Liquid-Phase Synthesis of Flower-like and Flake-like Titanium Disulfide Nanostructures

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Three-dimensional *flower-like* nanostructures of TiS_2 and two-dimensional *flake-like* nanostructures of crystalline TiS_2 have been synthesized using a facile solution method. On the basis of time-dependent experimental results, a growth mechanism has been proposed for these nanostructures. The injection temperature of the precursor plays a key role in the formation of the flower-like and flake-like morphology. The nanostructures have been characterized by X-ray powder diffraction, scanning electron microscopy, and transmission electron microscopy. The surface area of the nanostructures is also reported.

Introduction

Metal chalcogenide materials with layered structures such as TiS_2, NbS_2, MoS_2, WS_2, and SnS_2 have attracted considerable interest in recent years because of their electronic properties and potential applications.[1−4] TiS_2 and its intercalation compounds have been studied intensively and shown to be promising cathode materials in rechargeable batteries[5] and as potential hydrogen storage materials.[6]

TiS_2, like the rest of the group IVA dichalcogenides, crystallizes in the hexagonal CdI_2 structure, a layered compound with repeating subunits, made by a layer of Ti atoms and two layers of S atoms.[7] There is strong bonding between atoms in the Ti and S layers, whereas weak van der Waals forces dominate the bonding between the S and S layers.

Various morphologies of TiS_2 such as nanotubes,[5] nanoclusters,[8] fullerenes,[9] nanodisks,[10] whiskers,[11] and thin films[12] have been successfully synthesized. With respect to the synthesis of three-dimensional (3D) nanostructures, morphologies such as *flower-like* patterns and dendritic crystals of TiS_2 have been synthesized, by a chemical vapor transport approach.[13,14] However, the controlled wet chemical synthesis of flower-like nanostructures of TiS_2 has not previously been achieved.

Reports have been observed for the synthesis of *flake-like* nanostructures for materials such as SnS_2 and MoS_2, their growth attributed to their crystal structure.[15,16] To our knowledge, the synthesis of flake-like nanostructures in TiS_2 is yet to be achieved.

Moreover, the facile control of whether materials adopt two-dimensional (2D) structures such as nanoflakes or nanoplatelets and 3D structures such as nanoflowers or nanorods is still difficult and requires complex synthetic techniques.[13,14] However, a colloidal synthesis offers a more promising approach with advantages of being low cost in preparation and suitable for large-scale production.

In this paper we report a simple one-step solution phase route to synthesize elegant 3D flower-like nanostructures of TiS_2 and 2D flake-like nanostructures. This is the first report of the synthesis of flake-like nanostructures and synthesis in solution of flower-like nanostructures of TiS_2. These nanostructures were obtained from the reaction of titanium tetrachloride with elemental sulfur in the noncoordinating solvent 1-octadecene. It was found that changing the injection temperature could easily control whether a 2D or 3D morphology of nanostructures was obtained. On the basis of the evolution of the structure and morphology with reaction time, a growth mechanism of the flower-like and flake-like nanostructures has been elucidated.

Experimental Section

All of the chemicals used in this experiment were of analytical grade. In a typical synthesis, 0.192 g (6.00 mmol) of sulfur was

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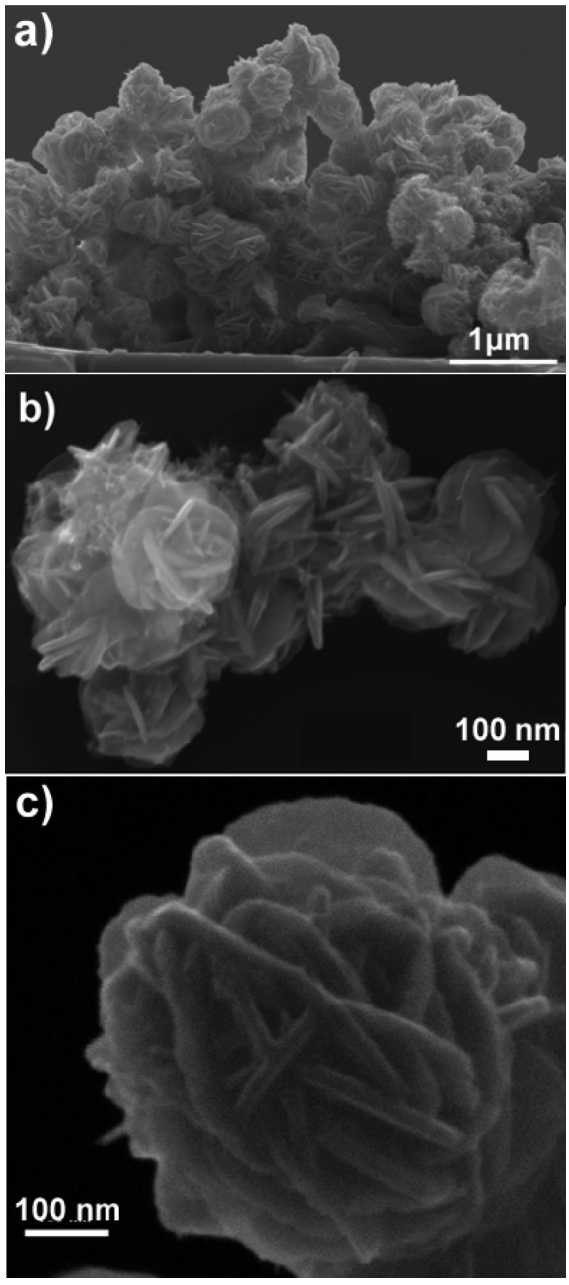

Figure 1. SEM images (a) and (b) are low-magnification images of flower-like TiS_2 nanostructures and (c) individual flower-like nanostructures.

dissolved in 20 mL of 1-octadecene (90%, Aldrich) and gradually heated to 300 °C and degassed for 30 min. Titanium tetrachloride (0.10 mL, 1.00 mmol) ($TiCl_4$ 98.5%, Aldrich) was injected swiftly into the stirring sulfur solution and the mixture turned black instantly. The solution was allowed to react for 10 min and then allowed to cool to room temperature. A black powder containing flower-like TiS_2 nanostructures was obtained. In a second reaction, titanium tetrachloride was injected at a temperature of 150 °C and then over 15 min the reaction temperature was increased to 300 °C and then allowed to react for 10 min. The reaction proceeded in a similar fashion with a rapid change in color followed by the formation of a black precipitate. The morphologies of the final product were observed to be flake-like. All experiments were conducted in a N_2 atmosphere, and the black solids obtained from both the reactions were collected by centrifugation and purified by washing with toluene and methanol repeatedly.

The resulting products were analyzed by scanning electron microscopy (SEM) on a JSM-6500F microscope. Transmission

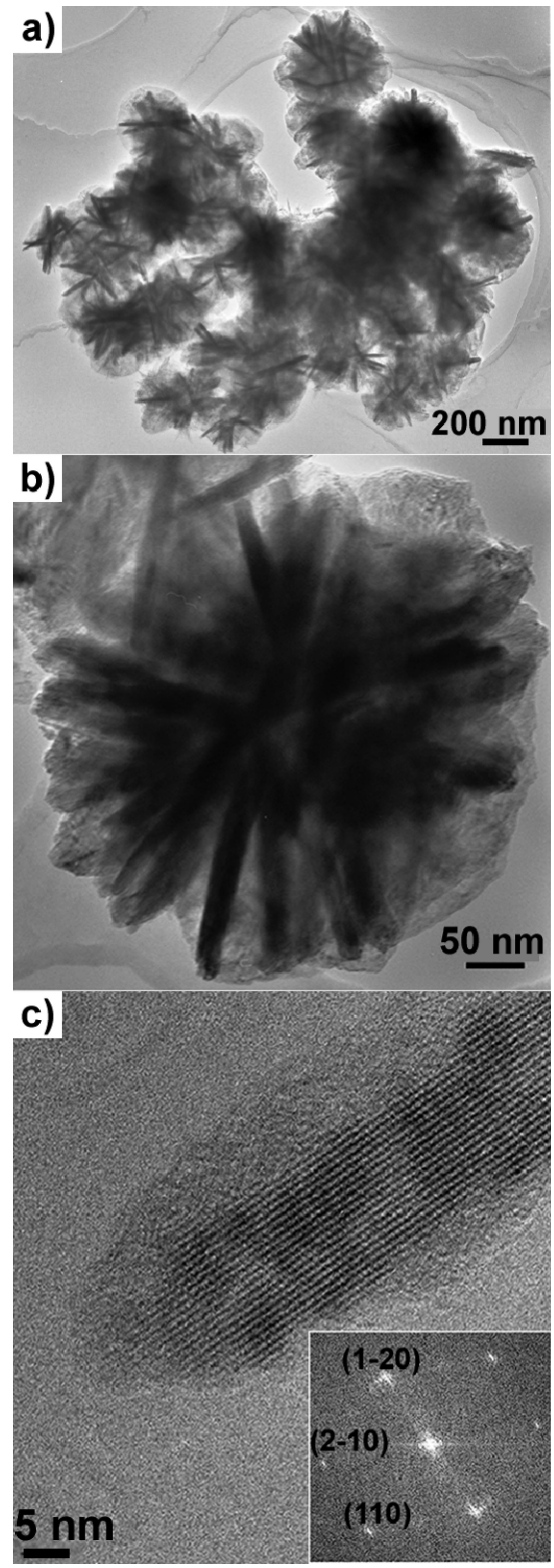

Figure 2. (a) Low-resolution TEM image of as-prepared TiS_2 nanoflowers; (b) a single nanoflower exhibiting rodlike growth originating from the center of the flake; (c) high-resolution TEM image of a nanopetal and (inset) FFT pattern of the corresponding image.

electron microscopy images (TEM) images and electron diffraction patterns were obtained using a JEOL 2010 transmission electron microscope operating at 200 keV equipped with a double tilt sample holder. Specimens for TEM investigations were sonicated in hexane and a drop of the solution was placed on a carbon-film-coated holey copper grid. The Brunauer−Emmett−Teller (BET) measurements

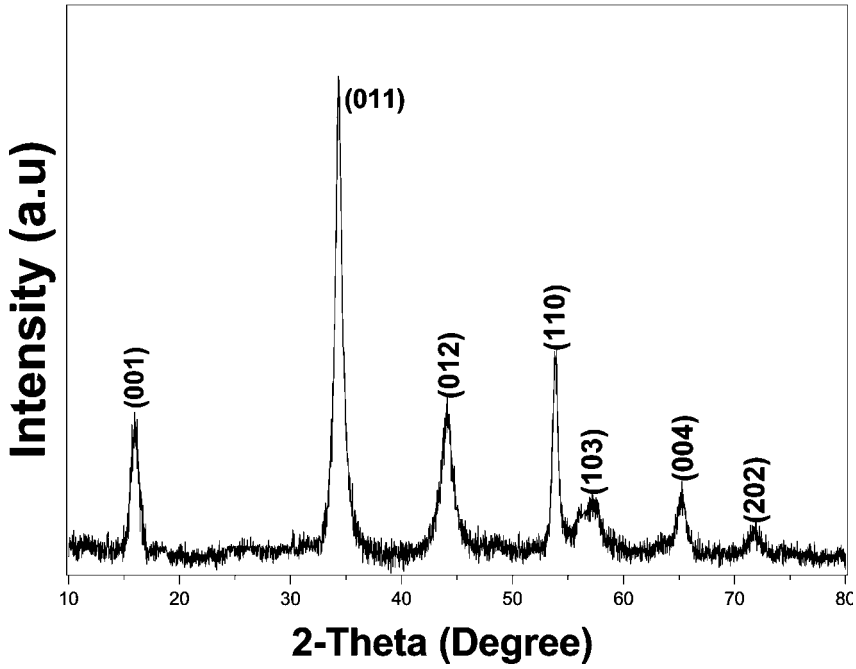

Figure 3. XRD pattern of the TiS_2 flower-like nanostructure.

were determined with a Micromeritics ASAP 2010 Accelerated Surface Area and Porosimetry System. Powder X-ray diffraction patterns were acquired on a Phillips PW 1720 X-ray generator using Cu Kα radiation.

Results and Discussion

The first reaction had both an injection and a reaction temperature of 300 °C of the titanium tetrachloride in the elemental sulfur solution. Low- and medium-magnification SEM images of the nanostructured materials formed are shown in Figure 1a,b.

From the images it may be observed that the structures are three-dimensional, partially spherical, and flower-like in appearance. Figure 1a is a typical SEM image and shows the flower-like nanostructures aggregated together. The flower-like nanostructures tend to cluster in groups of around 10−50. Individual flower-like nanostructures are typically between 100 and 500 nm in size. Higher magnification images showing more detailed morphology of the flower-like nanostructures are shown in Figure 1b,c and indicate that the flower-like nanostructures are built from tens of nanopetals. As can be seen in Figure 1c, individual flowers are made of randomly aligned nanopetals of about 100−500 nm in length and 20−50 nm in width. Sonication of the nanostructures did not break them into discrete petals, suggesting that the nanostructures are integrated and not an aggregation of nanopetals.

Further insight into the morphology and structure of the flower-like nanostructures was gained using low- and high-resolution transmission electron microscopy (TEM). The TEM images in parts (a) and (b) of Figure 2 show aggregates of flower-like nanostructures and an individual flower-like nanostructure, respectively. From the images it may be seen that the petals are about 25 nm in width and taper toward the edge. The nanopetals are crystalline and the TEM image in Figure 2c shows clearly observable lattice fringes. Fast Fourier transform (FFT) analysis (inset) of the corresponding image matched the crystal structure of titanium disulfide viewed down the [001] orientation.

An X-ray powder diffraction pattern of the TiS_2 flower-like nanostructure is shown in Figure 3. The reflections could be readily indexed to the hexagonal phase of TiS_2.[17]

Variation of Reaction Time and Growth Mechanism. To investigate the growth mechanism of the flower-like TiS_2, experiments were performed at 300 °C where small aliquots were removed from the reaction flask at times of 30, 60, and 90 s and quenched in an ice bath. The SEM images shown in Figure 4 are of the samples obtained at these different reaction times and illustrate the evolution of the morphology of the TiS_2 flower-like nanostructure. The sample taken after a 30 s reaction time is shown in the image Figure 4a. The products consist of a spherical core of size 200−300 nm with blisters growing from this core. We define these structures as *spheres with surface blisters*. The surface blisters are roughly semispherical in shape with diameters typically less than 35 nm. Energy-dispersive X-ray (EDX) analysis in both SEM and TEM of the spheres with surface blisters showed that their composition was $TiS_{1.3}Cl_{0.8}$.

An SEM image of a typical particle from the sample with a reaction time of 60 s is shown in Figure 4b. From SEM analysis it was found that over 80% of the product were particles similar to the one shown in Figure 4b, which we call *spheres with protuberances* and 20% of the product still remained as spheres with surface blisters. As shown in Figure 4b, a typical sphere with protuberances has a spherical core of similar size and structure to the spheres with surface blisters. As can be seen in Figure 4b, the protuberances are made of platelets that are randomly oriented, growing off the spherical core. From high-resolution TEM it was

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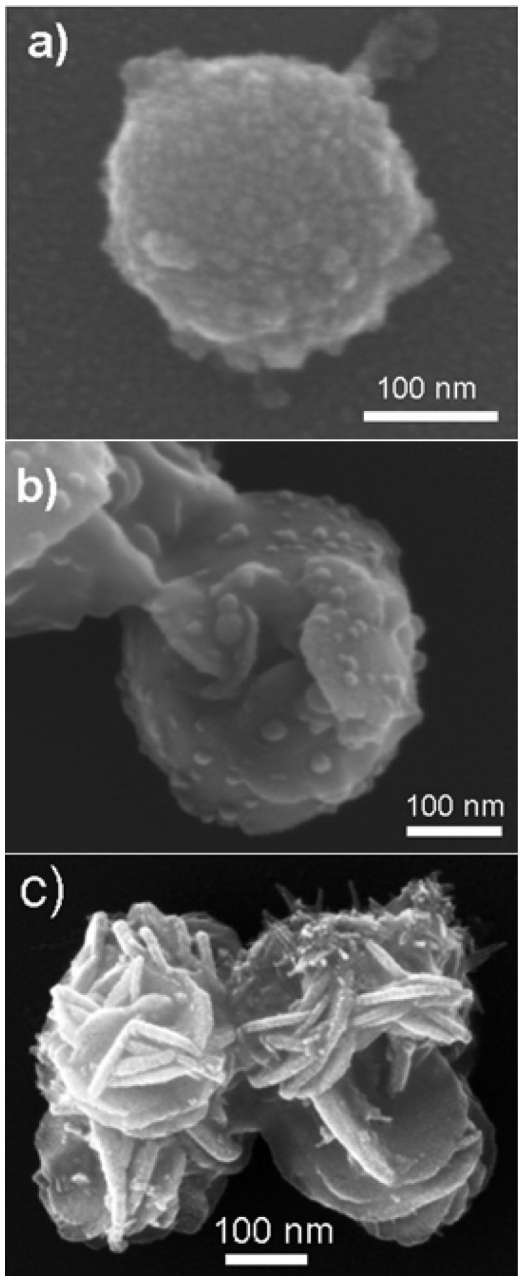

Figure 4. SEM images of the products obtained at different growth stages: (a) 30 s, (b) 60 s, and (c) 90 s.

discovered that they are 10−100 atomic layers in thickness and typically 35−250 nm horizontally. TEM studies on both surface blisters and protuberances showed that they were crystalline and were composed of stoichiometric TiS_2. However, from selected area electron diffraction (SAED), the spherical core was found to be amorphous.

At 90 s, the sample contained flower-like nanostructures of TiS_2 in a 100% yield. A typical flower-like nanostructure is shown in Figure 4c. As can be seen from Figure 4c, these structures are made of randomly aligned nanopetals originating from the center that are so large that the spherical core is no longer evident. SAED indicated that the flower-like nanostructures were highly crystalline. Reactions for longer time periods were also found to form identical flower-like nanostructures, suggesting that they are the final

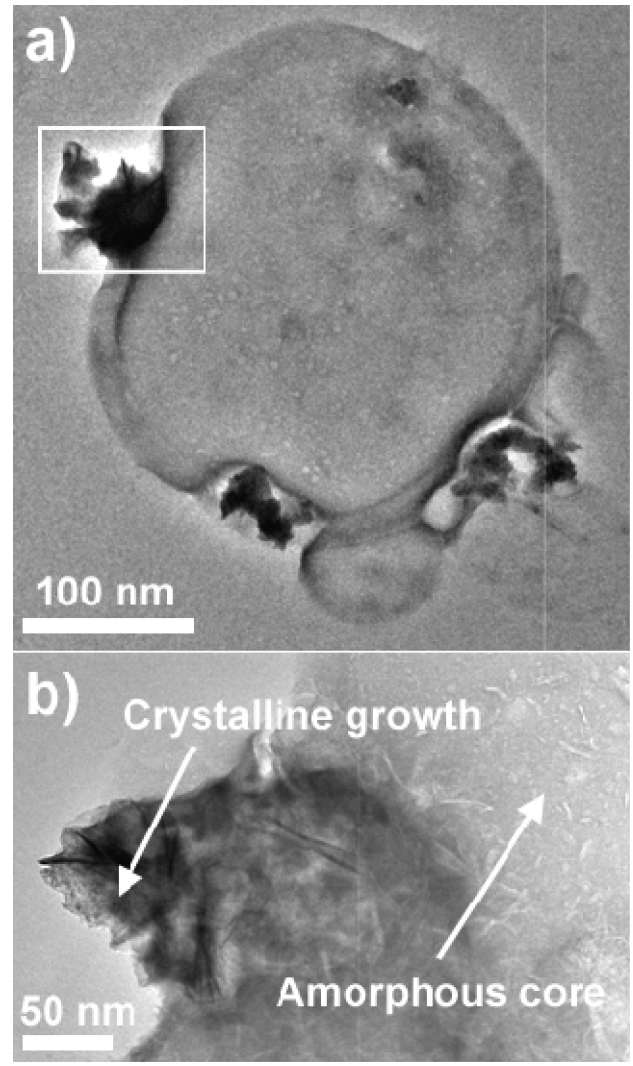

Figure 5. (a) Low-magnification TEM image of a sphere isolated at 60 s. (b) Higher magnification image of the rectangular section in Figure 5a, indicating the crystalline and amorphous part of the sphere.

Scheme 1. Reaction for the Synthesis of TiS_2 Flower-like Nanostructures

$$TiCl_4 + 6S \rightarrow TiS_2 + 2S_2Cl_2$$

thermodynamic product. EDX analysis in SEM and TEM of the final flower-like nanostructures indicated a composition of $TiS_{1.8}$.

TEM analysis of the spheres with surface blisters was undertaken to further characterize the intermediate structure. The TEM image of a typical sphere with surface blisters isolated at 60 s is shown in Figure 5a and a higher magnification image in Figure 5b. SAED of the area boxed in white containing the surface blister indicated that the surface blister was crystalline and SAED of the spherical core gave an amorphous diffraction pattern.

Chemical Reaction. The formation of crystalline TiS_2 from $TiCl_4$ and elemental sulfur most likely occurs through the overall reaction shown in Scheme 1. Sulfur has been known to act as both the reductant and sulfiding agent at high temperatures.[18−21] The $TiS_{1.3}Cl_{0.8}$ stoichiometry of the spheres

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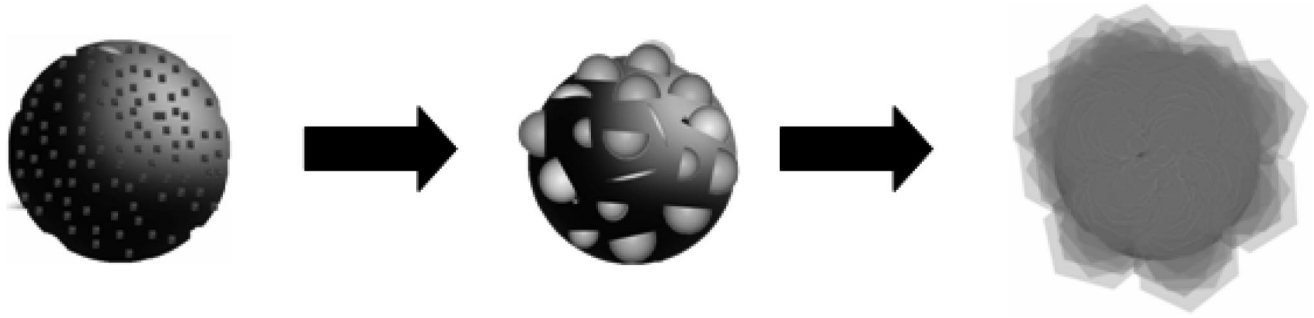
Scheme 2. Growth Mechanism of the TiS_2 Flower-like Nanostructures



with surface blisters indicates that a reaction may also occur to form amorphous TiS_xCl_y compounds.

Growth Mechanism. On the basis of the electron microscopy results shown in Figures 4 and 5, the growth mechanism for the formation of the flower-like nanostructures was elucidated and is depicted schematically in Scheme 2.

During the initial stages of nucleation, amorphous spheres between 200 and 300 nm with an approximate composition of $TiS_{1.3}Cl_{0.8}$ form. These spheres have small crystalline blisters of TiS_2 on the surface to give spheres with surface blisters. As the reaction continues, the inner amorphous spherical core remains constant in size and the growth occurs on the surface of the spheres as the surface blisters grow into bigger protuberances. As the reaction continues to 90 s, these protuberances have continued to grow in size to become full crystalline flower-like petals. These observations agree with previous reports of growth mechanisms involving a multistage growth process.[22−25]

Thus, the growth and morphology of the flower-like nanostructures may be understood as follows. The initial particles formed are amorphous and thus adopt a spherical shape. The surface of the spheres act as nucleation sites for the formation of small crystalline blisters of TiS_2. As the reaction proceeds, it is energetically more favorable for the crystalline TiS_2 blisters to grow, which they do via protuberances into full crystalline flower-like petals with the blisters on the surface of these spheres providing high-energy sites for crystalline growth.[26,27] The platelike 2D shape of the protuberances and flower-like petals originates from the layered structure of TiS_2, which grows preferentially along the *a*- and *b*-axes compared to the *c*-axis.

Flake-like Nanostructures. In a second reaction the injection temperature of the titanium source into the elemental sulfur was decreased to 150 °C. After injection at 150 °C, the temperature of the solution was gradually increased to 300 °C over a period of 15 min and the reaction further heated for 10 min. The as-synthesized product was purified and dispersed in hexane for analysis by SEM and TEM. SEM and TEM images of the products are shown in Figure 6. As can be seen from Figure 6a, the product was highly irregularly shaped TiS_2 fragments, which we refer to as TiS_2 flake-like nanostructures that were typically tens of micrometers in size. The higher magnification SEM image shown in Figure 6b shows that each of these flake-like nanostructures were made of smaller flakes about a micrometer in size attached to each other in random orientations to form discrete flake-like nanostructures and do not disintegrate upon sonication. Figure 6c is a representative TEM image in in which Figure 6c shows an individual flake-like nanostructure of TiS_2, showing good agreement with SEM images, and illustrates that the nanostructures are made of flaky protrusions. The light contrast in many areas of the TEM image in Figure 6c indicates the thin 2D nature of the flake-like nanostructures. The flake-like nanostructures were found to be crystalline and SAED patterns could be indexed to the hexagonal phase of TiS_2. EDX analysis was carried out on individual flakes of TiS_2, which showed good agreement with 1:2 molar ratios of titanium to sulfur.

Growth Mechanism. To understand the formation of the flake-like nanostructures, the reaction was repeated with small aliquots removed at different reaction times in a fashion similar to the method used for the flower-like nanostructures. The product in all the aliquots removed were analyzed by SEM and TEM and even those taken after only 1 s were flake-like nanostructures with the same size and morphology of those found at the longer reaction times and shown in Figure 6. These results show that the flake-like nanostructures are formed immediately after injection and prevented the isolation of initial products.

The formation of 2D flake-like nanostructures in dichalcogenide systems originates from the layered crystal structure. Flake-like nanostructures form with growth along the [100] and [010] directions, these directions being more favorable because of stronger bonding than that seen from growth in the longer [001] direction.[28]

Morphological Control. The results show that the final morphology of the TiS_2 nanostructure can be controlled by the nature of the initial nuclei. At a lower injection temperature of 150 °C flake-like nanostructures are obtained, most likely from the instant nucleation of TiS_2 flakes. At a higher injection temperature of 300 °C, flower-like nanostructures are obtained through the formation of spherical nuclei of TiS_xCl_y. This understanding of the controlled and

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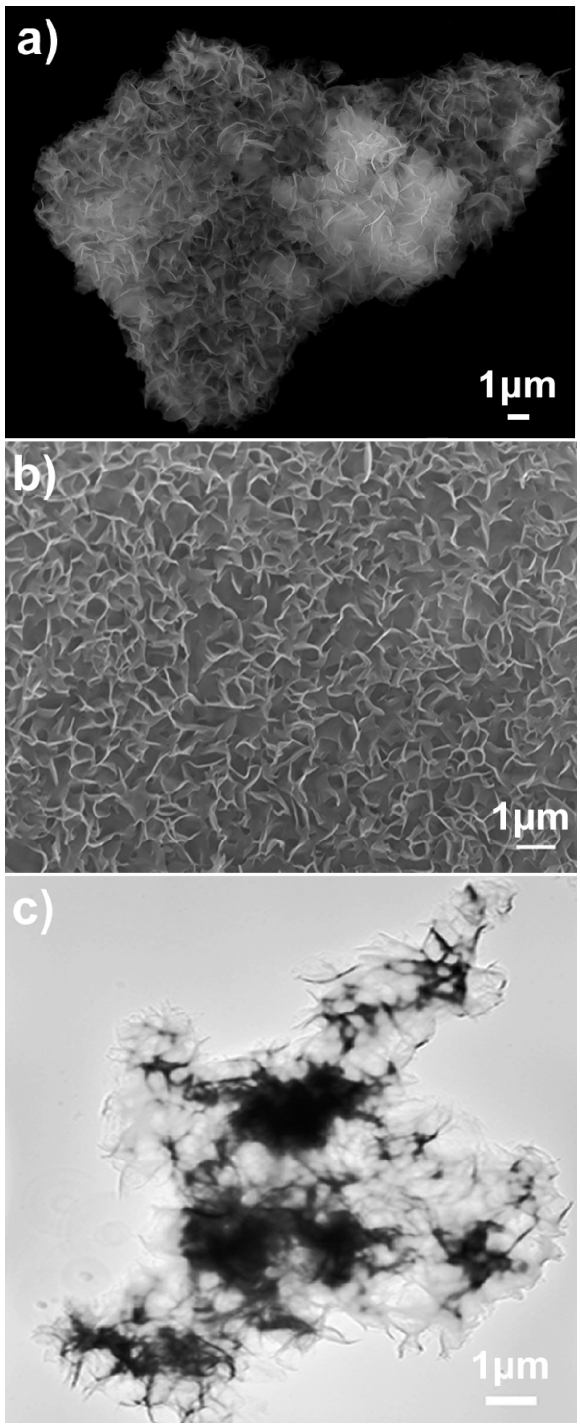

Figure 6. (a) Low-resolution SEM image of the flake-like nanostructures; (b) higher magnification view of the flakes; (c) TEM image of a single TiS_2 flake.

selected growth of both flower-like and flake-like nanostructures is highly significant for understanding the growth of all materials with similar layered structures including industrially important MoS_2, NbS_2, and WS_2.

BET Surface Area Measurements. TiS_2 is known to have possible applications as hydrogenation catalysts and hydrogen storage devices. For these applications high surface area is important. Hence, surface area measurements were conducted on both flower-like and flake-like nanostructures and were found to be 32 and 19 m^2g^{-1}, respectively (Figure 7). The surface area of our flower-like nanostructures were found to be more than that reported for TiS_2 nanotubes by Chen et al.[29] This high surface area indicates that these materials should have excellent performance as catalyst carriers and hydrogen storage devices.

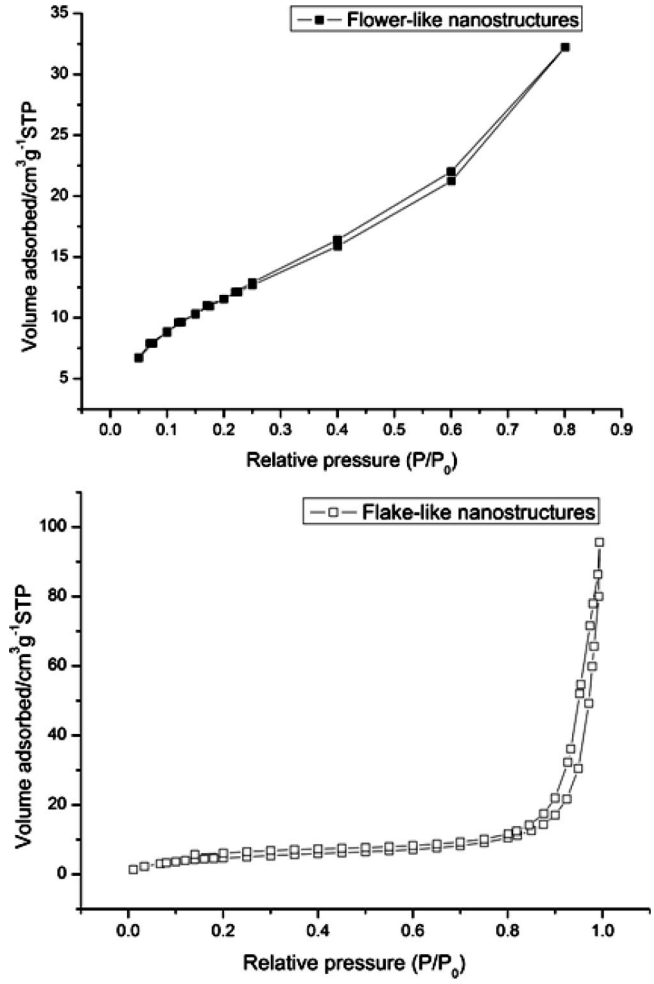

Figure 7. BET (isothermal adsorption/desorption plot) surface area measurements of TiS_2 nanostructures.

Conclusion

In summary, elegant flower-like and flake-like nanostructures of TiS_2 were, for the first time, synthesized by a colloidal route. The morphology and chemical composition of the as-synthesized nanostructures are characterized, and a possible growth mechanism for the formation of these nanostructures has been elucidated. The key factors in controlling the morphologies were discussed based on a clear understanding of the growth mechanism. The surface area of flower-like and flake-like TiS_2 nanostructures have also been reported. The synthetic route is expected to be applicable in the synthesis of other metal dichalcogenide layered systems.

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