

Preparation of a New Polyoxometalate-based Nanoparticles

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Abstract: Polyoxometalates (POMs) α -K₈H₆ [Si₂W₁₈Ti₆O₇₇] (Si₂W₁₈Ti₆) loaded starch nanoparticles have been prepared and structurally characterized by elemental analyses, IR spectra and ²⁹Si spectroscopy. The particle size of Si₂W₁₈Ti₆/starch was estimated by a Transmission electron microscope (TEM) and a 1000HSA MALVERN Zetasizer instrument. The result shows that the polyoxometalate retained the parent structure after encapsulated by starch microspheres.

Keywords: Polyoxometalate, nanoparticle, synthesis.

In recent years, considerable progress has been made to synthesize polyoxometalates (POMs) with nanosize^{1,2}, but these methods were still limited in application of POMs used as drugs delivery^{3,4}.

Such microspheres starch and liposome used as drug carrier for therapeutic applications are biocompatible, biodegradable and physically stable^{5,6} and show some benefits including solubilization of poorly soluble drugs, local depot for the sustained release of topically effective drugs, or reduction of side effects or incompatibilities.

Currently, we are exploring the possibility of combining drug delivery technology and POMs syntheses to prepare new POMs complexes materials in order to solve the problem that most POMs compounds are not stable at physiological pH conditions. Here in, we report the preparation of starch loading POMs α -K₈H₆ [Si₂W₁₈Ti₆O₇₇]⁷ nanoparticles.

In the synthesis, starch microspheres have been prepared from low cost raw materials-soluble starch by reversed-phase microemulsion polymerization methods using phosphorous oxychloride as the linking agent⁸. The titanium polyoxotungstates Si₂W₁₈Ti₆ loaded starch nanoparticles have been prepared by an enveloping method. 1.5 g of soluble starch was added to 10 mL of water to form a 15% mixture. The mixture was heated in boiling water-bath at a certain time until the mixture turned to transparent to form starch water aqueous. This aqueous solution was then cooled to room temperature, 200mg of α -Si₂W₁₈Ti₆⁸ was added to it to form a water phase. This water phase was added drop-wise to an oil-phase (the oil phase contains 200 mL of C₆H₅CH₃, 200 mL of CHCl₃ and a certain amount of surfactant Span-80) with stirring. It was kept stirring until

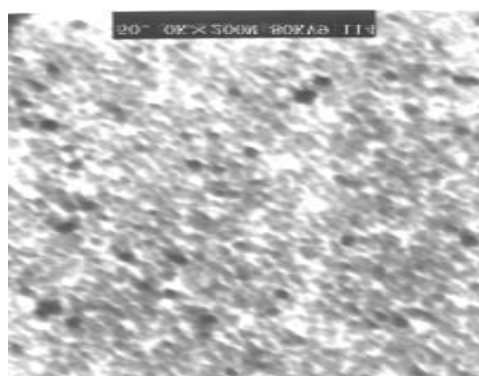
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a microemulsion was formed, the microemulsion was then treated by supersonic for 30 min in order to obtain smaller size nano-starch particles. To this microemulsion, 3 mL of POCl_3 was added and stirring was continued for another 1h. The microemulsion was left statically to obtain two layers. The water phase was separated and washed with acetone and ethanol to obtain the white solid (1g), and then the solid was washed with small quantities of water for four times in order to separate the unencapsulated $\alpha\text{-Si}_2\text{W}_{18}\text{Ti}_6$. The solid was dried at 60°C under vacuum to obtain the dry powder. The contents of $\alpha\text{-Si}_2\text{W}_{18}\text{Ti}_6$ were analyzed by ICP-absorption spectroscopy.

From the elementary analytic results of the POMs/starch, the contents of every elements are W, 7.30; Si, 0.13; Ti, 0.64; P, 1.66%. It can be seen that during the POMs were encapsulated by starch microspheres, the ratio of W: Ti: Si is still 9:3:1 consistent with the encapsulation of $\alpha\text{-Si}_2\text{W}_{18}\text{Ti}_6$, indicating that the $\text{Si}_2\text{W}_{18}\text{Ti}_6$ did not change during the reaction. The content of $\text{Si}_2\text{W}_{18}\text{Ti}_6$ in starch microspheres was 12.0%, according to the amount of $\text{Si}_2\text{W}_{18}\text{Ti}_6$ used in the experiment, the encapsulating effectiveness of starch microsphere to $\text{Si}_2\text{W}_{18}\text{Ti}_6$ can be calculated to be 60%. The IR spectrum of the POMs/starch nanoparticles showed the absorption peaks at 993, 953, 896, 783 and 720 cm^{-1} , which are characteristic asymmetric stretching vibrational peaks for heteropoly-anions with (dimeric) Keggin structure of W-O_d , $\text{W-O}_b\text{-W}$, $\text{W-O}_c\text{-W}$ and Si-O_a . The peak in 1158 cm^{-1} shows a C-O-P vibration peak, which shows that during the starch reacting with POCl_3 , the cross-linking reaction occurred. The content of P atom in $\text{Si}_2\text{W}_{18}\text{Ti}_6$ /starch microsphere (1.45%) also confirms this point.

The ^{29}Si MAS NMR spectrum of the POMs/starch nanoparticles shows one peak at -84.90 ppm as the same as that of pure $\alpha\text{-Si}_2\text{W}_{18}\text{Ti}_6$ (δ : -83.20 ppm). This shows that the primary $\alpha\text{-Si}_2\text{W}_{18}\text{Ti}_6$ structure is retained after encapsulation of the POMs.

Figure 1 The TEM of the POMs / starch



The transmission electron micrographs (TEM) (**Figure 1**) show that the POMs / starch forms relatively uniform nanometer particles of average diameter about 40–60 nm, and the shape of the nanoparticles is round and the particles did not agglomerated. The range of nanoparticles estimated by Zatesizer is from 100 nm to 20 nm, the size of the most nanoparticles is 40 nm.

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