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# Starlike nanostructures of polyoxometalates $K_3[PMo_{12}O_{40}]\cdot nH_2O$ synthesized and assembled by an inverse microemulsion method†

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**In a nonionic inverse microemulsion system, surfactant ($C_{12–18}EO_9$)/cyclohexane/water, heteropolyanions $[PMo_{12}O_{40}]^{3-}$ react with $K^+$ to form $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods and assemble as three-dimensional starlike nanostructures.**

Polyoxometalates (POMs) constitute a significant class of inorganic compounds with potential applications in catalysis,[1] conductivity,[2] molecular electronics, photoelectronic and electronic devices.[3] Among a wide variety of POMs those belonging to the so-called Keggin series are of the most importance for recent applications. They include heteropolyanions $XM_{12}O_{40}{}^{x-8}$ where X is the central atom ($Si^{4+}$, $P^{5+}$, *etc*.), *x* is its oxidation state, and M is the metal ion ($Mo^{6+}$, $W^{6+}$, *etc*.).[4] Of great technological interest is the photochemistry and electrochemistry of the Keggin-type POMs; they can return to their original state either thermally, upon irradiation with light of a frequency corresponding to the induced absorption, or electrochemically, upon reversing the polarity of the externally applied electric field.[3,5] In recent years, POM nanostructural materials have attracted increasing attention owing to their remarkable properties.[6–12] Previous reports, however, have rarely focused on the fabrication and assembly of one-dimensional POMs, which may play a critical role in developing nanotechnologies related to POMs, such as photoelectric switches at the nano-scale level. Herein we report the first effort to synthesize a three-dimensional starlike structure of POM ($K_3[PMo_{12}O_{40}]\cdot nH_2O$) nanorods using an inverse microemulsion method.

A nonionic inverse microemulsion system, surfactant/cyclohexane/water, was selected for this study. The surfactant used in the experiment was chemically pure $C_{12–18}$ fatty alcohol polyoxyethylene(9) ether ($C_{12–18}EO_9$, also referred as AEO-9), which was purchased from JiLian (JiLin) Petrochemicals Ltd. (China). All the other chemicals (of analytical grade) were also commercially available. The $K_3[PMo_{12}O_{40}]\cdot nH_2O$ starlike nanostructure was synthesized as follows: 5 ml surfactant ($C_{12–18}EO_9$) was mixed with both 40 ml cyclohexane and 0.5 ml *n*-amyl alcohol in a beaker. Then 1 ml $H_3[PMo_{12}O_{40}]$ aqueous solution (0.01 M) was added dropwise into this beaker to obtain solution 1. Meanwhile, solution 2 was prepared following the same procedure as solution 1, except that 0.01 M $H_3[PMo_{12}O_{40}]$ was replaced by 0.05 M KBr. Both solution 1 and solution 2 were stirred continuously until clear microemulsion solutions were observed. A greenish-yellow precipitate was formed gradually after mixing solution 1 with solution 2 under slow stirring. The elemental composition of the greenish-yellow product, including K, P, Mo and O, was unambiguously determined by Auger electron spectroscopy (AES) using a PHI Model 660 spectrometer (the AES pattern is deposited in the ESI†). Accordingly, the chemical reaction of heteropolyanions ($[PMo_{12}O_{40}]^{3-}$) and $K^+$ in the water pool of the inverse microemulsion can be expressed by eqn. (1):

$$3\,K^+ + [PMo_{12}O_{40}]^{3-} \rightarrow K_3[PMo_{12}O_{40}]\downarrow \qquad (1)$$

In our preliminary experiments, the volume ratio of the surfactant ($V_s$) to water ($V_w$) was varied to evaluate the influence of preparation conditions on the nanostructure formation. Mixtures of nanoparticles and irregular nanorods were observed when $V_s/V_w$ was 2.5, while slice shaped products were synthesized when the surfactant/water volume ratio was increased to 7.5 (corresponding TEM morphologies are given in ESI†). High yields of (>95 wt%) and uniform $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods, with diameters of *ca*. 60–90 nm and lengths of *ca*. 400–700 nm, were obtained for $V_s/V_w$ values of 5.0. These results indicate that the shape of the $K_3[PMo_{12}O_{40}]\cdot nH_2O$ products depends on the ratio of $V_s$ to $V_w$, and uniform nanorods can be prepared with good reproducibility using a suitable $V_s/V_w$ range.

A LEO1530 SEM system was employed for the field-emission scanning electron microscopy (FE-SEM) analyses. As shown in Fig. 1, a typical FE-SEM image of the original greenish-yellow product without additional pretreatment, one can observe several nanorods linked to each other at one end to form a vivid star with a size of about 0.8–1.3 μm. The nanorods in each star are approximately equivalent in length, though the radii of the two stars shown in the Fig. 1 are markedly different (*ca*. 400 and 600 nm, respectively). The junction of the star seems to be weak as seen by the visible split in the center. This weak junction might lead to the collapse of the starlike structure, which would result in the appearance of some unattached nanorods in the FE-SEM image. The formation mechanism of the starlike nanostructure remains to be investigated.

Transmission electron microscopy (TEM) images were taken using a JEM-100CXII TEM instrument. Owing to the interference of the surfactant left in the products, the TEM images were always dark and blurred if the original greenish-yellow precipitate was not pretreated to remove the surfactant. Accordingly, we washed the products using absolute ethanol, followed by centrifugating to remove the surfactant. This pretreatment procedure was repeated ten times before the TEM analyses. As shown in Fig. 2, a high yield (>95 wt%) and

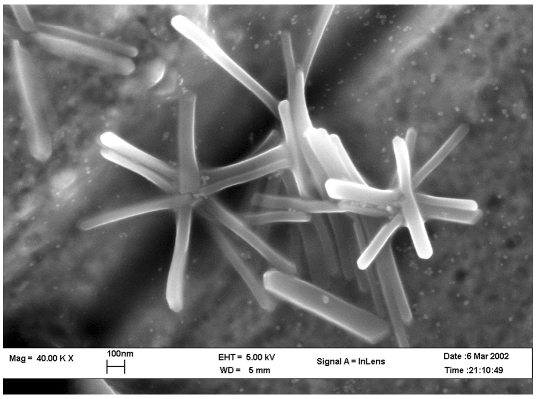

**Fig. 1** Typical FE-SEM image of the $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanostructure, scale bar: 100 nm.

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† Electronic supplementary information (ESI) available: Auger spectrum, TEM images and IR spectrum of surfactant. See http://www.rsc.org/suppdata/cc/b2/b205089g/

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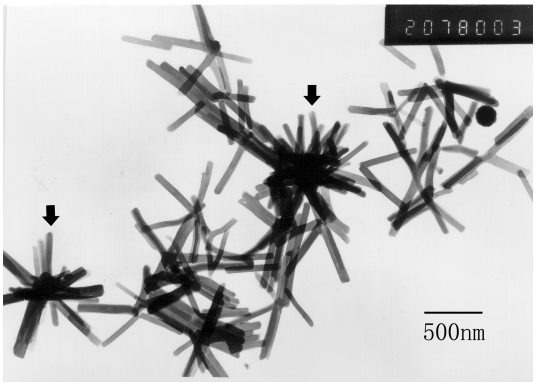

**Fig. 2** Typical TEM image of the $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods.

uniform $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods, with diameter ranging from 60 to 90 nm and length of *ca.* 400–700 nm, are observed. Most starlike nanostructures, however, were destroyed during the pretreatment process and only a few $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods exhibited the original star arrangement in the TEM image.

The nanorod products pretreated *via* ethanol washing were further investigated by IR and XRD analyses, carried out on a Nicolet AVATAR FT-IR spectrometer with KBr pellets and a Rigaku DMAX/RC X-ray diffractometer using Cu-K$\alpha$ radiation ($\lambda$ = 0.154178 nm), respectively. As shown in Fig. 3, the IR spectrum of the $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods matches well with the standard spectrum observed in macro-scale $K_3[PMo_{12}O_{40}]\cdot nH_2O$, with the exception of the peaks in the region 1100–1400 cm$^{-1}$ a contribution of which originates from the little surfactant remaining in the nanorod surfaces (IR spectrum of the surfactant is provided in the ESI†). There are four characteristic IR bands within the 600–1100 cm$^{-1}$ region, reflecting the different vibrations of oxygen atoms in the Keggin-type structure $[PMo_{12}O_{40}]^{3-}$: 4 $O_i$ (internal oxygen connecting P and Mo), 12 $O_e$ (edge-sharing oxygen connecting Mo), 12 $O_c$ (corner-sharing oxygen connecting $Mo_3O_{13}$ units), and 12 $O_t$ (terminal oxygen bonding to 1 Mo atom).[13] The XRD pattern (Fig. 4) shows diffraction peaks corresponding to cubic $K_3[PMo_{12}O_{40}]\cdot 4H_2O$ phase (JCPDS No. 09-0408), and these peaks are all indexed. These results indicate that the heteropolyanions in the as-prepared nanorods retain their original Keggin-type molecular structure.

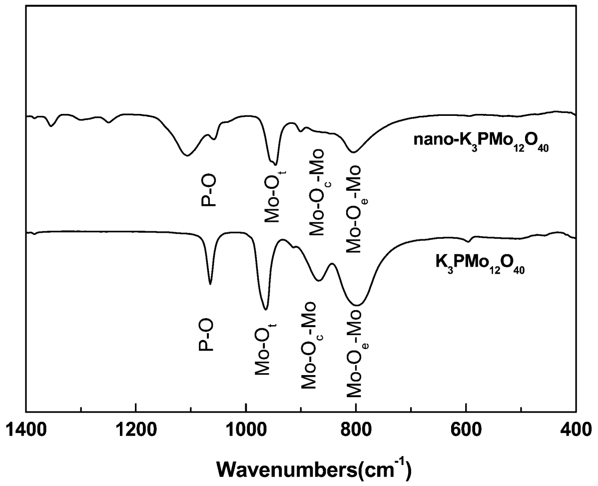

**Fig. 3** IR spectra of $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nano- and macro-scale samples.

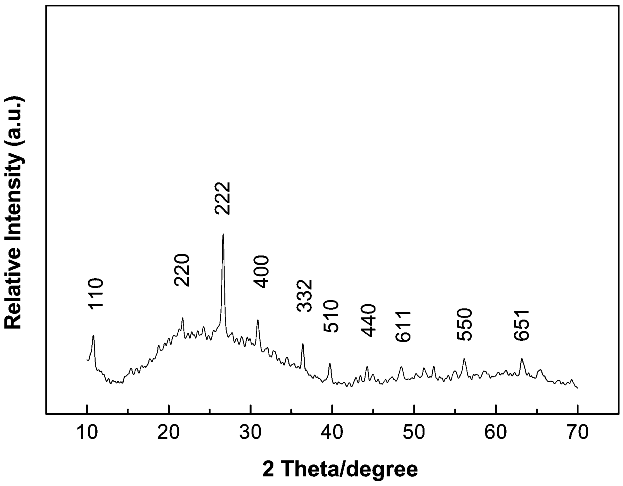

**Fig. 4** XRD pattern of the $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods.

Our ongoing research shows that $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods prepared using the reverse micelle method are not unique and the proposed method is widely applicable for the synthesis of other POMs. We have conducted similar experiments with $K_4[SiW_{12}O_{40}]\cdot nH_2O$ and $K_3[PW_{12}O_{40}]\cdot nH_2O$; the corresponding nanorods were obtained in high yields and the nanorods were of uniform dimensions.

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## Notes and references

1 (*a*) I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171; (*b*) N. Mizuno and M. Misono, *Chem. Rev.*, 1998, **98**, 199; (*c*) E. F. Kozhevnikova, E. G. Derouane and and I. V. Kozhevnikov, *Chem. Commun.*, 2002, 1178.

2 (*a*) M. Sadakane and E. Steckhan, *Chem. Rev.*, 1998, **98**, 219; (*b*) I. A. Weinstock, *Chem. Rev.*, 1998, **98**, 113.

3 (*a*) T. Yamase, *Chem. Rev.*, 1998, **98**, 307; (*b*) Y. H. Guo, Y. H. Wang, C. W. Hu, Y. H. Wang, E. B. Wang, Y. C. Zhou and S. H. Feng, *Chem. Mater.*, 2000, **12**, 3501.

4 I. V. kozhevnikov, *Catal. Rev.-Sci. Eng.*, 1995, **37**, 311.

5 R. A. Prados and M. T. Pope, *Inorg. Chem.*, 1976, **15**, 2547.

6 T. Ito, K. Inumaru and M. Misono, *Chem. Mater.*, 2001, **13**, 824.

7 C. Sanchez, G. J. D. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chem. Mater.*, 2001, **13**, 3061.

8 L. Xu, E. B. Wang, Z. Li, H. Y. Zhang and C. Qin, *Chinese Chem. Lett.*, 2001, **12**, 1127.

9 L. Cheng and J. A. Cox, *Chem. Mater.*, 2002, **14**, 6.

10 H. Murakami, T. Kozeki, Y. Suzuki, S. Ono, H. Ohtake, N. Sarukura, E. Ishikawa and T. Yamase, *Appl. Phys. Lett.*, 2001, **79**, 3564.

11 A. Muller, E. Krickemeyer, H. Bogge, M. Schmidtmann, P. Kogerler, C. Rosu and E. Beckmann, *Angew. Chem., Int. Ed.*, 2001, **40**, 4034.

12 D. G. Kurth, P. Lehmann, D. Volkmer, A. Muller and D. Schwahn, *J. Chem. Soc., Dalton Trans.*, 2000, **21**, 3989.

13 C. Rocchicciolideltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207.