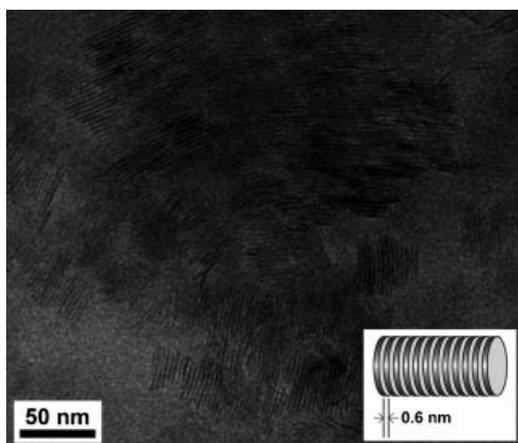
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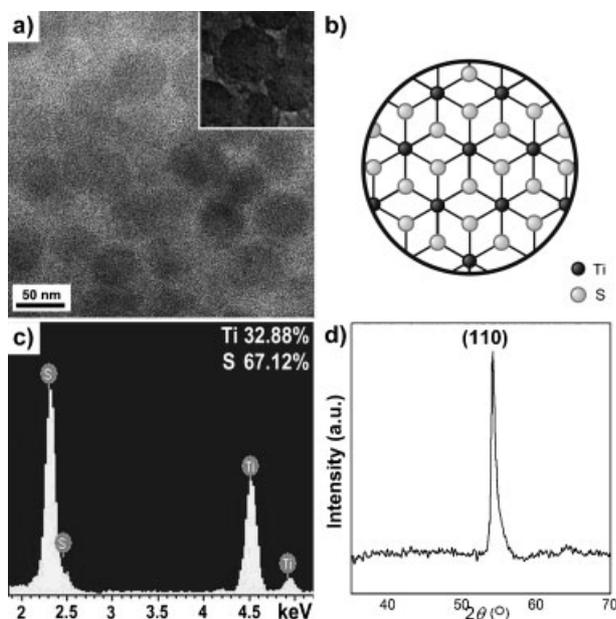
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**Figure 1.** TEM image of single-layered titanium sulfide nanodisks with an average width of 34 nm.

distance of S–Ti–S in a single layer (0.57 nm, JCPDS#15-0853). The average distance between the plates was  $1.9 \pm 0.3$  nm (based on the counting of 38 selected distances), evidence that the plates are separated by organic surfactants.<sup>[17]</sup> Most of the TEM images show both the side view and top view of the disks (see the Supporting Information for typical examples).

A typical top view of the plates is shown in Figure 2a, which reveals that the plates have circular-shaped disks. The low-contrast image in Figure 2a results from the very small thickness of the materials.<sup>[18]</sup> To confirm their shape, we removed the organic materials remaining in our sample using a plasma cleaner installed in the TEM (Figure S2). With the help of this technique, we were able to confirm the shape of the low-contrast materials. It is believed that the formation of circular single-layered structures is attributed to the stabilization of surface via interaction with organic surfactants.



**Figure 2.** a) TEM image showing top view of 50-nm nanodisks, b) structural diagram, c) EDS spectrum, and d) PXRD pattern.

As shown in Figure 2c, energy-dispersive spectroscopy (EDS) in conjunction with scanning electron microscopy (SEM) showed that the stoichiometric ratio of Ti to S was very close to 1:2. Powder X-ray diffraction (PXRD) patterns showed a single peak at  $53.8^\circ$ , which was assigned as the (110) crystal plane of the disks (JCPDS#15-0853; Figure 2d). Because these nanomaterials are very thin, it was speculated that the peaks related to the thickness direction could not be detected in the XRPD pattern.

The sizes of the nanodisks could be controlled by adjusting the experimental conditions, such as reaction time, concentration of precursors, and the rate of increase of temperature, and the results are summarized in Table 1.

As the reaction time became longer, the sizes of the nanodisks became bigger (entries 1–4 in Table 1). When the concentration of sulfur was increased from 2 to 4 equivalents the resultant size of the nanodisks decreased from 50 to 34 nm (entries 3 and 5 in Table 1). When the rate of increase of the reaction temperature was changed from  $4^\circ\text{C min}^{-1}$  to  $8^\circ\text{C min}^{-1}$ , the resultant size of the nanodisks decreased slightly (entries 3 and 6 in Table 1). According to this observation, it can be reasoned that a higher concentration or rapid increase in temperature is helpful in generating more nuclei, resulting in the reduction of the size of the disks. We selected three samples (entries 1, 3, and 5 in Table 1) to study the properties of these materials. Figure 3 shows the typical TEM images and the size distribution diagram of these three samples (Figures S6–8 for the TEM images of the wider region).

During the investigation of the possible size-dependent physical properties of these three disks, including the bandgap measurement using X-ray radiation, we discovered that the nanodisks are not a stable system but rather show dynamic structural changes. When the synthesized nanodisks were stored in a refrigerator under nitrogen, there was no significant change in the appearance of the samples. However, under exposure to air, the color of the materials (originally black) changed slightly from black to brown at room temperature. The rate of this color change was size dependent. In the case of the 18-nm disks, a significant color change was observed within one day. In the case of the 50-nm disks, it took around a month to obtain a similar brown-colored powder. We were curious about the origin of this color change in our samples.

It is well known that the surface layer of titanium sulfide is quite different from that of the bulk. In the bulk, the van der

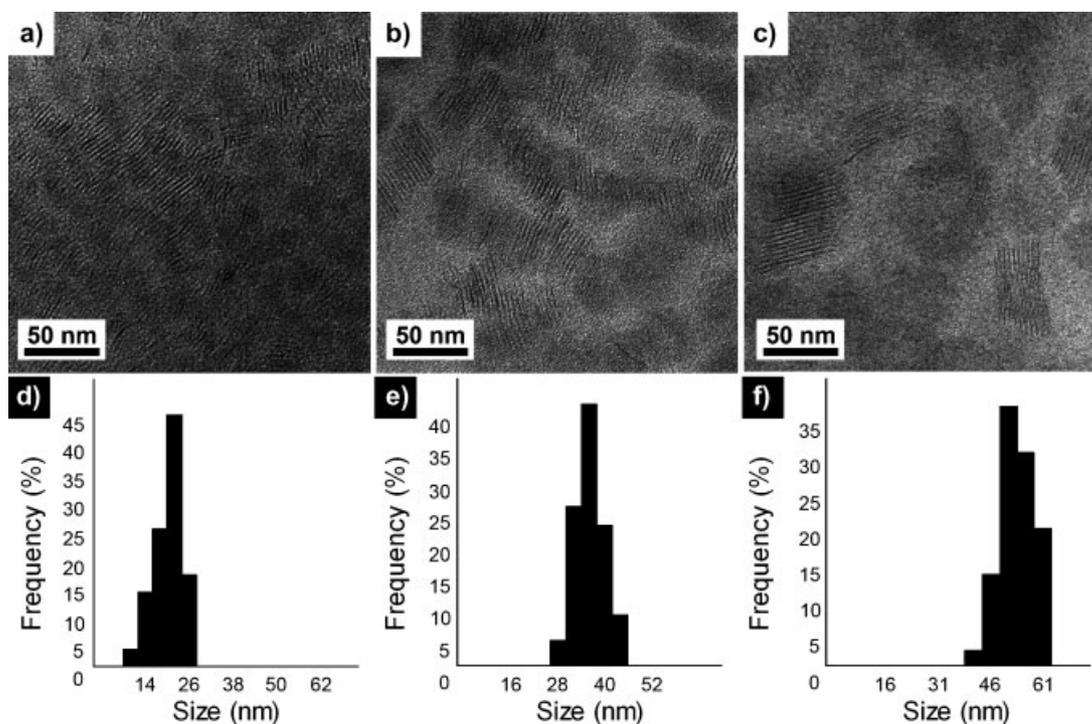
**Table 1.** Synthesis of titanium sulfide nanodisks.<sup>[a]</sup>

Entry	TiCl <sub>4</sub> [mL]	Sulfur [eq.]	Increase rate <sup>[b]</sup> [ $^\circ\text{C min}^{-1}$ ]	Time <sup>[c]</sup> [h]	Size [nm]
1	0.1	2	4	1	$18 \pm 5$
2	0.1	2	4	6	$37 \pm 8$
3	0.1	2	4	12	$50 \pm 7$
4	0.1	2	4	24	$57 \pm 9$
5	0.1	4	4	12	$34 \pm 4$
6	0.1	2	8	12	$41 \pm 5$

[a] 9 mL oleylamine was used as a solvent.

[b] The reaction temperature was increased from  $110^\circ\text{C}$  to  $215^\circ\text{C}$ .

[c] Aging time at  $215^\circ\text{C}$ .



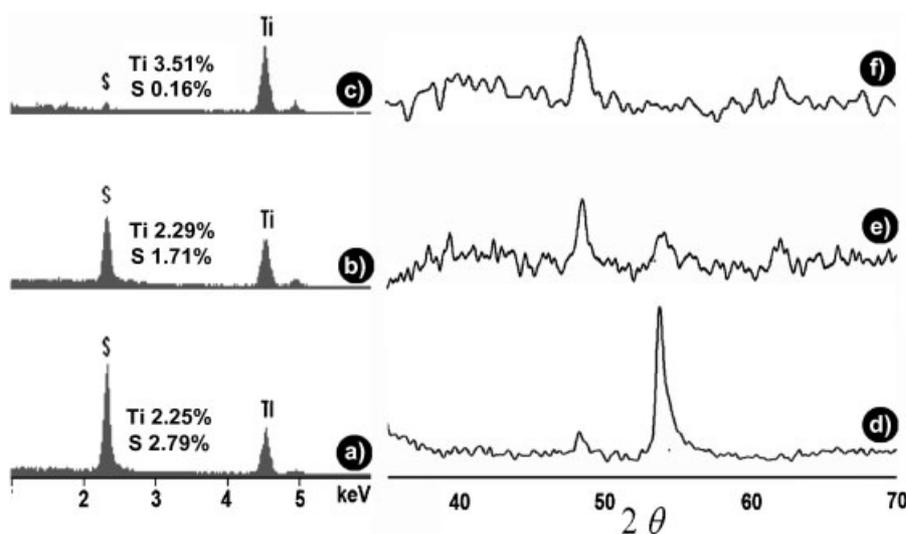
**Figure 3.** TEM images and size-distribution diagrams for the a,d) 18-nm nanodisks (entry 1 in Table 1), b,e) 34-nm nanodisks (entry 5 in Table 1), and c,f) 50-nm nanodisks (entry 3 in Table 1).

Waals interaction between the layers stabilizes the [001] surface. Also, it has been documented that the Madelung energy of the titanium atoms on the surface is about 0.35 eV lower than that of the titanium in the bulk.<sup>[15]</sup> Thus, it can be speculated that in the case of a single-layered structure, the system would be highly unstable because it is full of surfaces.

To characterize the origin of the color change of the nanodisks, several basic analysis tools were applied. First, we performed time-dependent SEM-EDS elementary analysis with the 34-nm nanodisks. As shown in Figure 4a, the stoichiometric ratio of sulfur to titanium gradually decreased over time. After one day of exposure to air, the ratio of sulfur to titanium decreased from 2.04 to 1.24. Also, the rate of change of the sulfur to titanium ratio gradually decreased and, after one month, the sulfur had almost completely disappeared. We also conducted time-dependent PXRD experiments. As shown in Figure 4b, the (110) peak of titanium sulfide slowly disappeared over time and new peaks for titanium dioxide appeared at 48.3, 53.9, and 62.1°. These new peaks are very close to those of anatase titanium oxide (JCPDS#21-1272). The peaks of titanium oxide started to be observed after one day of exposure to air. It

took about two weeks to observe the complete disappearance of peak of titanium sulfide and about one month to obtain clear titanium dioxide peaks.

Time-dependent XRD experiments gave some information about the structural change in the nanodisks, which indicated that the sulfur was displaced by oxygen in the air. The X-ray photoelectron spectroscopy (XPS) study confirmed that the oxidized materials are titanium oxides; the Ti 2p



**Figure 4.** Time-dependent SEM-EDS experiments of 34-nm titanium sulfide nanodisks at room temperature after a) one day of exposure in air, b) 3 days, and c) one week. Time-dependent XRPD studies of 34-nm titanium sulfide nanodisks at room temperature after d) one day of exposure to air, e) 12 days, and f) one month.

orbital peaks at 458.25 and 464.1 eV are well matched with known  $\text{TiO}_2$  materials.<sup>[19]</sup>

In the literature, there have been several reports on the sulfurization of titanium oxide to titanium sulfide and vice versa at high temperature (420–640 °C).<sup>[20]</sup> It is well known that these two materials have different and unique physical properties. Because titanium oxides usually absorb UV and titanium sulfide absorbs visible light, mixtures of these two materials hold promise as photocatalysts that absorb light over a wider region of the spectrum than either of these materials alone.<sup>[21]</sup> It was reported that the heat treatment of titanium sulfide under air resulted in the formation of titanium oxide.<sup>[22]</sup> However, in the literature there are no reports on the desulfurization of titanium sulfide at room temperature. It is well known that titanium sulfide is usually less stable than titanium oxide because the latter forms a stable three-dimensional (3D) structure. Moreover, it is reasoned that the destabilized surface in the monolayered titanium sulfide nanodisks makes these materials more unstable even at room temperature.

In order to identify the driving force for the structural change via oxidation, we performed the theoretical calculations using a plane-wave pseudopotential method based on density functional theory (Vienna ab initio simulation package (VASP) code<sup>[23]</sup>). As shown in Figure 5, it can be speculated

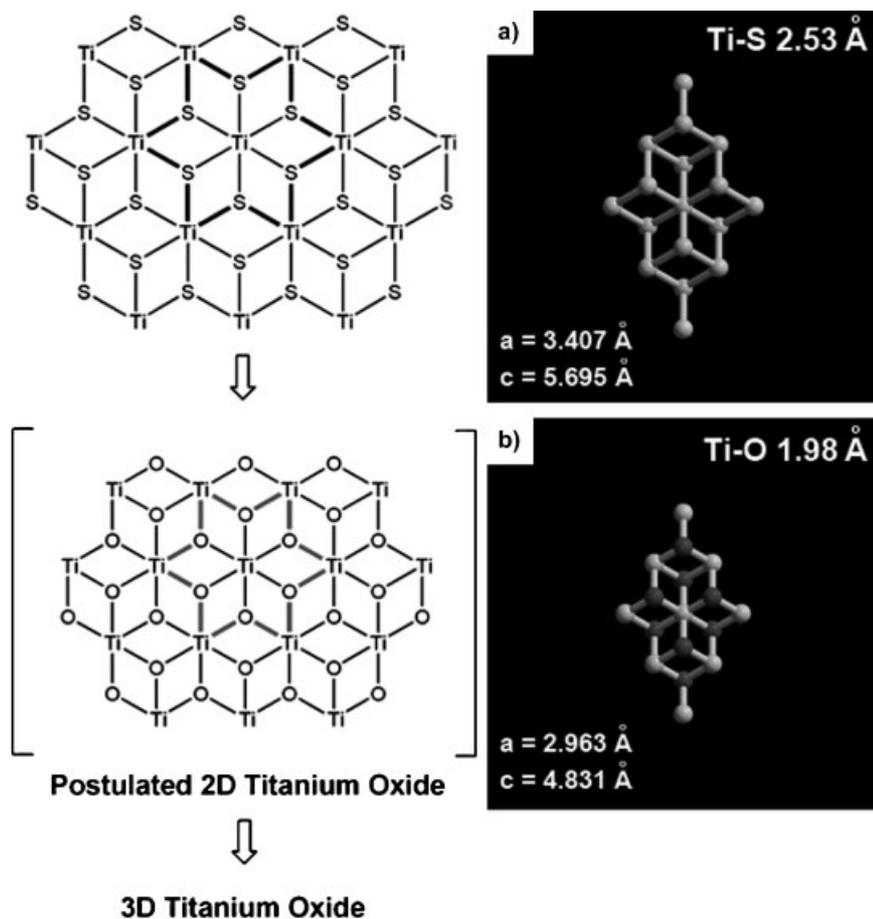
that the sulfur in titanium sulfide was displaced by oxygen to form a 2D structure. It is believed that this displacement would occur gradually and the resultant titanium oxide species would be further converted to 3D titanium oxide before the complete displacement of all sulfur atoms. However, to simplify the system, we postulated that all sulfur atoms in titanium sulfide were replaced with oxygen atoms. Figure 5b shows the postulated structure in which the titanium oxide has a 2D structure and the titanium atoms are located in the same plane. Firstly, the structure of the postulated 2D titanium oxide was theoretically optimized for further calculation on the stability. Secondly, we compared the stabilities of the single-layered titanium sulfide with the postulated single-layered titanium oxide, which showed that the monolayered titanium oxide is much more stable than titanium sulfide by 3.8 eV per unit cell (see the Experimental Section for the procedure of calculation).

The rate of structural change was significantly dependent on the amount of surfactant. The repeated washing of the nanomaterials using alcohol gradually removes the protective groups on their surface, which accelerates the structural change of the nanodisks. Thus, it can be expected that the rate of structural change can be controlled by adjusting the size of the nanodisks and the concentration of surfactant.

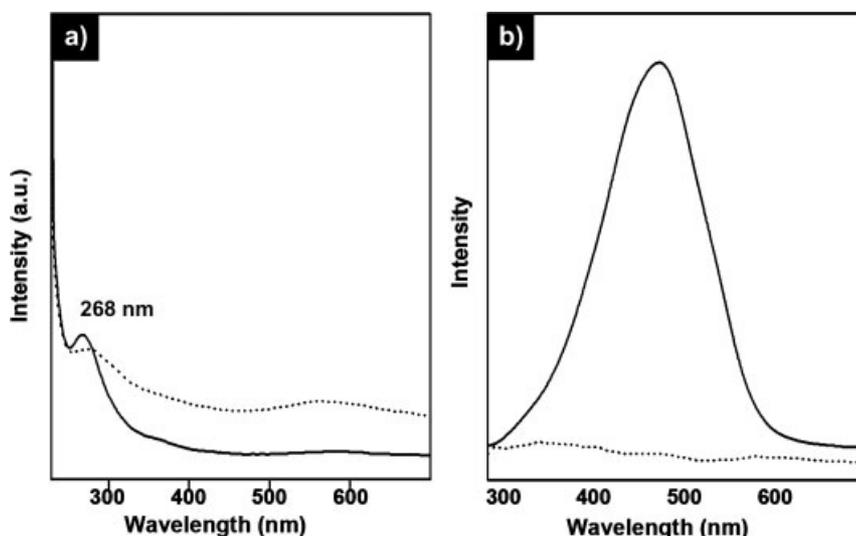
The time-dependent optical properties studies using UV/

Vis and photoluminescence (PL) spectroscopy showed interesting results. Figure 6 shows the changes in the UV/Vis absorption and PL spectra of the 18-nm nanodisks in methylene chloride solution. Interestingly, after the titanium sulfide was converted to titanium oxide, a clear absorption peak appeared at 268 nm, as shown in Figure 6a. In the PL studies, with increasing time, a strong new emission peak was detected at 475 nm (with a 268-nm excitation wavelength), as shown in Figure 6b. It has been reported that nanometer-sized titanium dioxide exhibits blue-light emission.<sup>[24]</sup> Thus, it can be concluded that the emission came from the titanium dioxide.<sup>[25]</sup>

Recently, there has been increasing interest in the development of oxygen sensors based on the change in the luminescent or electrical properties of materials caused by their interaction with oxygen. It has been reported that the partial desulfurization of titanium sulfide resulted in an increase of the photocurrent.<sup>[26]</sup> The single-layered titanium sulfide in this report has a 2D shape that could be incorporated into devices and the change in its optical properties and possible changes in its electrical properties brought about by the structural change from titanium sulfide to titanium oxide could



**Figure 5.** Illustration of transformation of the single-layered titanium sulfide nanodisks into titanium oxide at room temperature; single-layered  $\text{TiS}_2$  disk (a) and postulated  $\text{TiO}_2$  disk (b).



**Figure 6.** Change in the optical properties after the structure change of the 18-nm nanodisks; a) UV/Vis spectra and b) PL spectra with 268-nm excitation wavelength in methylene chloride solution. Dotted line: as prepared, solid line: after exposure to air.

be applied to the development of new oxygen sensors.<sup>[27]</sup>

In conclusion, single-layered titanium sulfide nanodisks with a thickness of 0.6 nm were prepared for the first time using the wet chemical method. Their size could be controlled by changing the experimental conditions. The time-dependent EDS and powder XRD studies demonstrated that the single-layered titanium sulfide nanodisks are unstable even at room temperature. They showed structural changes to form titanium oxide, which resulted in the observation of an emission at 475 nm.

## Experimental Section

TEM and HRTEM images were recorded with a JEOL 2100F unit operated at 200 kV. The samples for TEM study were prepared by drop casting nanomaterials dispersed in hexane on carbon-coated copper grids. The TEM studies were performed on as-prepared samples without employing a size-selection process. EDS was performed on a TEM (JEOL2100F) and an FE-SEM (JS6700F). PXRD patterns were obtained on a Rigaku Max-2200 with filtered  $\text{CuK}\alpha$  radiation. XPS was obtained using a Thermo VG and Monochromatic  $\text{AlK}\alpha$  radiation. UV/Vis and PL studies were performed using Jasco-630 and Jasco-FP6200, respectively. All calculations were performed using a plane-wave pseudopotential method based on density functional theory (VASP code<sup>[23]</sup>). In the calculation, potentials for electron–electron and for electron–ion pairs were described by a generalized gradient approximation (GGA)<sup>[28]</sup> and the projected augmented wave (PAW) method,<sup>[29]</sup> respectively. The plane waves to describe electronic wavefunction were expanded up to 400 eV. We sampled  $4 \times 4 \times 4$  Monkhorst-Pack (MP) meshes in the Brillouin zone.<sup>[30]</sup> Titanium chloride, sulfur, and oleylamine were purchased from Aldrich.

**Synthesis of 50-nm nanodisks:** 0.10 mL (0.91 mmol)  $\text{TiCl}_4$  was dissolved in well-dried oleylamine (2 mL) by sonication for a hour. 58.8 mg (1.83 mmol) of sulfur powder was dissolved in oleylamine

at 110 °C (7 mL). The solution was cooled to room temperature. These two solutions were combined in flame-dried 50 mL Schlenk tube under argon and the color of the reaction mixture became blue-black. The temperature of the reaction mixture was increased rapidly to 110 °C and then slowly increased ( $4^\circ\text{C min}^{-1}$ ) to 215 °C. At this temperature, the reaction mixture was stirred for an additional 12 h. After cooling to room temperature, the reaction mixture was poured into excess methanol. Black precipitates were collected by centrifugation and washed with methanol several times and dried under vacuum. For the preparation of 34-nm and 18-nm nanodisks, the same synthetic procedure was used except that twice the amount of sulfur (116.5 mg, 3.63 mmol) was used and the reaction mixture was stirred for 1 h at 215 °C.

## Keywords:

colloids · nanodisks · nanomaterials · semiconductors · titanium sulfide

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