A general strategy toward the rational synthesis of metal tungstate nanostructures using plasma electrolytic oxidation method

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A B S T R A C T
A new method based on conventional plasma electrolytic oxidation (PEO) technology has been developed for the rational synthesis of metal tungstate nanostructures. Using this method, ZnWO4 and NiWO4 nanostructures with controllable morphologies (nanorods, nanosheets and microsheets) and superior crystallinity have been synthesized. It has been found that the morphology diversity of ZnWO4 nanostructures can be selectively tailored through tuning the electrolyte concentration and annealing temperatures, showing obvious advantages in comparison to traditional hydrothermal and sol–gel methods. Precise microscopy analyses on the cross section of the PEO coating and ZnWO4 nanostructures confirmed that the precursors initially precipitated in the PEO coating and its surface during plasma discharge process are responsible for the nucleation and subsequent growth of metal tungstate nanostructures by thermal annealing. The method developed in this work represents a general strategy toward the rational synthesis of metal oxide nanostructures and the formation mechanism of metal tungstate nanostructures fabricated by the PEO method is finally discussed.

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1. Introduction

Metal tungstate nanostructures with diverse morphologies have received significant research interest in the past years due to their technologically important applications in the fields of photocatalysis [1–3], electrochromism [3,4], and photoluminescence [5]. Among all these tungstates, ZnWO4 with wolframite-type monoclinic structure and P2₁ space group is of particularly important for its high thermal stability, excellent optical and electrical properties [2] and its promising applications in photo-degradation [1], high-performance luminescent devices [5], Li ion battery [6], solid-state laser host, as well as for optical fibers [7]. It has been reported that porous ZnWO4 film and nanorods have excellent performance in organic solution degradation under UV and visible irradiances [8,9], and the photocatalytic efficiency can be further enhanced by F-doping [10,11]. In addition, ZnWO4 nanorod synthesized from hydrothermal method is a promising anode material in lithium battery for its outstanding charge–discharge performance and the decent capacity as high as 420 mAh g⁻¹ [6].

In search for ZnWO4 crystals with excellent properties and diverse functions, a variety of methods involving either physical sublimation or chemical routines have been developed [8,9,12–14]. Extensive efforts have been spent on the morphology controlling and photocatalytic efficiency enhancement of ZnWO4 nanostructures using hydrothermal reaction and sol–gel method [15–17] and it has been demonstrated that the two methods are rather facile in synthesizing ZnWO4 nanocrystals. However, the limitation of hydrothermal and sol–gel methods in controlling the morphology of ZnWO4 nanostructures is still obvious and only nanorods, nanowires and nanoparticles can be obtained. Most importantly, the large yield production of ZnWO4 nanocrystals with superior crystallinity is confined by the above-mentioned two methods in the viewpoint of industrial applications in the future. To overcome this disadvantage, some novel modification techniques for ZnWO4 nanocrystals including the hybridization with graphene, WO3 and C3N4 [18–21], the heterostructuring with SnO2, BiO1 and C3N4 [14,22,23], and the doping with fluorine have been developed for a significant performance improvement [10,24].

On the other hand, plasma electrolytic oxidation (PEO) technology has been proved to be a successful and versatile strategy in producing various functional composite coatings. It has been widely used in diverse fields ranging from medical to mechanical engineering [25,26]. For instance, multi-functional films such
as bioceramic coatings, abrasion-resistant coatings, and corrosion-resisting coatings on metals can be obtained using the PEO method [27]. In a typical fabrication process, the PEO coating is featured as porous layers with numerous micro-cracks randomly distributed inside. Such porous layers and micro-cracks with large surface area will enable the accumulation of large amount of electrolyte ions during the PEO process at higher temperature and serve as ideal media for cation and anion storage. In addition, more precursor ions will also penetrate into the porous coatings through numerous narrow channels (micro-cracks and pores) by dipping the coating into designated chemical solutions. These chemical ions stored in porous PEO coating can be used as the precursors for the synthesis of metal oxide nanostructures through a solid-diffusion reaction at high temperature. In addition, our previous studies on nitride semiconductor nanostructure growth have demonstrated that chemical vapor deposition (CVD) technology generally has inherent advantage in producing single crystalline nanostructures at high temperature [28]. Inspired by the PEO process and taking full advantage of CVD technology, a new method based on PEO technology is developed for the fabrication of metal oxide nanostructures. In this work, the rational synthesis of ZnWO₄ and NiWO₄ nanostructures using PEO method has been attempted. It is found that this technology enables a facile controlling of the morphology, size, dimension, orientation and crystallinity of ZnWO₄ nanostructures. Furthermore, this method represents a general synthesis routine to the growth of various metal oxides nanostructures and thus can be applied to the rational fabrication of tungstate, molybdate, vanadate, titinate nanostructures for specific applications in energy harvesting and environmental processing.

2. Experimental procedure

2.1. Materials preparation

To prepare ZnWO₄ nanostructures, commercially available titanium plates with grade 1 purity (10 mm x 10 mm x 1 mm, Shanxi Baotai Group) are used as the substrate for producing porous TiO₂-based coating via PEO method (abbreviated as PEO coating). In a typical experiment, the Ti plate is connected to the positive pole of the power supply as anode and conductive graphite electrode is linked with the negative pole as cathode. Aqueous solutions comprising of 0.7 mol L⁻¹ Na₃PO₄·12H₂O, 0.034 mol L⁻¹ Na₂B₄O₇·10H₂O, 0.01 mol L⁻¹ Na₃WO₄·2H₂O, and 0.1 mol L⁻¹ Zn(CH₂COO)₂·2H₂O are employed as the electrolyte for producing plasma discharge and subsequent porous PEO coating. The optimized PEO time, applied current density and frequency are fixed as 10 min, 0.1 A/cm² and 1000 Hz, respectively. The electrolyte temperature is maintained at around 25 °C to enable a uniform coating formation by means of a magnetic stirring cooling system. To enhance the full absorption/precipitation of Zn ions in porous PEO coating, the coating layer is dipped into Zn(NO₃)₂ solution at room temperature for further increasing the Zn⁺² contents. Following this step, the impregnated samples are transferred to a resistance furnace immediately for promoting the nucleation and subsequent crystallization of ZnWO₄ nanostructures. After annealing at the temperature of 650–850 °C for 30–240 min in ambience, ZnWO₄ nanostructures with high-phase purity and diverse morphologies can be obtained on the surface of porous PEO coating.

2.2. Morphology and structure characterization

The structure and phase of all samples are examined by X-ray diffractometer (XRD, Rigaku D/max 2400) with Cu kα as the X-ray source (λkα = 0.154056 nm). The binding energies of the W4f and Zn2p orbitals are acquired by an X-ray photoelectron spectroscopy (XPS. Thermal VG/ESCALAB250). The morphology, microstructure and composition of the PEO coating and metal tungstate nanostructures are characterized by a field-emission scanning electron microscopy (FE-SEM, FEI Inspet F50) equipped with a Quanta 600 Energy Dispersed X-ray spectrometer (EDS) system and a 200 kV transmission electron microscopy (TEM, FEI, Tecnai G2 F20).

3. Results and discussion

As described in the previous work, the formation of initial PEO coating in solution involves a complicated deposition and crystallization process, and the electrolyte ions will be absorbed into the porous PEO coating. In this work, all these precursor ions deposited into the PEO coating will diffuse into the coating surface to react with oxygen during the thermal annealing process, leading to the nucleation and growth of ZnWO₄ nanostructures. To examine the phase purity and structure of the PEO coating and ZnWO₄ nanostructures, XRD measurements scanned from 10° to 60° are carried out. It can be seen that titanium dioxide in the forms of mixed rutile and anatase phases are formed after the PEO process. Typically, anatase-TiO₂ is the predominant phase in the PEO coating and shows strong intensity (red curve in Fig. 1a). In addition, the porous PEO coating still contains some amorphous-like component as a wide dome exists in the range of 20–40°, which is produced as a result of repeatedly shock heating and cooling during the PEO process. Composition analysis performed on the PEO coating indicates that it is comprised of Zn, W, Ti, P and O elements (Fig. 1b), in which Ti comes from Ti substrate, whereas Zn, W, P and O elements are directly from the Zn(CH₂COO)₂·2H₂O, Na₃PO₄ and Na₂WO₄ electrolyte. It is a little surprising that no obvious peaks related to Zn or W-containing compound are found from the XRD pattern even though the two elements show rather intensive intensity in EDS spectrum (Fig. 1b). It is thus speculated that these W and Zn elements are possibly involved in these small size aggregates and are uniformly distributed in the porous PEO coating in the form of amorphous phase during plasma discharge, as evidenced in Fig. 1a (red curve).
After dipping the PEO coating in 0.5 M Zn(NO₃)₂ aqueous solution and annealing at 800 °C for 1 h, it is found that the diffraction peaks of anatase TiO₂ phase have almost disappeared from the XRD pattern. The disappearance of anatase-TiO₂ phase suggests that it has been completely converted into rutile-TiO₂ phase at high temperature. Most obviously, some new peaks with predominant intensity appear (blue curve in Fig. 1a) and these peaks can be well indexed to ZnWO₄ with wolframite-type monoclinic structure and P2₁c space group. The XRD result of ZnWO₄ phase is also in good agreement with the standard structure data of ZnWO₄ crystal (No. JCPDS: 15-0774), implying that a solid-diffusion reaction for the formation of ZnWO₄ has occurred on the surface of the PEO coating.

Fig. 2 shows the SEM images of PEO coating and ZnWO₄ nanostructures formed at 800 °C. Typically, the PEO coating exhibits an obvious porous morphology with different pore sizes (Fig. 2a). Such pores which are produced during the PEO process contribute to a significant increase of the surface area of the coating, enabling the absorption of precursor ions to the full extent during dipping process. It can be still found that some nanoparticles with an average diameter of tens of nanometers are homogeneously distributed on the PEO coating surface (Fig. 2a). It is supposed that these nanoparticles are also generated during the PEO process under high-energy discharge. Composition analysis performed on these nanoparticles indicates that they are mainly composed of Zn, W, and O elements; in consist with our assertion on the amorphous ZnWO₄ dendrite in XRD pattern. It is reasonable to understand that the electrolytes surrounding on the Ti substrate undergo a huge temperature variation during and after plasma discharge, leading to the non-equilibrium amorphous phase formation. Fig. 2b shows the representative appearance of PEO coating after heated at 800 °C for 1 h in ambience. It can be seen that the surface of PEO coating has been densely covered with flower-like nanosheets and nanowires with a length up to 50 μm. The obvious morphology evolution implies that ZnWO₄ nanostructures have been formed on the PEO coating via an in situ high-temperature solid-diffusion reaction, as evidenced in the XRD data shown in Fig. 1a.

As described in experimental section, the electrolyte containing different cations and anions are used for producing the plasma discharge and supplying the precursors of ZnWO₄. The phase analysis using XRD recording has demonstrated the obvious phase transition after PEO process and annealing. Therefore, it is essential to examine the composition and chemical states of PEO coating and annealed samples. Fig. 3 shows the XPS spectra of Zn, W, and O elements after PEO and thermal annealing at 800 °C. All the binding energies of the three elements are referenced to the C1s peak binding energy at 284.6 eV. Fig. 3a and d shows the Zn2p₃/₂ XPS spectra with characteristic peaks centered at 1021.8 eV and 1021.4 eV, respectively. These two peaks correspond to the typical Zn²⁺ oxidation states in oxides, in which the Zn atom is surrounded by neighboring O atoms to form Zn-O bond [12]. Fig. 3b shows the emission peak of W4f recorded from PEO coating. The strong two peaks located at 35.2 eV and 37.3 eV can be assigned to W4f₇/₂ and W4f₅/₂ signals and are in consistence with the W⁶⁺ in ZnWO₄ [29], indicating that ZnWO₄ species have been generated by means of high-energy discharge during PEO process. Such ZnWO₄ material which may exist in the form of amorphous phase uniformly distribute in porous PEO coating, as discussed earlier (Fig. 2a). After annealing process, the XPS peak of W4f is slightly broadened and presented by two components with binding energies of W⁴f₇/₂ at 35.2 eV and at 33.5 eV, respectively (Fig. 3e). The higher binding energy value at 35.2 eV can be assigned to the W⁶⁺ oxidation state, which is the characteristic of W element in WO₃ octahedron. Meanwhile, the lower binding energy value of 33.5 eV can be attributed to the W⁵⁺ oxidation state [30]. It has been suggested that W⁶⁺ can be transformed to the lower valence state such as W⁵⁺ and W⁴⁺ at high temperature of 800 °C through capturing the electrons in oxygen [31]. Similar to W4f, the emission peaks of O1s for PEO coating and the sample after annealing also show some obvious differences in XPS spectrum configuration, as shown in Fig. 3c and f. The O1s peak collects from PEO coating can be divided into four distinct small bands by Gaussian multiplet deconvolution procedure. The four separated bands demonstrated that different kinds of O binding energies are involved in the PEO coating. The peak A with its binding energy centered at 529.6 eV can be assigned to the Ti-O bond in porous PEO coating [32], whereas the binding energy of peak B at 530.6 eV matches well with the O1s in ZnWO₄ and corresponds to the W-O bond [33]. The peak C with its center at 531.6 eV represents the oxygen chemical state in hydroxyl groups (O—H). The peak D located at 532.5 eV is attributed to oxygen-related H₂O molecules which are usual for porous coating grown in aqueous solutions [34]. After annealing at 800 °C, it is found that peak D has disappeared from the separated bands and the other three peaks still remained. The absence of peak D in Fig. 3f implies that the H₂O molecular attaching on the PEO coating has been completely removed through high-temperature treatment. The XPS results are in good agreement with the data reported in previously published work [7]. Meanwhile, these XPS results also imply that ZnWO₄ has been generated during PEO process and is further crystallized during the post heat treatment. It is anticipated that Zn²⁺ and WO₄²⁻ in the electrolyte will react with each other to form ZnWO₄ at high temperature during PEO process. The tiny ZnWO₄ nanoparticles in amorphous phase will then be incorporated into porous PEO coatings and absorbed on the PEO coating surface by the strong electric field (in the order of ~10⁻⁶ V m⁻¹) [35]. After annealing at 800 °C, the W and Zn precursors will diffuse from the inside of the porous PEO coating to the surface to form ZnWO₄.
nanostructures with different morphologies. As a result, apparent XPS emission peaks from ZnWO₄ are detected from both PEO coating and annealing sample.

During the synthesis of ZnWO₄ nanostructures, it has been found that the annealing temperatures have significant influence on the morphology evolution of ZnWO₄ nanostructures. The growth of ZnWO₄ nanostructures is carried out in the heat-treatment temperature range of 650–850 °C and their corresponding morphologies are shown in Fig. 4. Typically, ZnWO₄ nanostructures with 3D flower-like morphology tend to assemble on the surface of porous PEO coating after heating at 650 °C, as shown in Fig. 4a. Further observation finds that these “flowers” are composed of high density of 2D tiny nanosheets with a length of ~1 μm and an average width of 100–300 nm. Interestingly, the ZnWO₄ nanosheets are densely grown from these nanoparticles preferentially nucleated at the porous coating rather than a uniform formation on the surface. This should be related to the local enrichment of W and Zn elements on the particle sites. When the temperature is increased to 750 °C (Fig. 4b), the 3D flower-like morphology has evolved into grass-like configuration, and the growth density of ZnWO₄ nanostructures also increase to completely cover the porous PEO coating. Meanwhile, the size of ZnWO₄ nanostructures is also several times larger than those obtained at 650 °C, implying that a higher temperature leads to a faster growth rate. It should be noted that the ZnWO₄ nanostructures still show a similar growth behavior with the ones at 650 °C, in which the tiny ZnWO₄ nanosheets are densely grown from particles. With the temperature further increases to 800 °C, mixed morphology including long nanorods and flat nanosheets are observed in the product (Fig. 4c). When the temperature is heated to 850 °C, microsheets with a length more than 10 μm, a width close to 10 μm and a sheet thickness of 100–300 nm are formed on the surface of large size particles. The significant width increase of ZnWO₄ nanosheets suggests that a faster growth rate along the radial direction has started as a result of the higher annealing temperature. At 850 °C, a large amount of ZnWO₄ microsheets with smooth morphology surface and regular rectangle shape have dominated the surface of PEO coating. Therefore, it can be concluded that the higher heat-treatment temperature not only results in the increase of growth density, but also leads to an obvious morphology evolution from long and narrow nanosheets to uniform microsheets.

Similar to the growth temperature, the thermal oxidation duration also has apparent impact on the morphology and size evolution of ZnWO₄ nanostructures. Further investigations on the topography of ZnWO₄ nanostructures are carried out to reveal the influence of thermal oxidation time. Fig. 5 shows the SEM images of PEO coatings heated at 650 °C for 30, 60 and 240 min, respectively. When the porous PEO coating is thermally oxidized for 30 min, flower-like microspheres with an average diameter of ~1 μm are first formed on the porous PEO coating surface (Fig. 5a), and later the tiny nanosheets with a thickness of dozens of nanometers and large nucleation density start to develop. Interestingly, these small sheets tend to construct on the particles with obvious ordering, which is guided by the initial preferential nucleation as a result of self-assemble process. The 30-min growth has paved a way for the subsequent morphology evolution of ZnWO₄ microsheets. With the prolonging of annealing time to 60 min (Fig. 5b and c), the size of the ZnWO₄ nanosheets increases along the axial and radial directions correspondingly and a maximum sheet width up to 1 μm can be obtained. In addition, the construction of the 2D nanosheets into cabbage-like 3D architectures becomes more obvious and all the nanosheets are regularly self-assembled on the particle surface. With the further increase of annealing time to 240 min, the morphology of ZnWO₄ nanostructures still maintain a sheet-like appearance, but the dimension and size exhibit a slight increase tendency until the depletion of W and Zn precursors inside the porous PEO coating (Fig. 5c and f).

To investigate the crystal quality of as-synthesized ZnWO₄ nanostructures, high-resolution TEM (HRTEM) analyses are carried out on all samples. Fig. 6 shows the typical TEM images of ZnWO₄ nanostructures with different morphologies by controlling the growth temperature in the range of 650–850 °C. It can be

![Fig. 3. XPS spectra of Zn2p, W4f, O1s (a–c) after PEO, and (d–f) annealing at 800 °C, respectively.](image)
seen that the ZnWO₄ nanostructures feature as three representative shapes: nanosheets with smaller size (Fig. 6a–c); long nanorods with an average diameter of 300–500 nm (Fig. 6e), and rectangular microsheets with larger size (Fig. 6g), as observed in SEM images (Fig. 4). Fig. 6a–c shows the TEM images of ZnWO₄ nanosheets synthesized at 650 °C, and one can see that different from the ZnWO₄ nanosheets synthesized from hydrothermal and sol–gel reactions [9,16,36,37], the ZnWO₄ nanostructures with diverse morphologies in current work possess a superior crystallinity. It is supposed that the high-temperature for solid-diffusion reaction is responsible for the ordering atom organization and excellent crystal quality. These nanoplates with length up to several micrometers and an
average width less than 500 nm are extremely uniform in morphology. HRTEM analysis performed on tens of nanosheets demonstrates that these ZnWO₄ nanosheets are well crystallized and show single crystal characteristic. No structural defects such as microtwins and stacking faults are found inside the ZnWO₄ samples, implying the single crystalline nature of ZnWO₄ nanostructures synthesized by PEO method. The distances measured from neighboring lattice fringes in HRTEM image (Fig. 6d) are 0.57 and 0.49 nm, respectively, matching well with the d-spacings of (010) and (001) planes of wolframite-type monoclinic ZnWO₄. Further crystallographic study confirms that the nanosheets are preferentially oriented along the [010] direction, as indicated in Fig. 6d. Furthermore, quantitative element analysis using EDS technology verified that the stoichiometric ratio in ZnWO₄ nanosheets approaches to the standard ratio with Zn:W:O = 1:1:4 (see supporting information, Fig. S1), demonstrating again the high phase purities of ZnWO₄ nanocrystals. Spatially resolved elemental mapping measurement indicates that each of the comprising elements inside the ZnWO₄ nanosheet has a uniform distribution, further verifying the composition and phase purity of as-synthesized nanostructures (see supporting information, Fig. S2). 

Fig. 6e and g shows the low-magnification TEM images of individual ZnWO₄ nanorod and microsheet at annealing temperatures of 750 °C and 850 °C respectively. The dimension expansion of ZnWO₄ nanostructures as a dependence of growth temperature can be confirmed again. From the HRTEM images of ZnWO₄ nanorod and microsheet shown in Fig. 6f and h, it can be seen that all the atoms inside the crystal are regularly arranged in good ordering. Different from ZnWO₄ nanosheets annealed at 650 °C, ZnWO₄ nanorods and microsheets crystallized at a higher temperature exhibit a preferential orientation along the [001] direction (c-axis of the monoclinic ZnWO₄). Compared with ZnWO₄ nanostructure growth is still in exploration. 

The PEO technology developed for the fabrication of functional coatings on metal surface has been established for dozens of years, and the formation mechanism of HA–TiO₂ [38], HA–ZrO₂–TiO₂ [39] coatings with PEO technique has been already developed. However, the application of this method for the rational synthesis of metal oxide nanostructures has rarely been reported [40]. Based on detailed structural and compositional analyses, a tentative growth model that interprets the formation process of tungstate nanostructures has been proposed, as schematically described in Fig. 7. At the first stage, the anodic oxidation reaction is started at the
surface of Ti substrate to generate a thin porous passive layer under the lower applied voltage. With the increase of working voltage, the spark ignition is observed and becomes more severe, implying that the anodic oxidation has evolved into the PEO process. During this stage, the negatively charged ions such as WO$_4^{2-}$ in the electrolyte solution are drawn toward the PEO coating under the high electric field, diffusion and electrophoresis. On the other hand, the cations such as Zn ions in the electrolyte may first react with OH$^-$ to form tiny Zn(OH)$_2$ precipitates in the solution and the Zn(OH)$_2$ will further react with additional OH$^-$ to produce negatively charged Zn(OH)$_4^{2-}$ groups as follows:

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2$$  \hspace{1cm} (1)  

$$\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-}$$  \hspace{1cm} (2)
These Zn(OH)₄²⁻ groups will also be transported into the anodic PEO coating to provide the Zn precursor. Concurrently, the high temperature produced by plasma discharge also results in strong chemical reactions in the local discharged area and leads to the formation of tiny ZnWO₄ nanoparticles, as schematically described in Fig. 7 (process “a”). Due to the huge temperature gradient on the PEO coating surface and the surrounded electrolytes, the tiny ZnWO₄ nanoparticles are generated in the form of amorphous phase and randomly distributed on the coating matrix and the surface of the porous PEO coating, as evidenced in SEM observation and XRD measurement. Following this step, the porous PEO coating was dipped into Zn(NO₃)₂ solution for further increasing the concentrations of Zn element in the porous coating (process “b”). Later, the sample is transferred to a resistance furnace for high-temperature solid-diffusion reaction. It should be noted that the tiny ZnWO₄ amorphous nanoparticles play a key role for the initial nucleation of ZnWO₄ nanostructures. At high temperature, these ZnWO₄ nanoparticles will organize into small seeds and assemble together to guide the subsequent growth of ZnWO₄ nanostructures. This assertion is solidly evidenced by the facts that all the ZnWO₄ nanostructures (nanorods, nanosheets and microsheets) are preferentially grown from the particles, as observed in SEM images. Meanwhile, the Zn and W species precipitated in the porous PEO coating will be evaporated and diffuse into the surface to participate the reaction (process “c”). The line-scan composition profile along the cross-section of the porous PEO coating demonstrates that Zn and W elements have a uniform distribution inside the PEO coating after PEO process (Fig. S3). After annealing at 850 °C, the concentrations of Zn and W elements increase obviously at the coating surface, implying the migration of Zn and W elements from PEO coating to the surface for ZnWO₄ nucleation and growth (Fig. S3).

The PEO approach has proven to be a versatile approach for the rational synthesis of ZnWO₄ nanostructures. Using this method, diverse morphologies of ZnWO₄ nanostructures including nanosheets, nanorods and microsheets can be selectively obtained under control. Most importantly, the ZnWO₄ nanostructures via high-temperature annealing exhibit decent crystallinity and show a single crystal characteristic. The PEO method can also be applied to the facile synthesis of other tungstate nanostructures with controllable morphology. As an example, Fig. 8a shows the SEM image of NiWO₄ nanorods annealed at 850 °C using the PEO method. The nanorods exhibit extremely uniform morphology and densely cover on the PEO coating. The sole difference from ZnWO₄ nanostructures in synthetic process is only the electrolyte and dipping solution we used. In the case of NiWO₄ nanorods, Ni(CH₃COO)₂ and Ni(NO₃)₂ precursors are utilized to replace the Zn(CH₃COO)₂ and Zn(NO₃)₂ in initial and dipping solutions whereas other electrolytes keep unchanged. The XRD result shown in Fig. 8b confirms the phase purity of as-synthesized NiWO₄ nanorods with extra peaks from rutile-TiO₂ phase (porous PEO coating) underneath. The purity of NiWO₄ phase can also be justified from the chemical analysis using EDS. The real molar ratio of Ni, W and O elements in the nanorods approaches well to the ideal stoichiometric ratio of NiWO₄, further demonstrating the predominant advantage of PEO method in improving the phase and composition purities of tungstate nanostructures. Fig. 8d-f shows a representative TEM image of NiWO₄ nanorods with an average diameter of 100 nm and their structural characterizations using HREM and selected area electron diffraction (SAED). It can be found that the NiWO₄ nanorods are also well-crystallized without obvious structural defects. The application of PEO method in the rational synthesis of ZnWO₄ and NiWO₄ nanostructures with controllable morphology and decent crystallinity demonstrates that this method can be regarded as a new general strategy toward the rational synthesis of various metal oxide nanostructures ranging from tungstate to titanate, molybdate and vanadate, and it will thus undoubtedly promote their applications for energy harvesting and environmental processing.

4. Conclusions

In summary, a new facile method to fabricate metal tungstate nanostructures based on PEO technology has been developed and this approach exhibits predominant advantages in the controlling of morphology, size and crystallinity in comparison with conventional sol–gel and hydro-thermal methods. Using this method, ZnWO₄ nanostructures with diverse morphologies such as nanorods, nanosheets and microsheets have been successfully synthesized and it is found that the morphology of ZnWO₄ nanostructures is strongly dependent on the annealing temperature and increasing the temperature from 650 °C to 850 °C will lead to the morphology evolution from nanosheets to nanorods, and to smooth rectangle micro-sheets. HRTEM analyses performed on several ZnWO₄ samples treated at different temperatures verify the single crystal characteristic of all as-synthesized nanostructures even though the temperature is as low as 650 °C. It is believed that the porous PEO coating with micro-cracks serves as an ideal media for the storage of anions and cations, and thus enables continuous precursor transportation for participating in the reaction on the coating surface during heat-treatment. Extension of this method to the growth of NiWO₄ nanowires demonstrates that it represents a general strategy toward the rational synthesis of numerous metal oxides ranging from metal tungstate to titanate, molybdate and vanadate compounds for promising applications in energy storage and environmental catalysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2015.08.080.

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