钨硅酸银纳米晶:形貌可控合成与表征

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摘要:通过聚电解质(表面活性剂)作为导向剂的液相合成路线,合成了多种形貌的多金属氧酸盐纳米晶,包括纳米球,纳米带,纳米片,纳米立方体,六角纳米粒子,三角纳米粒子,雪花状纳米粒子。形状独特的六角形空心纳米粒子也通过相似的方法合成出来。在反应过程中,银离子通过配位作用吸附在聚电解质的组装结构上,通过与氮原子或氧原子的配位作用被定位在聚电解质上,从而导致规则形貌的多酸纳米粒子的形成。结果表明,产物的形貌极大地取决于表面活性剂的组装结构和它们与反应物间的配位作用。

关键词:纳米粒子;多金属氧酸盐;可控合成;聚电解质
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$Ag_4SiW_{12}O_{40}$ Nanocrystals: Shape-controlled Synthesis and Characterization

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Abstract: A large-scale synthesis of Polyoxometalates (POMs) crystalline nano-ball, -belt, -flake, -cube, -hexaprism, trigonal and snowflake-like nanocrystals was performed by a solution-phase route using polyelectrolyte (surfactant) as a structure modifier. The uniform hollow hexangular nanoparticles were also obtained by a similar solution-phase route. In this approach, Ag^+ introduced into the solution-phase system was adhered to the polymer assembly structure by the coordination reaction. During the reaction, the coordination reaction between Ag^+ and N or O atom makes Ag^+ located on the aggregates of the surfactant (polyelectrolyte), which directs the formation of regular-shaped POMs nanoparticles. The results suggest that the morphology of the product is largely dependent on the assembly structure of the surfactant and the coordination between the polyelectrolyte (surfactant) and the reactant.

Key words: regular-shape; nanoparticles; polyoxometalates; controllable-synthesis; polyelectrolyte

Nanocrystals are of great fundamental and practical importance owing to the dependence of their novel properties on special sizes and shapes. The properties of nanocrystals depend not only on their composition, but also on their structure, phase, shape, size, and size distribution. Furthermore, the architectural control of nanosized materials with well-defined shapes is important for the success of "bottom-up" approaches towards futures nanodevices[1~3]. The intrinsic properties of inorganic nanocrystals are mainly determined by their size, shape, composition, crystallinity and structure (solid versus hollow). In principle, it is possible to control the diameters of each kind of the nanocrystals properly so that their properties can be tuned accordingly. Therefore, the exploration of synthesis method for controlling the sizes and shapes of nanocrystals becomes one of the major focuses for the development of synthesis

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chemistry[4~10]. Many efforts have been concentrated on the preparation of nanomaterials, including template-assisted [11], vapor-liquid-solids (VLS)-assisted [12], and electrochemical processes[13]. Recently, the introduction of polyelectrolyte (surfactant) as a structure modifier to induce the formation of nanostructures has provided a relatively simple and powerful method for controlling the size, shape and surface texture of nanoparticles and nanorods[14~16].

POMs have received increasing attention in the domain of materials science attributing to their chemical, structural and electronic versatility. As one of the typical inorganic metal oxide clusters[17~23], POMs can be regarded as one of the extremely versatile inorganic entities for the construction of functionally active solids and the favorite candidates for nano-sized building blocks. Numerous well-characterized POMs are available, and then it is extremely significant to the preparation of POMs nanocrystals in order to explore their novel properties. Size, shape, and structure control of POMs nanoparticles is technologically needed because of the tight correlation between these parameters and optical, electrical, and catalytic properties[24~27].

In this paper, we report the large-scale synthesis of POMs crystalline nano-ball, -belt, -flake, -cube, -hexaprism, trigonal and snowflake-like nanocrystals and uniform hollow hexangular nanoparticles based on the assembly structure and coordination effect of polymer.

1 Experimental

The SEM images were obtained on a JEOL JSM-840 operated at 20 kV. The XRD patterns were recorded on a Rigaku D/max 2500V PC diffractometer with graphite monochromatized Cu $K\alpha$ radiation (λ= 0.154 06 nm). JEM-2010 transmission electron microscope was used to examine the morphologies of the POMs nanocrystals.

In this work, all reagents were purchased from Beijing Chemical Reagent (Beijing, China). All reagents were of analytical grade and used as received. A general preparation procedure of $Ag_4SiW_{12}O_{40}$ nanocrystals was as follows. 0 .25 g $AgNO_3$ and 1 g $H_4SiW_{12}O_{40}\cdot nH_2O$ were dissolved in two triton-X 100/H_2O systems with w of 1 and 1.5 ($w=V_{\text{triton-X 100}}/V_{H_2O}$), respectively. The two systems were then mixed and four times of ethanol in volume were added in the system. Large amount of white flocculent precipitates contained POMs nanoballs was formed. The white precipitate was separated by centrifuge, the solid was washed with ethanol and dried in air at 50 ℃ for 1 h. The yield was 60%~80%. Very similar approaches were employed to prepare the $Ag_4SiW_{12}O_{40}$ nano-hexaprism, and hollow nanohexaprism: (PVP (Poly Vinyl Pyrrolidone, $M\approx$55 000)-$AgNO_3$ solution (PVP / H_2O=1∶4 (V/V), C_{Ag^+}: 0.1 and 10^{-3} mol·L^{-1}) and PVP-$H_4SiW_{12}O_{40}nH_2O$ solution (PVP/H_2O=1∶4(V/V)) mixture was used, the precipitates were washed with ethanol and then dried in air. The yield was 50%~70%. Another system used was PAA (polyacrylic acid, $M\approx$ 1 000) /H_2O =1∶4 (V/V) and PAA-$H_4SiW_{12}O_{40}\cdot nH_2O$ solution (PAA/H_2O=1∶4 (V/V), C_{Ag^+} : 0.08, 0.03, and 10^{-3} mol·L^{-1}) mixture. The yield was 60%~70%.

2 Results and discussion

2.1 Assembly structure and morphology

In our previous study, PEG/water system, the chain-like structure of PEG assembly in water was used for the controllable synthesis of POMs 1D nanocrystals with various diameters and lengths, nano/microtubes and 3D ordered-tube system. Typical $Ag_4SiW_{12}O_{40}$ hollow particles obtained from PEG-200/H_2O system have an approximate hollow spheroid structure. The aggregates of PEG 200 in water are so soft that they cannot be the template for the synthesis of POMs nanorods but lead to the formation of hollow particles due to their soft and crimped characteristics [4]. A similar hollow spheroid structure is also obtained in the PEG-100/H_2O system. In the PEG molecule, as we know, oxygen atom connects two ethylene units. Hydrogen atom with little volume makes the oxygen atom lain in a free chemical environment. The coordination reaction between the oxygen atom and Ag^+ cannot be neglected. Fig.1 shows the SEM images of the belt-like nanocrystals of $Ag_4SiW_{12}O_{40}$ obtained from the PEG-400/H_2O (2.5 mL/3 mL) system.

Here, Ag^+ adheres to the PEG aggregates due to the weak interaction between Ag^+ and oxygen atoms. The reaction happens in the aqueous phase in the surface of cylinders assembled from many PEG aggregates. Therefore, the nanobelts can also be obtained in PEG/H_2O system. Fig.2 shows the SEM images of the flake-like nanocrystals of $Ag_4SiW_{12}O_{40}$ obtained from the PEG-400/H_2O (2.5 mL / 3~4 mL) system.

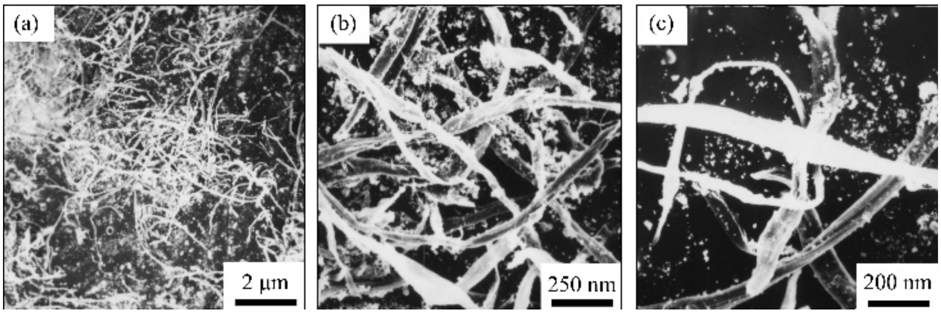

Fig.1　SEM images of the belt-like nanocrystals of $Ag_4SiW_{12}O_{40}$

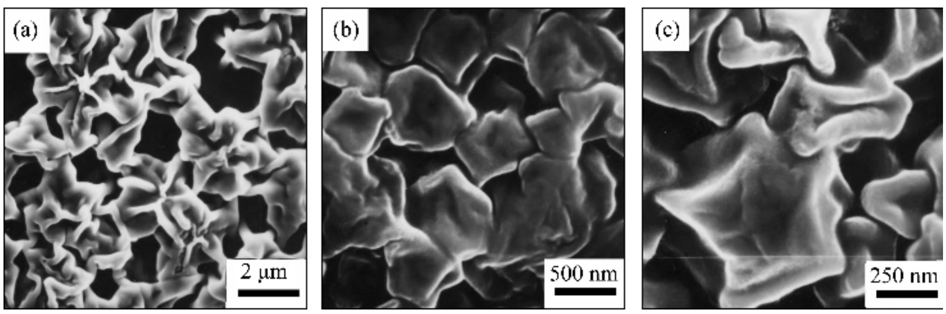

Fig.2　SEM images of the flake-like nanocrystals of $Ag_4SiW_{12}O_{40}$

Synthesis of nanoparticles in Triton-X 100/cyclohexane water-in-oil microemulsions was reported in 1996[28]. Triton-X 100 has a short chain of ethylene oxide units with a large alkyl unit, it is similar to PEG in structure, which makes the assembly structure of Triton-X 100/water different from that of PEG in water. From this we can see that large alkyl units can destroy the ethylene oxide chains assembly structure in water. Then it provides a very good reference system to discuss the contribution of non-ionized surfactant assembly structure in water to the shape control. Monodispersed samples of $Ag_4SiW_{12}O_{40}$ nanoballs are synthesized in large quantities by the reactions of $AgNO_3$ and $H_4SiW_{12}O_{40} \cdot nH_2O$ in the presence of Triton-X 100. The TEM images of $Ag_4SiW_{12}O_{40}$ nanoballs obtained from the triton-X 100/H_2O system are showed in Fig.3. It is a solid spheroid with diameter about 80 nm. So the morphology of the product is largely dependent on the assembly structure of the PEG aggregates in the PEG/H_2O system.

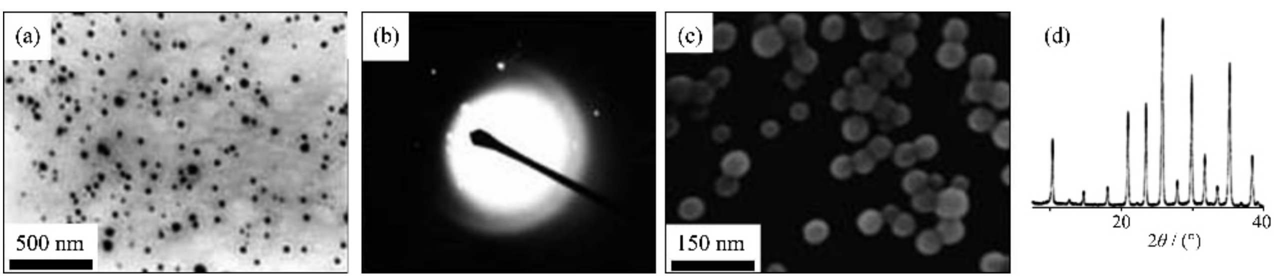

Fig.3　(a) TEM image of $Ag_4SiW_{12}O_{40}$ nanoballs, (b) Electron-diffraction pattern of the nanoballs of $Ag_4SiW_{12}O_{40}$, (c) SEM image of $Ag_4SiW_{12}O_{40}$ nanoballs, (d) XRD patterns of $Ag_4SiW_{12}O_{40}$ nanoballs

2.2 Coordination reaction and morphology

The subsequent experiments suggest that the morphology of the product is mainly dependent on the coordination reaction. Poly Vinyl Pyrrolidone (PVP), cationic polyelectrolytes, with a lot of nitrogen and oxygen atoms exhibit many interesting unique properties in the synthesis of the silver nanocrystals. Many interesting and very important works are based on the coordination reaction between Ag^+ and PVP. It gives us an apocalypse that this coordination reaction may have an influence on the morphology of the products, which are synthesized through the reactions of $AgNO_3$ and $H_4SiW_{12}O_{40}\cdot nH_2O$ in the solution-phase system. At a very low concentration of silver nitrate (about 10^{-3} mol·L^{-1}) the products of $Ag_4SiW_{12}O_{40}$ nanoparticles are cubes. Fig.4a, 4b show the SEM images of the $Ag_4SiW_{12}O_{40}$ nanocubes. The mean edge length of these nanocubes is 250 nm. When the concentration of silver nitrate increases to about 0.1 mol·L^{-1}, the morphology of the product is transferred into hexaprism. Fig.4c, 4d, 5a, 5d show the SEM images of the $Ag_4SiW_{12}O_{40}$ nanohexaprism. Fig.5b gives the TEM image and Electron-diffraction pattern of $Ag_4SiW_{12}O_{40}$ nanohexaprism. The mean edge length of these nanohexaprism is 150 nm. Fig.5c shows the XRD patterns. If the concentration of silver nitrate increases (more than 0.2 mol·L^{-1}), irregular particles with the diameter in the micrometer scale are obtained. It is reasonable that at a low concentration there exists extensive interaction between most of Ag^+ and the PVP polymer. Ag^+ is free in the solution when silver nitrate has a high concentration. So the irregular particles are formed without the strong coordination reaction. Although the fundamental basis of the shape selectivity for this system has still to be further understood, it is important to point out that the

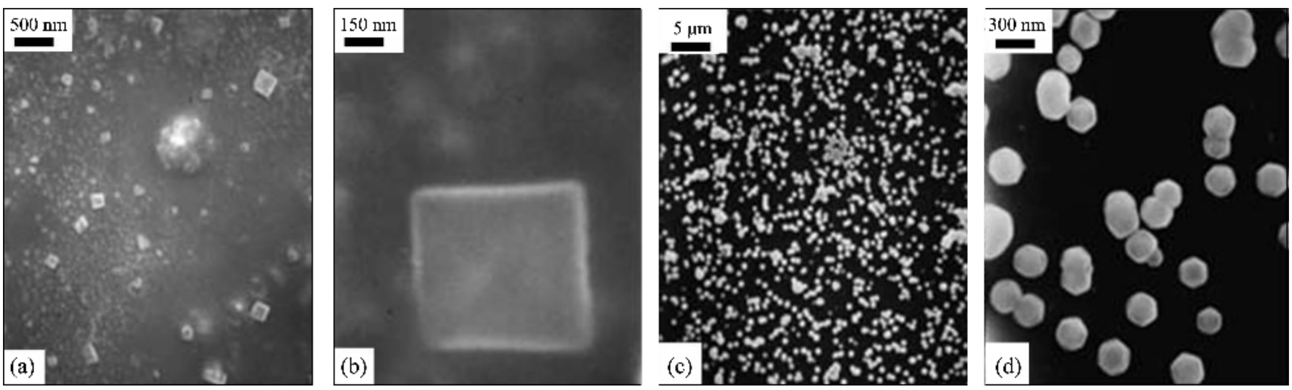

Fig.4 SEM images of $Ag_4SiW_{12}O_{40}$ nanocubes (4a, 4b), and nanohexaprism (4c, 4d)

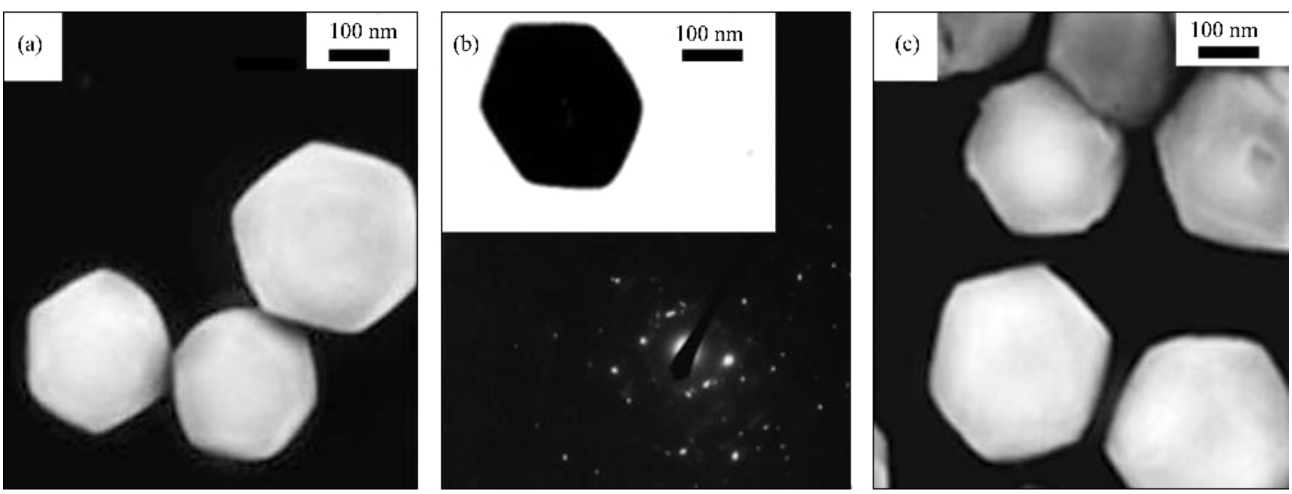

Fig.5 (a, d) SEM image of $Ag_4SiW_{12}O_{40}$ nanohexaprism, (b) TEM image and Electron-diffraction pattern of $Ag_4SiW_{12}O_{40}$ nanohexaprism, (c) XRD patterns of $Ag_4SiW_{12}O_{40}$ nanohexaprism coordination reaction between the polyelectrolyte (surfactant) and the reactant may play a major role in determining the morphology of the $Ag_4SiW_{12}O_{40}$ particles.

Another powerful case is that the $Ag_4SiW_{12}O_{40}$ hollow nanohexaprisms are obtained in the presence of PAA through this solution phase approach. PAA is a kind of anionic surface active agents. A lot of carboxyl units with oxygen atoms exist in the PAA chains. The strong coordination reaction between Ag^+ and PAA is also very important for the morphology of the products. This experiment also suggests that the morphology of the products is tightly related to the reaction conditions. At a very low concentration of silver nitrate (about 10^{-3} mol·L^{-1}), the products of $Ag_4SiW_{12}O_{40}$ nanoparticles are trigonal. Fig.6 shows the SEM images of the trigonal $Ag_4SiW_{12}O_{40}$ nanocrystals. When the concentration of silver nitrate increases to about 0.03 mol·L^{-1}, the morphology of the product is transferred into snowflake-like nanocrystals. Fig.7 shows the SEM images of the $Ag_4SiW_{12}O_{40}$ snowflake-like nanocrystals. Fig.8, a, b and c, exhibit SEM images of a typical sample of $Ag_4SiW_{12}O_{40}$ hollow nanohexaprisms and indicate that large quantity and good uniformity are achieved in this approach provided that the concentration of silver nitrate increases to about 0.08 mol·L^{-1}. The mean edge length of these hollow nanohexaprisms is about 200 nm with homogeneous wall thickness (80 nm). Fig.8d is the XRD pattern. This pattern confirms that the $Ag_4SiW_{12}O_{40}$ hollow nanohexaprisms are crystalline. When the concentration of $AgNO_3$ is increased to the extent that the molar ratio between $AgNO_3$ and the repeating unit of PAA is more than 3.5, the irregular particles are formed without the strong coordination action.

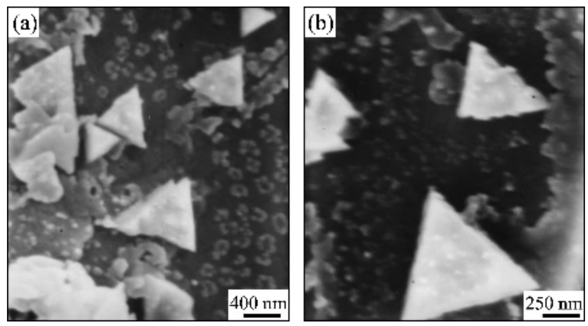

Fig.6 SEM images of the trigonal $Ag_4SiW_{12}O_{40}$ nanocrystals

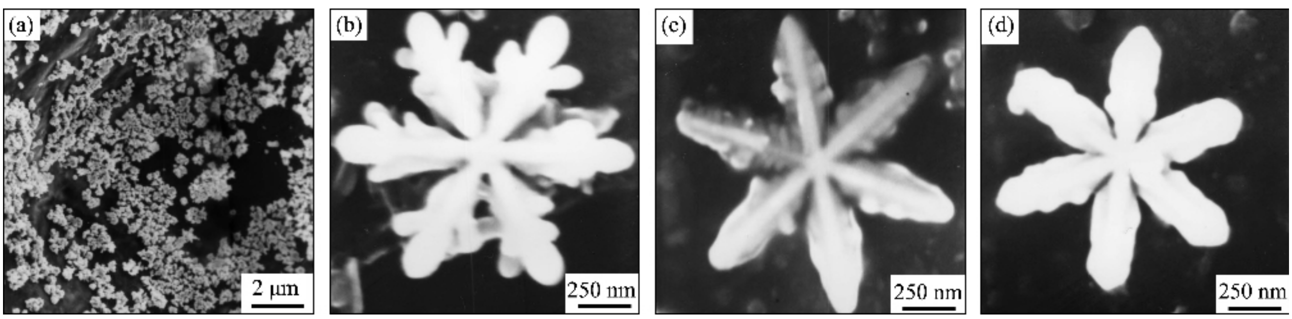

Fig.7 SEM images of the $Ag_4SiW_{12}O_{40}$ snowflake like nanocrystals

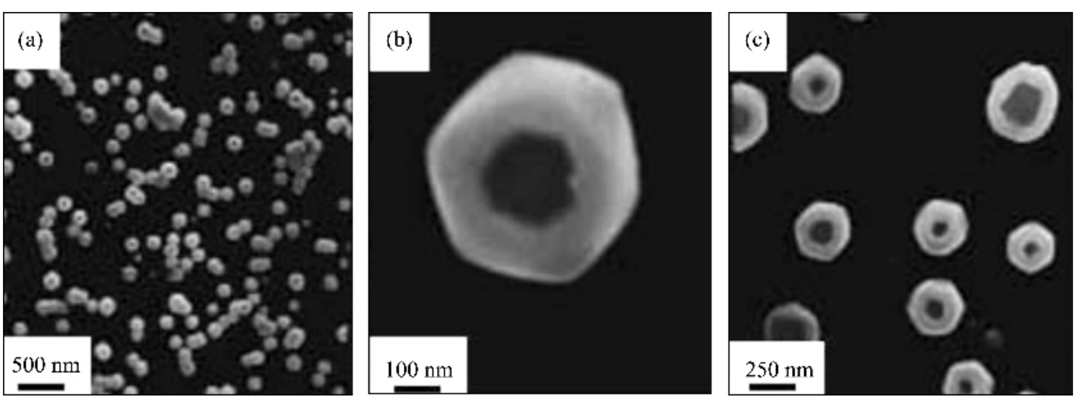

Fig.8 SEM images and XRD pattern of $Ag_4SiW_{12}O_{40}$ hollow nanohexaprisms particles

Elemental analysis results of the white products give the molar ratio of Ag:Si:W=4:1:12. FTIR spectrum exhibits the characteristic peaks at 1 100, 1 011, 970, 919, 882 and 795 cm^{-1}, which are attributed to the $\nu(Si=O_a)$, $\nu(W=O_t)$, $\nu(W\text{-}O_b\text{-}W)$ and $\nu(W\text{-}O_c\text{-}W)$ of Keggin-type structure, respectively. In the hollow nanohexaprisms there exists many very large cavums. These POMs hollow particles would be useful in a rich variety of applications. For instance, they may be suggested or demonstrated as extremely small containers for microencapsulationa process that plays an important role in many areas such as catalysis, delivery of drugs, development of artificial cells and protection of biologically active materials (e.g., enzymes, proteins, or deoxyribonucleic acids, DNAs)[29]. On the other hand, these uniform monodispersed samples of POMs nanoparticles with regular shape may provide an opportunity to realize the construction of complex nano/micro system with multiple functions and can be used as good templates for the synthesis of nanocrystals.

From the above results, we can see that the coordination between Ag^+ and PVP/PAA has a great influence on the form of POMs nanoparticles shapes. Ag^+ is pre-located on PVP/PAA in solution through the coordination reaction between Ag^+ and N, O atoms before the chemical reactions occur, and during the growth of $Ag_4SiW_{12}O_{40}$ nanoparticles the located Ag^+ will adjust and control the shapes of the products. The control experiment suggests that irregular particles are formed without such coordination reaction. Further shape control for other inorganic nanocrystals is undergoing in the similar routes using different polyelectrolyte (surfactant) containing lots of O, N, S atoms.

3 Conclusions

In summary, POMs (inorganic) crystalline nano-belt, -flake, -ball, -cubes, -hexaprism, trigonal and snowflake-like nanocrystals and uniform hollow-structured nanoparticles were obtained through a convenient solution-phase route. It suggests that the morphology of the product is closely related to the assembly structure of the surfactant and the coordination reaction between polyelectrolyte (surfactant) and the reactant.

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References:

[1] Xia Y N, Rogers J A, Paul K E, et al. *Chem. Rev.*, **1999**,**99**(7):1823~1848

[2] Duan X F, Huang Y, Cui Y, et al. *Nature*, **2001**,**409**:66~69

[3] Huang M H, Mao S, Feick H, et al. *Science*, **2001**,**292**:1897~1899

[4] Kang Z H, Wang E B, Jiang M, et al. *Eur. J. Inorg. Chem.*, **2003**,**2**:370~376

[5] Jiang M, Wang E B, Kang Z H, et al. *J. Mater. Chem.*, **2003**,**13**(4):647~649

[6] Shi H T, Qi L M, Ma J M, et al. *J. Am. Chem. Soc.*, **2003**,**125**(12):3450~3451

[7] Puntes V F, Krishnan K M, Alivisatos A P. *Science*, **2001**,**291**:2115~2117

[8] Li M, Schnablegger H, Mann S. *Nature*, **1999**,**402**:393~395

[9] Wang R Y, Yang J, Zheng Z P, et al. *Angew. Chem. Int. Ed.*, **2001**,**40**(3):549~552

[10]Sun Y G, Xia Y N. *Science*, **2002**,**298**:2176~2179

[11]Martin B R, Dermody D J, Resis B D, et al. *Adv. Mater.*, **1999**,**11**(12):1021~1025

[12]Hu J T, Odom T W, Lieber C M. *Acc. Chem. Res.*, **1999**,**32**(5):435~445

[13]Mohamed M B, Ismail K Z, Link S, et al. *J. Phys. Chem. B*, **1998**,**102**(47):9370~9374

[14]Vaucher S, Li M, Mann S. *Angew. Chem. Int. Ed.*, **2000**,**39**(10):1793~1796

[15]Hopwood J D, Mann S. *Chem. Mater.*, **1997**,**9**(8):1819~1828

[16]López-Quintela M A, Rivas J. *J. Colloid Interface Sci.*, **1993**,**158**(2):446~451

[17]Pope M T, Müller A. *Angew. Chem. Int, Ed.*, **1991**,**30**(1):34~46

[18]Müller A, Petters F, Pope M T, et al. *Chem. Rev.*, **1998**,**98**(1):239~272

[19]Rhule J T, Hill C L, Judd D A, et al. *Chem. Rev.*, **1998**,**98**(1):327~358

[20]Coronado E, Gomez-Garcia C J. *Chem. Rev.*, **1998**,**98**(1):273~296

[21]Mizuno N, Misono M. *Chem. Rev.*, **1998**,**98**(1):199~218

[22]Müller A, Shah S Q N, Bogge H. *Nature*, **1999**,**397**:48~50

[23]Müller A, Das S K, Kögerler P, et al. *Angew. Chem. Int, Ed.*, **2000**,**39**(19):3413~3417

[24]Ito T, Inumaru K, Misono M. *Chem. Mater.*, **2001**,**13**(3):824~831

[25]Bi L H, Wang E B, Peng J, et al. *Inorg. Chem.*, **2000**,**39**(4):671~679

[26]You W S, Wang E B, Xu Y, et al. *Inorg. Chem.*, **2001**,**40**(21):5468~5471

[27]Bi L H, Huang R D, Peng J, et al. *J. Chem. Soc., Dalton Trans.*, **2001**,**2**:121~129

[28]Haram S K, Mahadeshwar A R, Dixit S G. *J. Phys. Chem.*, **1996**,**100**(14):5868~5873

[29]Lu Y, Yin Y D, Xia Y N. *Adv. Mater.*, **2001**,**13**(4):271~274