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Synthesis of flake-like crystals by a hydrothermal process

Liangbao Yang[1,2], Yuhua Shen*[1], and Anjian Xie[1]

[1] School of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui 230039, P. R. China
[2] The Key Laboratory of biomimetic Sensing and Advanced Robot Technology, Anhui Province, Institute of Intelligent Machines, Chinese Academy of Science, Hefei, 230031 Anhui, P. R. China

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In this study, a hydrothermal method for formation of flake-like nanocrystals is described. This approach with appropriate surfactant CTAB can be successfully synthesized of compound, noble metals, and semiconductors simple substance, such as lead sulfate, gold and selenium. The products were characterized by SEM image and XRD pattern. The results show that TSA acting as a new class of inorganic scaffolds for the synthesis of materials in crystal engineering and composites design for different applications is versatile reactor and may be extended to the creation of other highly novel inorganic structures with applications in catalysis, novel optical materials and other fields.

1 Introduction

Recent advances have demonstrated that it is possible to control the growth processes of nanocrystals and their nanoarchitectures with complex forms and different compositions [1, 2]. The presence of organic additives or surfactants [3–6], self-assembled organic superstructures and templates with complex functionalization patterns [7] can direct the growth of inorganic crystals with controlled morphologies and architectures [8]. Searching for new strategies toward one dimensional nanosized building blocks has attracted intensive interest because of their distinctive geometries, novel physical and chemical properties, and potential applications in nanodevices [9, 10]. These systems are expected to display the size and shape dependent optical, magnetic, and electronic properties [11-15].

Utilizing Tungstosilicate acid ($H_4SiW_{12}O_{40}$, TSA) ion to synthesize nanoparticles is an important method. TSA ions form a subset of polyoxometalates of keggin structure. It is well known that Keggin ions undergo stepwise multielectron redox processes without a structural change [16]. They may be reduced electrolytically, photochemically and chemically (with suitable reducing agents). They are a large category of metal oxygen cluster anions with well-defined structures and properties and have diverse applications in the fields of analytical chemistry, biochemistry and solid state devices, and have been used as antiviral and antitumor reagents. Their redox chemistry is characterized by their ability to accept and release a certain number of electrons, in distinct steps, without decomposition [17]. Recently, we have used TSA as a UV-switchable reducing agent for making Se network [18]. We have also used TSA as a template for different crystals [19-21].

In this study, we report how to selectively synthesize low dimensional materials (including $PbSO_4$, Au, and Se) with similar hexahedron flake-like structure in large scale through a simple hydrothermal approach. This approach can be successfully extended further, for the convenient and large-scale synthesis of families of compound, noble metals, and some semiconductors simple substance flake-like materials.

* Corresponding author: e-mail: s_yuhua@163.com

2 Experimental

Tungstosilicate acid ($H_4SiW_{12}O_{40}$), lead oxide (PbO_2), selenious acid (H_2SeO_3), chloroauric acid ($HAuCl_4$), Na_2SO_4, cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfonate (SDS), and isopropanol ($CH_3CH(OH)CH_3$) were all A.R. grade and obtained from Shanghai reagent Co.. All the reagents in the experiment were used as received.

Preparation of $PbSO_4$ particles In a typical experiment, 2 mL of propan-2-ol, 4.78 mg PbO_2 and 20 ml of a 1 mM aqueous solution of Na_2SO_4 were added to a 20 mL of 1 mM aqueous solution of TSA under continuous stirring. The solution was transferred into a 50 mL capacity stainless Teflon-lined autoclave after stirring for 30 min at room temperature. The autoclave was sealed, maintained at 160 °C for 6 h, and then allowed to cool to room temperature naturally. The obtained precipitates were centrifuged, washed several times using distilled water and absolute ethanol, and dried in a vacuum at 60 °C for 6 h. The process of corresponding experiments adding different surfactants to reaction solution is similar to above experiments.

Preparation of Se particles 20 mL of 1mM aqueous deaerated solution of tungstosilicate acid was taken in a test tube along with 20 mL of 1 mM aqueous deaerated solution of H_2SeO_3 and 2 mL of propan-2-ol. The solution was transferred into a 50 mL capacity stainless Teflon-lined autoclave. The next steps are similar to above.

Preparation of Au particles 20 mL of 1mM aqueous deaerated solution of tungstosilicate acid was taken in a test tube along with 20 mL of 1 mM aqueous deaerated solution of $HAuCl_4$ and 2 mL of propan-2-ol. The solution was transferred into a 50 mL capacity stainless Teflon-lined autoclave. The next steps are similar to above. XRD analysis of drop-coated films of the Au solution on glass substrates was carried out on a MAP18AHF instrument (Japan MAC Science Co.). SEM measurements were performed on a Leica Stereoscan-440 scanning electron microscope.

3 Results and discussion

A representative Keggin structure $(SiW_{12}O_{40})^{4-}$ was chosen to study the reaction between $[SiW_{12}O_{40}]^{5-}$ and PbO_2, $HSeO_3^-$ and $AuCl_4^-$ ions. The $(SiW_{12}O_{40})^{5-}$ ion was obtained by heated of a deaerated isopropanol/ $(SiW_{12}O_{40})^{4-}$ aqueous solution, in the presence of, for instance, isopropanol as a sacrificial reagent [22] [Eq. (1)].

$$2(SiW_{12}O_{40})^{4-} + (CH_3)_2CHOH \rightarrow 2(SiW_{12}O_{40})^{5-} + (CH_3)_2C{=}O + 2H^+ \quad (1)$$

After hydrothermal treatment, the PbO_2, $HSeO_3^-$ and $AuCl_4^-$ ions can be reduced to $PbSO_4$, Se, and Au [Eq. (2)].

$$2[SiW_{12}O_{40}]^{5-} + PbO_2 + 4H^+ + SO_4^{2-} \rightarrow PbSO_4\downarrow + 2[SiW_{12}O_{40}]^{4-} + 2H_2O \quad (2a)$$

$$4(SiW_{12}O_{40})^{5-} + HSeO_3^- + 5H^+ \rightarrow 4(SiW_{12}O_{40})^{4-} + Se + 3H_2O \quad (2b)$$

$$(SiW_{12}O_{40})^{5-} + AuCl_4^- \rightarrow (SiW_{12}O_{40})^{4-} + Au + 4Cl^- \quad (2c)$$

Furthermore TSA ions as oxidizing agent or reducing agent can be cyclically utilized via Eq. (1) and Eq. (2). Figure 1 shows the X-ray diffraction (XRD) patterns of the as-prepared products after hydrothermal treatment. All diffraction peaks shown in figure 1A can be indexed as a pure primitive orthorhombic lattice of $PbSO_4$ (anglesite) with cell parameters a = 6.97, b = 8.47, and c = 5.39 Å, which are in good agreement with those reported in the literature (JCPDS card number 36-1461). The XRD pattern recorded from a drop-coated film of the Se sample on a glass substrate is shown in figure 1B. All of the strong and sharp reflection peaks can be readily indexed to a single phase of trigonal-structured selenium (t-Se, space group P3121 (152) with infinite, helical chains of selenium atoms packed parallel to each other along the c-axis), with cell parameters a = 0.4367 nm and c = 0.4959 nm. These values are consistent with the values reported in the literature (JCPDS Cards No. 86-2246). The XRD pattern recorded from a drop-coated film of the Au sample on a glass substrate is shown in figure 1C. The measurement has proven the successful synthesis of face-centred cubic structured Au (JCPDS 4-784). The sharp and strong diffraction peaks indicate the high crystallinity of the particles.

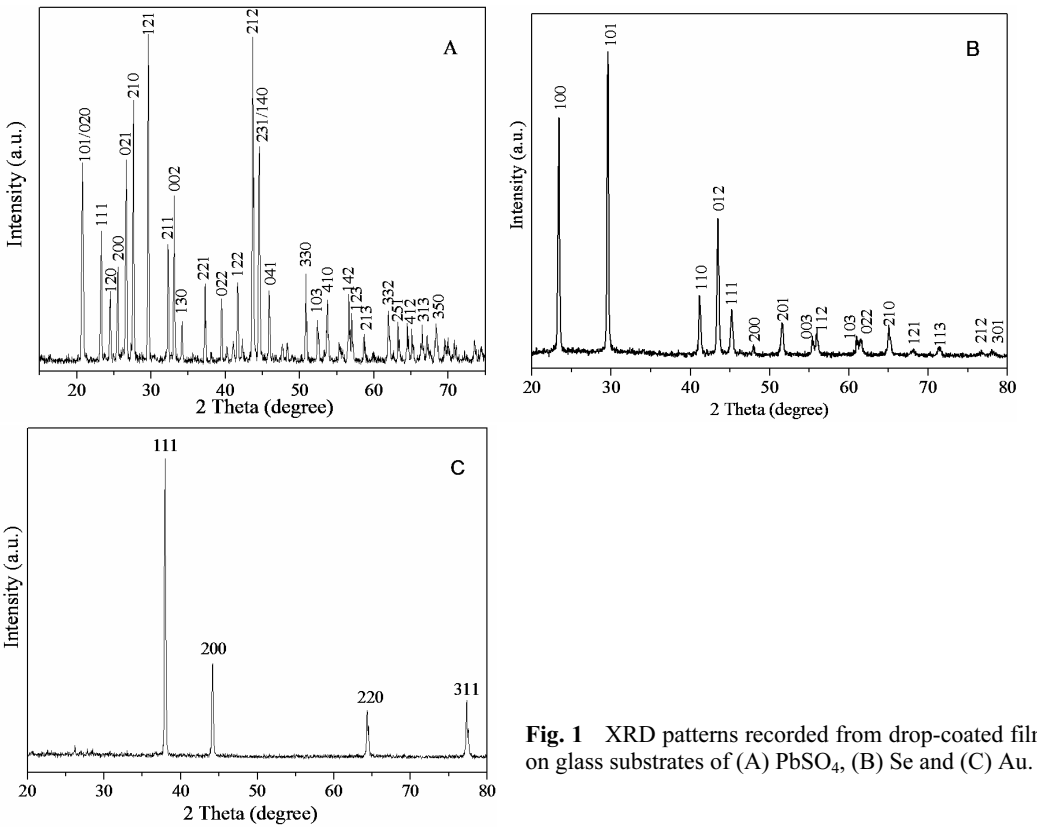

Fig. 1 XRD patterns recorded from drop-coated films on glass substrates of (A) $PbSO_4$, (B) Se and (C) Au.

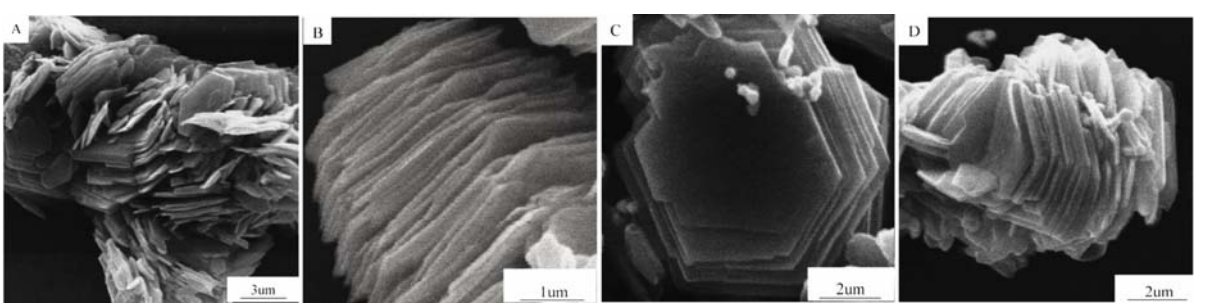

Fig. 2 SEM images of the $PbSO_4$ synthesized by hydrothermal treated method with CTAB (0.1M).

Figure 2A shows Scan electron microscope (SEM) images of typical samples of $PbSO_4$ crystals. The image reveals that large quantity crystals were achieved using this approach. The borders of the flakes are rough (Fig. 2B). Most of the flakes are hexagons (Fig. 2C). The structures of the surface are quite flat and smooth (Fig. 2C). Average thickness is about 125 nm and length of side of hexagons is about 3 μm. Some of the flakes are vertical (Fig. 2D). The surfactants were found to significantly affect the shape of the particles. When the other conditions are kept the same but decreased the concentration of CTAB (0.01 M), there are many large scales hexagon flakes and a lot of little irregular $PbSO_4$ crystals are achieved. When the other conditions were kept constant but with added SDS instead of CTAB, at concentration with 0.1 M, a lot of short rods are obtained. Different from the particles obtained in the solution without surfactant, the sample of the product consists of homogeneous polyhedron of side 0.3–1.2 mm at the panel. Most of the surfaces of the polyhedrons are smooth. All these show that the surfactant CTAB plays an important role in controlling the morphology of $PbSO_4$. This observation can be explained CTAB is adsorbed on specific facets of the $PbSO_4$ crystal, when the amount of CTAB is appropriate. In contrast, the no-adsorbed facets of crystals will grow rapidly [23].

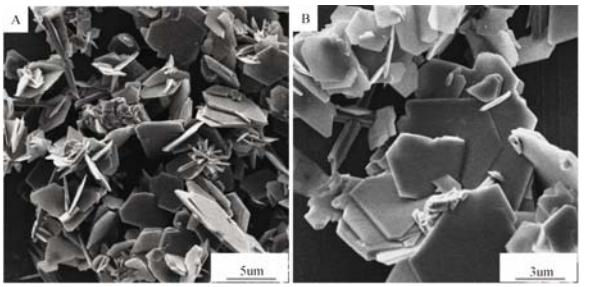

Fig. 3 SEM images of the Se synthesized by hydrothermal treated method with CTAB (0.1M).

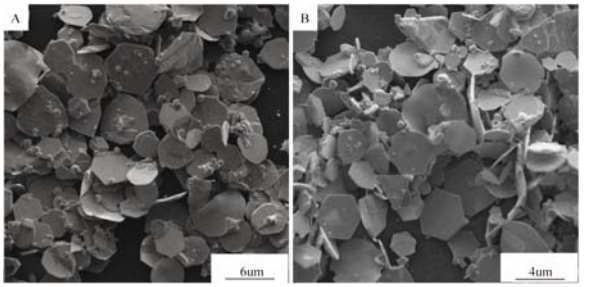

Fig. 4 SEM images of the Au synthesized by hydrothermal treated method with CTAB (0.1M).

Figure 3 shows the SEM images of the Se particles synthesized by reaction of hydrothermal treatment with CTAB (0.1 M). Most of the products are hexagons. The length of side is 2-6 μm and the thickness is 200-500 nm. From figure 3B, we observe that the surface is smooth and most of the border is straight. When the concentration decreases to 0.01 M, there is little effect to the morphology of the Se crystal. When the other conditions are kept constant but with addition of 0.1 M SDB instead of CTAB, a lot of microrods and microbands are obtained. At the reaction conditions without any surfactant, spherical t-Se particles were formed and some of the spheres were broken, showing an interesting core-shell structure. All above observations can be explained that CTAB or SDB is adsorbed on specific facets of the Se crystal. In contrast, the no-adsorbed facets will grow rapidly. When the concentration of CTAB is too low, there will be no adsorbed surfactant on all of the facets and it loses the ability to control the morphology of the growing crystals.

Figure 4 shows the SEM images of the Au particles synthesized by reaction of hydrothermal treatment with CTAB (0.1 M). Plenty of flakes can be observed. Most of the flakes are hexagons. The length of side is 3-5 μm. the thickness of the flakes is about 150-400 nm. There are some little particles on the surface of the flake. These particles may be little Au particles, indicating that the larger particles (flakes) grow from the small ones. While the Au particles synthesized by reaction of hydrothermal treatment without CTAB, the images are very different. Many compactly combined spherical urchin-like Au architectures are seen on the surface of the substrate. The sphere is built up by many interleaving slightly bending flakes with the thickness of 80–150 nm, which entangle together to behave like a network in the sphere. The urchin-like morphological Au forms as the interleaving thin flakes aggregate into microspheres due to minimizing the interfacial free energy to the lowest state. At the other hand, the surfactant CTAB is proved to be very important in forming flake-like structure Au.

Based on the above analyses, we conclude that the surfactants significantly affect the shapes of the particles. The shape when the surfactants were added was completely different from that observed without surfactants. The surfactant of CTAB plays an important role in controlling the morphology of $PbSO_4$, Se and Au. Though the reasons why form hexagons flake-like superstructures in TSA system are not clear yet.

4 Conclusions

In conclusion, we have demonstrated a simple hydrothermal synthesis of unique hexagon flake-like crystals in large quantities with using the same surfactant in TSA solution. This approach with appropriate concentrate surfactant CTAB can be successfully synthesized of lead sulfate, gold and selenium. TSA is been proven as a soft template in the experiments. This strategy shows great potential in the synthesis of flake-like materials.

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