Synthesis and Optoelectronic Properties of Two-Dimensional FeS$_2$ Nanoplates

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Supporting Information

ABSTRACT: There is a growing interest in the earth abundant and nontoxic iron disulfide (FeS$_2$) photovoltaic materials. Here, we report the synthesis of FeS$_2$ nanoplates with different spectral features which we have associated with thicknesses and crystallization. The structure and crystalline order of ultrathin FeS$_2$ nanoplates have a strong influence on the carrier lifetime, electronic and optical properties. We demonstrate that two-dimensional FeS$_2$ nanoplates show great promise for fabrication of hybrid bulk heterojunction solar cells. This opens up a host of applications of these materials as inexpensive solar cells and photocatalysts.

KEYWORDS: colloidal synthesis, iron disulfide (FeS$_2$), nanoplates, carrier lifetime, hybrid solar cells

1. INTRODUCTION

Iron disulfide (FeS$_2$), with a pyrite structure, has significant scientific interest and technological applications.1−3 On the application side, FeS$_2$ is the major sulfur mineral in coal, and has demonstrated a significant increase in photoelectrochemical activities.4 Owing to their large potential capacities for solar cell applications, iron-based materials have been extensively studied as possible alternatives for commercially available silicon or gallium arsenide solar cells.5 Compared with other multi-composition photovoltaic materials such as Cu$_2$ZnSnS$_4$,6,7 binary FeS$_2$ nanocrystals allow solution-processed solar cells. Recent efforts on research and development of pyrite FeS$_2$ nanocrystals have been driven by remarkable performance improvements of low cost solar cells to meet ever-increasing energy demands.8 However, the main drawback of this system is stemming from oxidation and due to the orthorhombic metastable marcasite structure that is detrimental to photovoltaic properties.9

Though various FeS$_2$ spherical nanoparticles have been fabricated using a variety of synthetic methods,10,11 thus far the preparation of high quality two-dimensional (2D) layered FeS$_2$ nanoplates has remained a significant challenge. The electronic structures of FeS$_2$ and other 3d transition metal dichalcogenides have been of considerable scientific interest because these materials straddle the localization-itinerant regimes for the 3d electrons.12−14 It is important to understand how this structure varies with electronic confinement, but apparently no earlier work exists on this subject. Especially, in layered FeS$_2$ nanoplates, the lateral confinement can remarkably enhance optoelectronic performance compared to their bulk counterparts because of nanoscale characteristics that include large surface areas, finite lateral sizes, and enhanced open-edge morphologies.

In this letter, we report the development of a facile synthesis of laterally confined, 2D, and layered FeS$_2$ nanoplates. Because of its unique morphology, consisting of a finite lateral sized and well-defined layered structure, this material is more suitable for many applications in comparison to its nanoparticle counterparts. In fact, as a material with layered crystal structure, FeS$_2$ nanocrystals with sheet or plate shape may be more attractive due to the probable quantum confinement at one dimension and the electrical continuity at the other two dimensions. Below, we discuss the morphological and optical properties of this substance and its potential utilization as a photovoltaic material.

2. EXPERIMENTAL SECTION

Laterally confined 2D FeS$_2$ nanoplates were synthesized by using thermal decomposition of the precursor, Fe(CO)$_5$, in an organic solvent at elevated temperature. All of the synthetic experiments were carried out under Ar atmosphere using standard Schlenk line techniques. In a typical synthesis of FeS$_2$ nanoplates, the sulfur stock solution was prepared by the coordinating solvent oleyamine (OLA) with elemental sulfur and deaerated at different temperatures (120 °C, 180 and 240 °C, referred as the reaction temperature later) for 15 min and then backfilled with Ar for 15 min. In a separate vessel, Fe(CO)$_5$ organometallic precursor is dissolved and heated under Ar. At the reaction temperature, Fe(CO)$_5$ was rapidly injected into the sulfur solution, while not permitting the temperature of the solution to decrease. The vessel with the resulting black mixture was continually stirred at this temperature for different aging time (3, 30, 60, 180, and 540 min). After the mixture was cooled to room temperature, methanol was added to precipitate the product. The black precipitate was then isolated via the centrifugation (3000 rpm).

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for 5 min. The washing process was repeated three times with methanol to ensure removal of any excess capping agent. The final FeS$_2$ nanoplates were obtained by dissolving into chloroform.

3. RESULTS AND DISCUSSION

The structure of the crystalline platelike FeS$_2$ is strongly dependent on the reaction temperature and aging time. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images show the FeS$_2$ morphologies with 180-min aging time at different reaction temperatures: 120 °C, 180 and 240 °C. At a low temperature of 120 °C, the reactants mostly form an amorphous precursor state without clear edges (Figure 1a,d). Irregular, continuous material is seen (Figure 1a), and no isolated particles can be found. This shows the presence of undecomposed precursor at this low temperature. Increasing the reaction temperature to 180 °C promotes the appearance of nanoplates with a clear edge. The FeS$_2$ nanocrystalline are 2D nanoplates with a lateral size of ca. 150 nm and size distribution of (20%) (Figure 1b and 1e). The FeS$_2$ samples prepared at 180 °C are mainly composed of nanoplates with irregular shapes. Upon increasing reaction temperature to 240 °C, the FeS$_2$ nanoplates have a truncated hexagonal and triangular shape with a large size variation from 200 to 500 nm, as shown in the SEM and TEM images (Figure 1c, f and Figure S1a in the Supporting Information). The increased reaction temperature plays an important role in the 2D planar growth but with a minor effect on the thickness of FeS$_2$ nanoplates, which is about 30 nm thickness. The anisotropic growth of the FeS$_2$ nanoplate may originate from the crystalline facets which tend to develop on the low-index planes to minimize the surface energy when growing. The platelike FeS$_2$ nanocrystals with regular shape are formed exhibiting mainly hexagonally shaped nanoplates (Figure 1f). This further demonstrates that the reaction temperature plays a very important role in the formation of nanoplates. The chemical components of the nanoplates have been identified by energy dispersive X-ray spectroscopy (see Figure S1 in the Supporting Information).

The FeS$_2$ nanoplate growth process can also be demonstrated by changing the aging time while keeping the same reaction temperature of 180 °C. We investigated the morphology and structure of FeS$_2$ nanoplates using TEM and high-resolution TEM. Figure 2 shows typical TEM images of the FeS$_2$ nanoplates with varied aging time. The particles show platelike shapes for the 3-min aging time (Figure 2a). The nanoplates had no uniform shape and size, demonstrating an incomplete reaction at this time. However, the crystal lattice fringes of this sample can still be observed, suggesting a fast crystallization at the beginning of reaction. At the same reaction temperature, the nanoplates start to grow larger and thicker with increasing aging time. Compared to the 3 min aging time, FeS$_2$ nanoplates aged for 180-min grow bigger and thicker but remain relatively thin (Figure 2b). After 540 min aging, nanoplates with regular shape and increased thickness can be obtained. A single hexagonal FeS$_2$ nanoplate with the HRTEM...
FeS₂ nanostructures, we have fabricated and tested the band to the conduction band. Given the layered nature of the distinct features are direct transitions from deep in the valence identified as the first excitonic transition does not change, only the absorption spectra as the temperature is increased. Under temperature but at longer aging time. Both of the two the other one can happen at a relatively low reaction temperature from small size to larger ones at high reaction temperature, and forming an irregular thick nanoplate. It should be noted that smaller, more stable crystalline lattice energy compared to the variation of nanoplate shape results from the different dimension of FeS₂ growth is through direct nanoplates growth can be obtained through two different paths. One path of two-dimensional FeS₂ growth is through direct nanoplates growth from small size to larger ones at high reaction temperature, and the other one can happen at a relatively low reaction temperature but at longer aging time. Both of the two pathways enable the formation of well-defined, regular FeS₂ nanoplates.

The photoabsorption behavior of FeS₂ nanoplates is essential for their optoelectronic applications. The absorbance spectra of FeS₂ nanoplates are shown in Figure 3. Panels a and b in Figure 3 show the sequence of optical absorption spectra of FeS₂ nanoplates with varied reaction temperatures and aging time. In the Figure 3a, the apparent absorption versus photon energy increased by the pump, which could be induced by free-carrier absorption. The signal decays exponentially, with a time constant of 2.4 ± 0.5 ps. After the transient time of about 20 ps, a positive steady signal is detected. It is likely induced by the heating effect of the pump pulse. By comparing the results from different pump fluences, we found that the signal is proportional to the pump fluence, as shown in Figure 4c. Because the injected carrier density is proportional to the pump fluence, we conclude that the signal is proportional to the carrier density. Hence, the measured decay time can be attributed to the carrier lifetime. The ultrashort lifetime of several ps is consistent with the low efficiency measured, and shows potential for further improvement since such a short lifetime is likely limited by the sample quality. In fact, similar measurements performed on nanoparticle samples show carrier lifetime of about 200 ps (see the Supporting Information). To further confirm the negative sign of the differential transmission signal, we have also detected the differential reflection signal,
and found it is positive during early probe delays. Other features of the signal are similar to the differential transmission, as shown in panels b and d in Figure 4.

4. CONCLUSIONS

In summary, we have demonstrated a novel approach for the colloidal synthesis of pyrite FeS$_2$ nanoplates. The FeS$_2$ synthesis at high reaction temperature and long aging time results in the formation of hexagonal-shaped crystalline nanoplates. Although the nanoplates exhibit photovoltaic behavior with the conjugated polymer P3HT, such hybrid solar cells show the power conversion efficiency of 0.03% with an open circuit voltage of 0.78 V under AM1.5 condition. The solar cells show the power conversion efficiency of 0.03% with an open circuit voltage of 0.78 V under AM1.5 condition. The synthetic protocol is under investigation (Supporting Information, Figure S2), and the results will be reported elsewhere.

**REFERENCES**