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SCIENTIFIC PAPER

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MORPHOLOGY CONTROL OF MnO₂ NANOPARTICLES: EFFECT OF P123 POLYMER IN ETHANOL-WATER SYSTEM

Article Highlights

- A series of MnO₂ nanoparticles were synthesized in the ethanol-water system
- The morphology changed from rod-like into sheet-like shape
- P123 polymer played a crucial role in controlling the morphology

Abstract

A series of MnO₂ nanoparticles were synthesized by two-step reaction in the ethanol-water system with urea as reducing agent. During the novel routine, P123 polymer plays a crucial role in controlling the morphology. Then, characterization and systematic investigations of the samples by transmission electron microscopy and scanning electron microscopy confirmed that the morphology of MnO₂ nanoparticles changed as the raw materials ratio changed. Finally, X-ray diffraction and X-ray photoelectron spectroscopy were employed to confirm the crystal structure and the exact components. These results indicated the particles showed a rod-like shape without P123 and changed into sheet-like shape after the addition of P123. Therefore, this idea could be developed for the controllable synthesis of other metal oxide-based nanomaterials.

Keywords: MnO₂, P123, morphology, nanoparticles.

MnO₂ nanoparticles, with good physical and chemical properties, have become attractive candidates for heterogeneous catalysis and energy storage systems, especially due to environmental awareness in the recent years [1-4]. This low-cost and environment-friendly material had attracted more and more attentions and many researchers engaged in synthesis of MnO₂ nanoparticles with various approaches [5-7]. However, in practical applications, the crystallinity and morphology of MnO₂ nanoparticles have direct effects on the performances.

Up to now, several morphologies of MnO₂ nanoparticles were reported, including hollow spheres, urchins, thin films, nanopillars and other one-dimensional (1D) or three-dimensional (3D) nanostructured MnO₂ [8-13]. These types of nanoparticles had spe-

cific surface area and good structural stability, leading to remarkable improvement compared with the traditional MnO₂ powder. Unfortunately, the synthesis methods are not well-controlled and there is a lack of studies on the relationship between the morphology and the raw materials.

It is known that P123, one type of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers, exhibits particular behavior in aqueous solution and has been introduced to synthesize loads of nanomaterials [14-17]. In fact, it is also a highly effective agent for controlling the nucleation and growth of crystals. In previous reports, it was employed as a template for the synthesis of MnO₂ nanoparticles [18-19]. However, the performances were still unsatisfying. In this study, a series of MnO₂ nanoparticles were synthesized with P123 polymer introduced into the novel ethanol-water system. The exact function of P123 polymer was also investigated.

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EXPERIMENTAL

Materials and reagents

Potassium permanganate and urea (CO(NH₂)₂) were purchased from Guangfu Fine Chemical Plant (Tianjin, China). Ethanol was purchased from Xilong Chemical Co., Ltd. Pluronic P123 (EO:PO:EO = 20:70:20, average *Mn* = 5800) was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals are of analytical grade and used without any further purifications. Water used in the experiment was distilled for three times before.

Preparation of MnO₂ nanoparticles

A certain amount of P123 was dissolved in 100 mL ethanol-water system (ethanol:water = 1:5) with continuous stirring on magnetic stirring devices. Then, KMnO₄ and CO(NH₂)₂ powder were added into the transparent colloidal dispersion sequentially and stirred for another 30 min. After aging for 24 h, the mixture was transferred into 80 mL Teflon-lined autoclave and maintained at 90 °C for 24 h. After cooling to room temperature, the as-obtained solid was filtered, and washed with water and ethanol for three times, respectively. Finally, the collected solid was dried in a vacuum oven at 60 °C for 12 h. The as-prepared samples were placed in a crucible and heated in a furnace at 500 °C for 2 h under the air atmosphere to obtain the product. In order to make a comparison, a series of the product were synthesized under different conditions, which were denoted as M-*X* (Table 1), where *X* represents the experiment number.

Transmission electron microscopy (TEM)

TEM was conducted on JEM-2000EX (JEOL, 200 kV). All samples for TEM tests were prepared by dropping a suspension of each sample onto the carbon holey grid (JEOL, 400 meshes). The suspension was prepared with the solid dispersed in ethanol using an ultrasonic bath for 15 min.

Scanning electron microscopy (SEM)

SEM images were obtained on JSM-5600 (JEOL, 25 kV) and each sample was gilded to enhance the conductivity before characterization.

X-Ray diffraction (XRD)

The samples were tested on the Rigaku D/max-2500 X-ray powder diffractometer using CuKα radiation ($\lambda = 0.1542$ nm) with scattering angles (2θ) of 5–80°, operating at 40 kV and a cathode current of 30 mA.

X-Ray photoelectron spectroscopy (XPS)

XPS was conducted on the Thermo Escalab 250 with a monochromatic AlKα source at room temperature with the sample (M-1) cleaned before. All the binding energies were referenced to the C1s peak at 284.8 eV.

RESULTS AND DISCUSSIONS

A series of MnO₂ nanoparticles, labeled as M-1 to M-6, were synthesized under various reaction conditions. The whole designed routine mainly included two stages, hydrothermal reaction and high-temperature thermal treatment. The growth of nanoparticles was conducted in the ethanol-water system in the presence of P123 polymer and urea. The product was obtained after P123 polymer was removed completely by calcination.

TEM studies were employed to reveal the morphology of the samples in details. As is shown in Figure 1a, the M-1 sample showed a rod-like structure with the length of 300 to 500 nm. However, as the addition of P123 polymer, the morphology witnessed significant changes. The remained samples presented the special sheet-like structure. By comparison from M-2 to M-4 (Figure 1b-d), excessive amount of P123 polymer would lead to serious agglomeration and the sheet-like structure was not obvious. Even some samples demonstrated other structural shapes. For example, in terms of M-4, some short rod-like structure could be found. Therefore, the P123 polymer played an important role on the morphology of MnO₂ nanoparticles. Actually, at the room temperature, after the addition of KMnO₄, P123 molecules were absorbed on the surface of MnO₄⁻ to form micelles in the presence of ethanol. As for P123 polymer, when the reaction temperature was above the critical micellar temperature (CMT), the PPO blocks would

Table 1. The various reaction conditions for synthesis of MnO₂ nanoparticles

Sample	CO(NH ₂) ₂ , g	P123, g	KMnO ₄ , g	H ₂ O, mL	C ₃ H ₆ O, mL
M-1	2.5	0	1.0	25	5
M-2	2.5	1.5	1.0	25	5
M-3	2.5	0.5	1.0	25	5
M-4	2.5	2.5	1.0	25	5
M-5	1.5	1.5	1.0	25	5
M-6	0.5	1.5	1.0	25	5

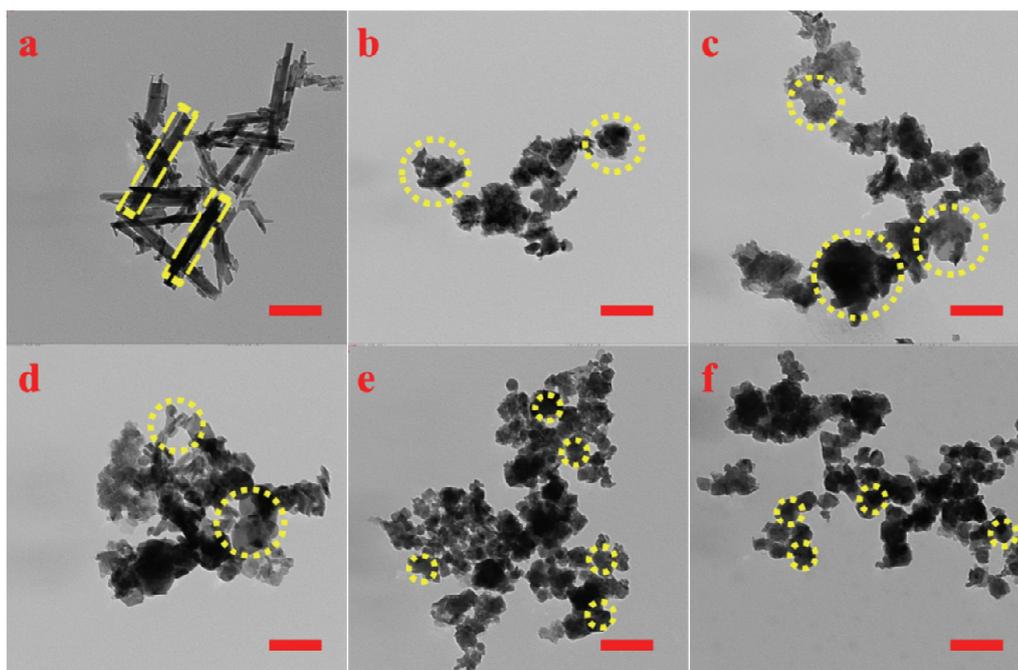


Figure 1. TEM images of the as-synthesized samples; a-d corresponds to the sample M-1 to M-6, respectively. The bar: 200 nm.

become insoluble while the PEO blocks would be still soluble. Hence, the previous growth kinetic would be modified, leading to a sheet-like structure from a rod-like one.

Interestingly, in the following experiments, if the amount of $\text{CO}(\text{NH}_2)_2$ decreased, the sheet-like structure became clear with an exact pentagon, as is shown in M-5 (Figure 1e) and M-6 (Figure 1f). Combined with the previous literature, the K^+ might also have effect on the structure of the product and the main idea was that high-concentration K^+ stacked

between the MnO_2 sheets, making the structure stable [20]. Meanwhile, the nanoparticles could be distributed around the P123 polymer under the action of hydrogen bonds between ethanol and water to form a uniform state.

SEM was used to confirm the state of aggregation of the MnO_2 nanoparticles. The shape showed in M-1 (Figure 2a) had obvious differences with other ones. On average, M-2 (Figure 2b) and M-3 (Figure 2c) found no uniform shapes and many blocks were relatively big. On contrary, the small blocks with uni-

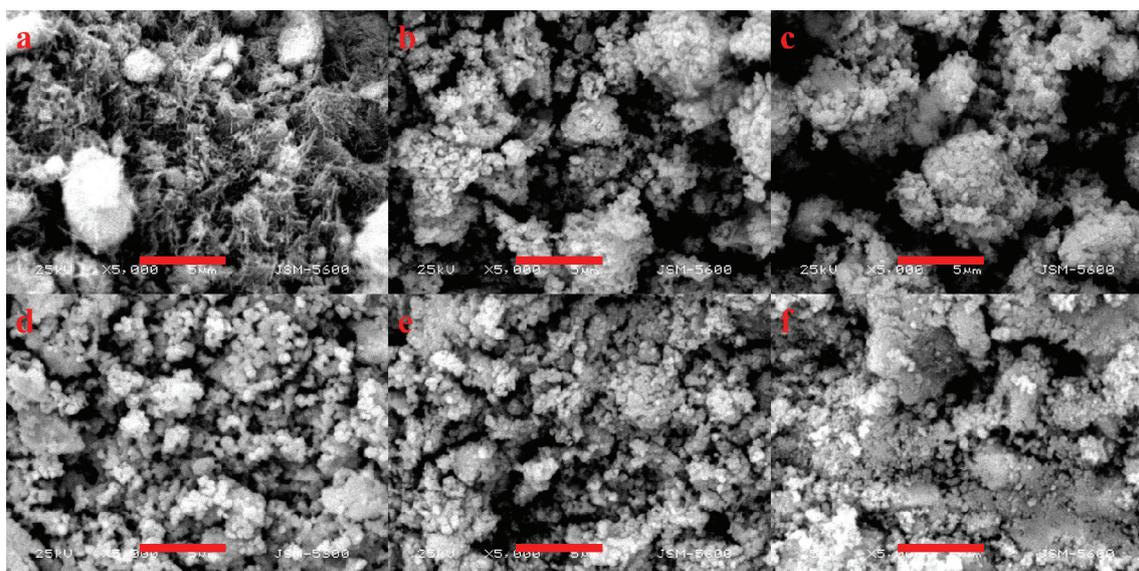


Figure 2. SEM images of the as-synthesized samples; a-d corresponds to the sample M-1 to M-6, respectively. The bar: 5 μm .

form shape appeared in M-4 (Figure 2d), M-5 (Figure 2e) and M-6 (Figure 2f). Therefore, the last three samples demonstrated more compact state and smaller particle sizes.

The crystal structure was confirmed by XRD analyses (Figure 3). M-1 showed the typical peaks corresponding to α -MnO₂, which held a tetragonal structure with $I4/m$ and lattice parameters of $a = b = 9.785$ Å, $c = 2.863$ Å (JCPDS card No. 44-0141). But after

the addition of P123 polymer, the crystal structure of M-2 to M-6 changed into K_{0.5}Mn₂O₄·1.5H₂O, a monoclinic structure with $C/2m$ and lattice parameters of $a = 5.15$ Å, $b = 2.844$ Å, $c = 7.159$ Å (JCPDS card No. 42-1317). That is to say, the growth kinetic was changed and the P123 could restrict the movement of K⁺, which also participated in the growth of sheet-like structure. Furthermore, the intensity of all diffraction peaks indicated that they were highly crystallized.

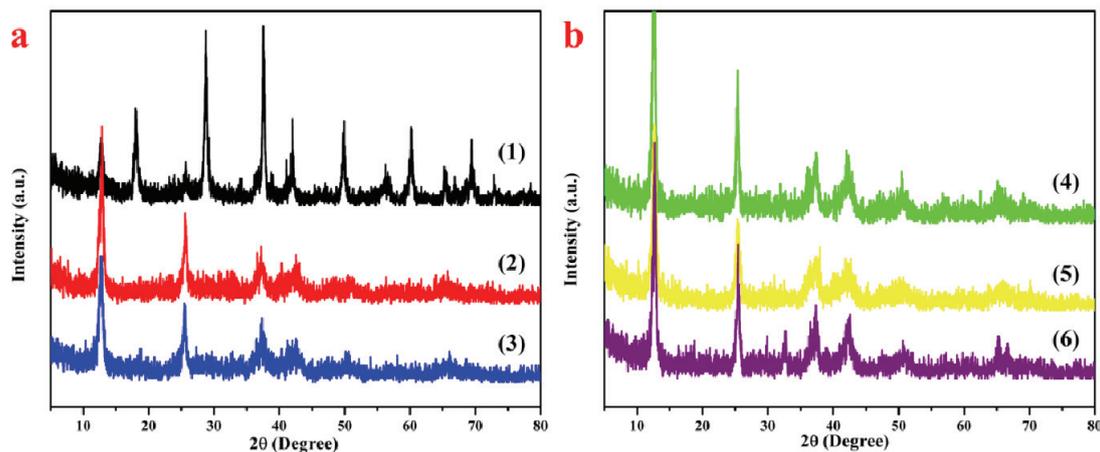


Figure 3. XRD patterns of the as-synthesized samples; 1-6 corresponds to the sample M-1 to M-6, respectively.

XPS, a powerful tool to identify the elements' states in bulk material, has been used to further elucidate the chemical composition of the as-synthesized MnO₂ nanoparticles. The peaks associated with Mn could be observed in the spectrum (Figure 4). The Mn 2p_{3/2} and Mn 2p_{1/2} peaks were centered at 642.3 and 654.0 eV, respectively. This indicated the presence of MnO₂ (Mn⁴⁺) with a spin energy separation of 11.7 eV, which was in good accordance with the previous data on MnO₂ [21].

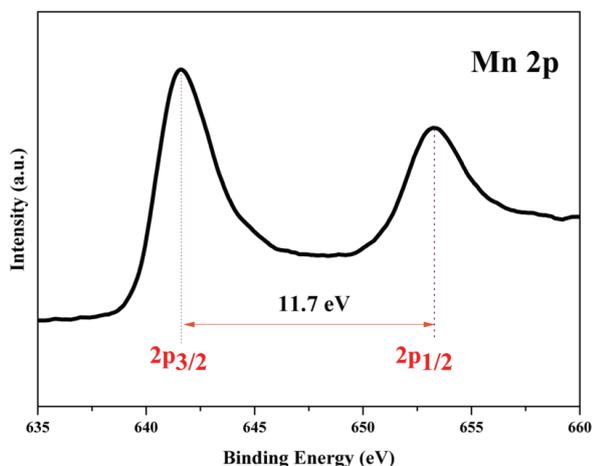


Figure 4. Mn 2p spectrum of the as-synthesized samples.

CONCLUSIONS

A series of MnO₂ nanoparticles were synthesized in the ethanol-water system and these results proved that P123 polymer played a crucial role on the morphology of the particles. Without the P123 polymer, the particles showed a rod-like shape and dense stacking state. However, the morphology changed into sheet-like shape and the density had a close relationship with the amount of P123 polymer. This is beneficial to control morphology of MnO₂ nanoparticles and this idea could be developed for the synthesis of other metal oxide-based nanomaterials.

Acknowledgements

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NAUČNI RAD

KONTROLA MORFOLOGIJE MnO_2 NANOČESTICA: UTICAJ POLIMERA P123 U ETANOLNO-VODENOM SISTEMU

Serijsa MnO_2 nanočestica je sintetisana dvostepenom reakcijom u etanolno-vodenom sistemu sa ureom kao redukujućem agensom. Za vreme novog postupka, polimer P123 igra ključnu ulogu u kontroli morfologije. Karakterizacija i sistematično istraživanje uzoraka pomoću transmisiona elektronske mikroskopije i skenirajuće elektronske mikroskopije pokazuje da se morfologija MnO_2 nanočestica menja sa promenom odnosa sirovina. X-difrakcionom i X-fotoelektričnom spektroskopijom su potvrđene kristalna struktura i komponente. Rezultati pokazuju da u odsustvu P123 čestice izgledaju poput štapića, a da se menjaju u pločasti oblik nakon dodatka P123. Zbog toga bi ovakav pristup mogao biti dalje razvijen radi kontrole sinteze ostalih nanomaterijala baziranih na metalnim oksidima.

Ključne reči: MnO_2 , P123, morfologija, nanočestice.