# Treatment of nanowaste via fast crystal growth: With recycling of nano-SnO$_2$ from electroplating sludge as a study case

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A B S T R A C T

The treatment of industrial sludge containing amorphous/nanophase metal oxides or hydroxides is one of the vital issues in hazardous waste disposal. In this work, we developed a strategy to recycle nano-SnO$_2$ from tinplate electroplating sludge. It revealed that the major components of this sludge were acid soluble Sn and Fe amorphous phases. By introducing NaOH as a mineralizer, a fast growth of amorphous Sn compound into acid-insoluble SnO$_2$ nanowires was achieved selectively. Thus, the as-formed nano-SnO$_2$ could be recycled via dissolving other solid compositions in the sludge by using acid. The role of NaOH on accelerating both the Oriented Attachment (OA) and Ostwald Ripening (OR) growth of SnO$_2$ was discussed, which was regarded as a critical factor for treating the sludge. A pilot-scale experiment was conducted to treat 2.3 kg original sludge and the recycling of about 90 g nano-SnO$_2$ was achieved. We anticipate this work can provide a good example for the recycling of valuable metals from industrial sludge containing fine metal oxides or hydroxides.

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## 1. Introduction

Electroplating sludge is a heavy metals-bearing byproduct from the plating industry, which is produced during precipitation of metal ions from wastewater via alkalization treatment [1]. In China, more than 100 kt of noble metals in electroplating sludge are discarded annually [2]. As in the case of Sn, which is an important industrial material in solder, tin plating, ceramic galzes and glass, it reveals that a large amount of Sn are disposed as waste in industry. For example, a waste tin stripping solution from printed circuit board manufacture contains 150 g/l SnO$_2$ [3]. An electroplating sludge from fluoroborate electrolyte produces is also mainly comprised of Sn [4]. Nevertheless, it is estimated that Sn might be run out in 20 years at current global consumption rates [5]. Thus, the recycling of Sn from sludge is an urgent and unnegligible task.

Over the past decades, many metals recycling techniques have been developed, including leaching–solvent extraction [6], electrolysis [7], ion exchange [8], membrane separation [9] and microbiological methods [10], etc. However, most of these methods have drawbacks such as high costs in operation or the disposal of the residual metal sludge. Furthermore, from the industrial point of view, the complexity and diversity of sludge make it hard to develop an effective and universal method for managing the wastes. Up to now, industrial sludge is still sent to landfill. In this situation, a more rational strategy is to develop specific treating method for specific type of sludge, aiming to achieve the following goals: (i) metals in the sludge could be transformed into reusable materials after the recycling, for instance, expensive nanomaterials. (ii) The strategy should be economically feasible in real system. So far, few work has been reported in this area.

Recently, the phase state of the industrial sludge has been carefully investigated. It has been revealed that the major components in the sludge are nanophase or amorphous metals oxides/hydroxides (hereinafter simply called "MOH") [11]. Since the growth of the low-solubility MOH nanoparticles are very slow, most sludge components can keep in small size for a long time in nature, and sometimes can adsorb other forms of heavy metals [11]. Actually, the metals recovery from the sludge is frequently hampered by the difficulties in the precipitation of the highly suspended small-sized MOH particles. Thus, a feasible approach for treating sludge is to artificially induce the fast crystal growth of amorphous/nanophase form into large ones, hence to make the precipitation of particles easier and reduce their adsorption capacities [11–13]. For example, the sludge from some chlor-alkali and chlorate plants contains Cr$^{VI}$-adsorbed 20 nm Mg(OH)$_2$ [11]. Taking advantage of the different Cr$^{VI}$ adsorption efficiency of nano-Mg(OH)$_2$ and bulk-Na$_2$Mg(CO$_3$)$_2$, a fast crystal growth of Mg(OH)$_2$

into bulk material proved its ability to realize the separation of $Cr^{VI}$ from the magnesium salt. In addition, the crystal growth may possibly promote changes in the physical or chemical properties (e.g. solubility) of specific MOH compound in sludge. Once different MOH compounds in sludge can show great discrepancy in solubility or other property, it will be easier to develop methods to selectively isolate the target compound from sludge.

Enlightened by above thought, this work was designed to explore a strategy for recycling of $SnO_2$ from tinplate electroplating sludge that mainly contains amorphous Sn and Fe compounds. Commonly, the isolate of Sn from other sparsely soluble solids is considered to be done by dissolving Sn under alkaline condition at high temperature [14]. However, such a method not only has disadvantage of a lower recovery efficiency of Sn, but also will face difficulties in the disposal of residual hazardous solid waste. Consequently, it is hampered for its application in real system. Additionally, an acid treatment in our experiment also proves infeasible to separate the high value Sn from Fe. In this work, through introducing NaOH as a mineralizer, we attempted to realize a fast and selective growth of amorphous Sn phase into acid-insoluble $SnO_2$ crystallites. Under such circumstance, the recycling of $SnO_2$ crystallites from acid-soluble Fe amorphous might be reached by a subsequent acid treatment. Additionally, the role of mineralizer on facilitating the crystal growth was discussed. We anticipate this work can provide a good example for the recycling of valuable metals from industrial sludge containing amorphous/nanophase MOH.

## 2. Experimental methods

### 2.1. Reagents

The reagents of sodium hydroxide (Alfa Aesar, China) and 69% $HNO_3$ solution (Alfa Aesar, China) used in experiments are of analytical grade.

### 2.2. The analysis of original electroplating sludge

Typical electroplating sludge comes from a tinplate manufacturing factory in Fujian Province of China. To calculate the water content, the original sludge was dried under 100 °C for 6 h. It is worthy to mention that, except for pilot-scale experiment, the sludge used hereinafter was all pre-dried in this way to achieve a precise analysis. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and X-ray diffraction (XRD) were used to determine the elemental content and phase composition of the sample, respectively. To evaluate the feasibility of an acid treatment in extraction of Sn from the original sludge, the sample was mixed with 40 ml 69% $HNO_3$, and the mixture was boiled and refluxed for 0.5 h. Till the sludge no longer dissolved, the residual solid part was collected. The phase character of the solid part was determined by fine XRD analysis.

### 2.3. Mineralization processing of the sludge

A mineralization processing of the sludge was done in the following way. The sample was stirred with 10 ml NaOH solution with concentration from 0.1 to 0.7 M, or with 10 ml $H_2O$ for 1 min. Subsequently, the mixture was transferred to a 23 ml Teflon-lined stainless steel autoclave and heated at 230 °C. For time series experiments within 96 h, autoclave containers were taken out at time interval of 12 h and quenched to room temperature. The suspension was centrifuged and rinsed with the distilled water for three times. The supernatant was collected for ICP analysis. The precipitate was dried for the following elemental analysis and phase determination.

### 2.4. Acid treatment of sludge after the mineralization

The sample obtained by the mineralization treatment was further stirred with 15 ml 69% $HNO_3$ for 1 min, then the mixture was boiled and refluxed for 0.5 h. The contents were partially dissolved in the acid solution. The residual precipitate was separated by centrifugation and dried for the following elemental analysis, phase determination, SEM and TEM observation.

### 2.5. Pilot-scale experiment

The pilot-scale experiment was carried out to examine the feasibility of the strategy. In a typical process, 2.3 kg original wet sludge, 200 ml $H_2O$ and 32 g NaOH were mixed and stirred for 0.5 h. The ratio of the ingredients was employed to ensure that the final concentration of NaOH was 0.4 M. After that, the mixture was transferred to a 5 l Teflon-lined stainless steel autoclave under 230 °C for 48 h. The following steps are similar with the above treatment of the small-scale sludge.

### 2.6. Characterization

The phase of the samples was identified by XRD pattern using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation (40 kV, 40 mA) in the continuous scanning mode. The scanning range $2\theta$ was from 15° to 75° in steps of 0.01° with a collection time of 100 s per step. The average crystallite size was calculated from the peak broadening using the Scherrer equation. The morphology and size of the solid product were characterized on a Scanning Electron Microscope (SEM LEO 1530), as well as a Transmission Electron Microscopy (JEOL JEM2010 HRTEM at 200 kV). The elemental content of both liquid and solid samples was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Jobin Yvon Ultima2).

## 3. Results

Typical electroplating sludge mainly consists of about 78% water, 5.4% Fe, 3.7% of Sn, 0.63% Ca, 0.59% Cr and 0.18% P. Further calculation reveals that the residual part may almost be O or OH that bind to the metals. The pH value of sludge is around 6. Fig. 1a shows the XRD pattern of the original sludge and no obvious diffraction peak related to Sn or Fe compounds can be found. This implies that most of Sn and Fe compounds in sludge are in amorphous phase.

Original sludge was found acid soluble. It showed that over 98.5% of the sludge could be dissolved. ICP analysis confirmed that most of Sn and Fe were released into the solution. Therefore, it is infeasible to extract the Sn simply by the acidization of the original sludge. Nevertheless, one thing attracting our attention is that, there was a small part of solid sludge remained after the acid treatment and a fine XRD analysis in Fig. 1b demonstrates that the residue was $SnO_2$ and $SiO_2$ in crystalline phase. This indicates that besides the amorphous Sn compound, a very small amount of $SnO_2$ crystallites also resided in the sludge. More importantly, this crystalline phase is acid insoluble.

Under this condition, if a selective transformation of amorphous Sn compound into crystalline-$SnO_2$ can be realized, then the extraction of Sn might be implemented by an acid treatment. To reach the goal, a hydrothermal treatment method was adopted, on consideration that the high temperature and pressure environment could facilitate the crystals growth. Moreover the introducing of a suitable mineralizer could accelerate the growth of a specific phase [11]. In this work, NaOH as a mineralizer was selected, since previously alkaline solution has proved its ability to improve the growth rate of $SnO_2$ [15], but has little impact on that of amorphous Fe compound [16].
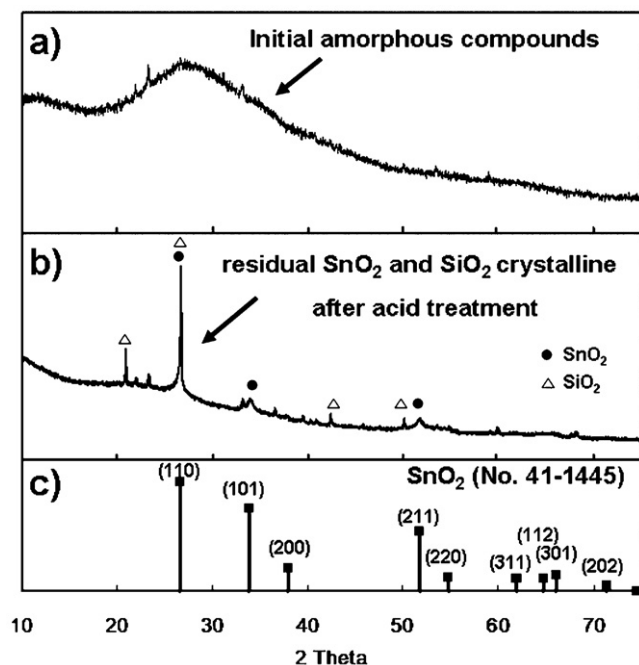
**Fig. 1.** XRD patterns of the original dried sludge (a) before and (b) after treated by 69% $HNO_3$. (c) The standard JCPDS card for tetragonal-$SnO_2$.

Fig. 2a and b shows the comparison of the XRD pattern of the sludge coarsened at 230 °C in distilled water for 144 h and in alkaline solution for 48 h, respectively. We can find that without a mineralizer, a weak diffraction intensity of tetragonal-$SnO_2$ appeared in XRD pattern of Fig. 2a, which implies that only a small quantity of $SnO_2$ crystallites was formed after a long-time coarsening process. Subsequent acid treatment reveals that a larger amount of Sn compound in sludge still dissolved in acid. In contrast, with the addition of only 0.1 mol/l NaOH, the XRD pattern in Fig. 2b shows that diffraction peaks related to tetragonal-$SnO_2$ were obvious. Additionally, it shows that the coarsening process also led to the appearance of a small amount of $Ca_5(PO_4)_3(OH)$ phase. However, no diffraction peak related to Fe compound can be found, suggesting that it is still in the amorphous state. Apparently, NaOH as a mineralizer can accelerate the transformation of amorphous Sn compound into crystalline phase selectively.

To examine the effect of NaOH on the crystal growth in more detail, the sludge was hydrothermally treated at 230 °C for 48 h in NaOH solution with concentration from 0.1 to 0.7 M. XRD patterns shown in Fig. 2b demonstrate that, as NaOH concentration rises from 0.1 to 0.4 M, particle size of $SnO_2$ increases approximately from 4.1 to 9.4 nm in [1 1 0] direction, and from 6.9 to 12.2 nm in [1 0 1] direction, calculated from peak broadening via Scherrer equation. It reveals that, the higher the NaOH concentration was, the faster the $SnO_2$ grew. However, once NaOH concentration is above 0.4 M, contrarily tetragonal-$SnO_2$ phase in XRD analysis is found disappeared gradually. As $SnO_2$ is an amphoteric compound,
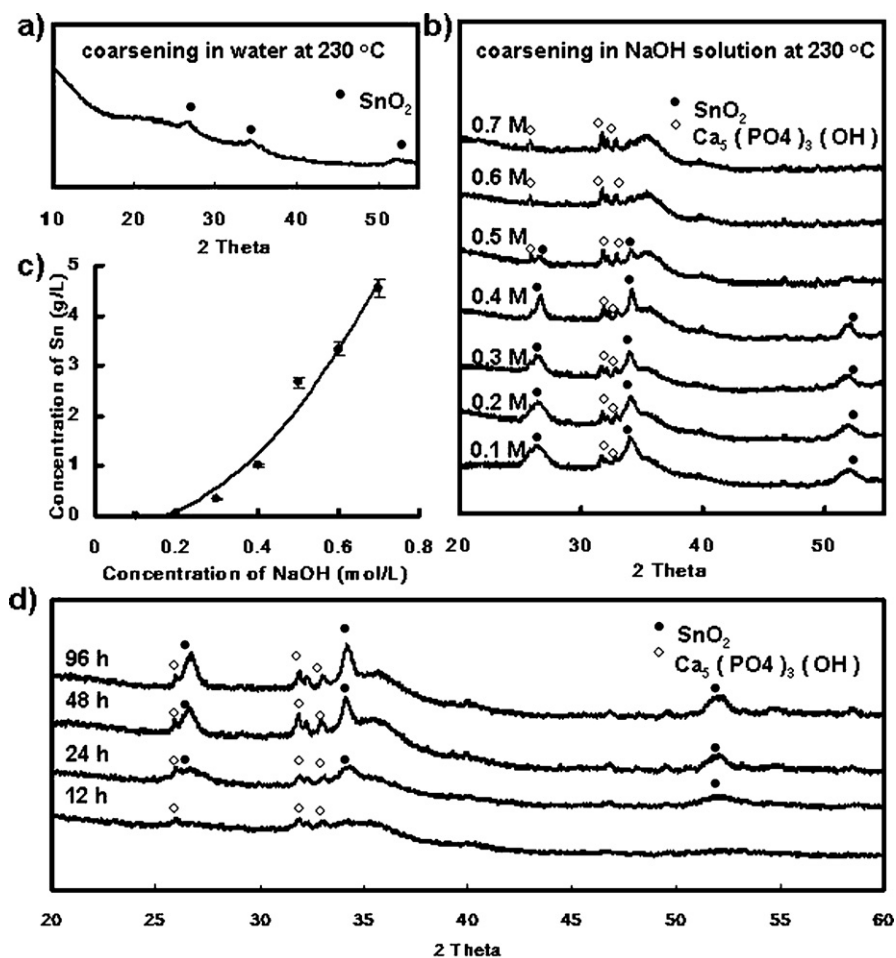


**Fig. 2.** XRD patterns of the sludge treated hydrothermally at 230 °C (a) in water for 144 h, (b) in NaOH solution with concentration from 0.1 to 0.7 M for 48 h. (c) The concentration of Sn ions in the supernatant of alkaline solutions against NaOH concentration, after a hydrothermal treatment at 230 °C for 48 h. (d) Time series XRD analysis of the sludge treated hydrothermally in 0.4 M NaOH at 230 °C for 12, 24, 48, and 96 h.
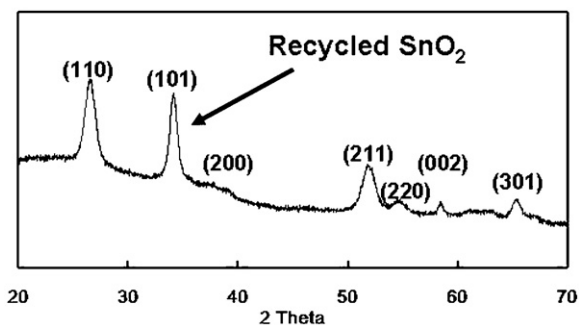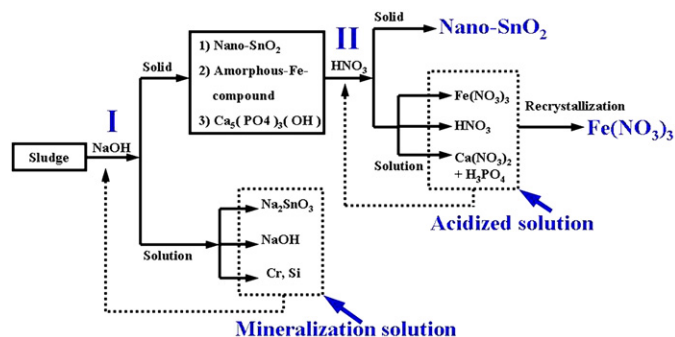
**Fig. 3.** XRD pattern of SnO₂ recycled from the electroplating sludge coarsened in 0.4 M NaOH at 230 °C for 48 h, followed with an acid treatment.



**Scheme 1.** Illustration of recycling of nano-SnO₂ from electroplating sludge in two steps: step (I) Fast Mineralization treatment of original sludge with an addition of NaOH, aiming at a fast and selective transformation of amorphous Sn phase into acid-insoluble SnO₂ crystallines; step (II) subsequent acid treatment of sludge to dissolve Ca₅(PO₄)₃(OH) and amorphous Fe compounds into solution.

we speculate that the SnO$_2$ might be dissolved again in higher-concentration NaOH solution, which will produce SnO$_3^{2-}$ ions. To verify this, we checked the concentration of Sn ions in alkaline solution against NaOH concentration. After a hydrothermal treatment at 230 °C for 48 h, as shown in Fig. 2c, in 0.4 M NaOH solution the content of Sn was found to be around 1.03 g/l (about 12% of Sn compound dissolved). As NaOH concentration increased to 0.7 M, the content of Sn was found to be around 4.54 g/l (about 54% of Sn compound dissolved). Thus to reach the fast growth of SnO$_2$ and keep Sn compound in solid part as much as possible, an optimal value of NaOH concentration is suggested to be 0.4 M. In addition, as shown in Fig. 2d, further time series XRD analysis of the sludge treated hydrothermally in 0.4 M NaOH indicates that the SnO$_2$ nanoparticles grow rapidly in the first 48 h. After that, little change can be found, suggesting that the growth rate of SnO$_2$ nanoparticles declined to a very low level after 48 h.

Based on above results, the optimized condition for realizing a selective transformation of amorphous Sn compound to SnO$_2$ crystallites could be the coarsening of the sludge in 0.4 M NaOH solution at 230 °C for 48 h. Next, the acid was used to examine the dissolution property of the sludge. Our experimental results reveal that, ∼40% of the solid sample could not be dissolved in the nitric acid. ICP analysis reveals that over 91.3% Fe, and most of Cr, P, and Ca in the sludge have been dissolved, while slight amounts of Sn can be detected in solution. XRD analysis (Fig. 3) further demonstrates that the residue was basically comprised of tetragonal SnO$_2$. It indicates that, after the acidification the amorphous Fe and Ca₅(PO4)₃(OH) were dissolved. Consequently, nano-SnO$_2$ powders with purity close to 90% can be obtained.

Furthermore, the extensive SEM and HRTEM observations were used to investigate the microstructure and growth behavior of the recycled SnO$_2$ particles. Fig. 4a shows the SEM image of the SnO$_2$ sample recycled from the sludge coarsened in 0.1 M NaOH solution. Small SnO$_2$ nanoparticles of size no more than several nanometers can be found. When NaOH concentration increased to 0.4 M, as shown in Fig. 4b, the dominant SnO$_2$ form were nanowires with over 200 nm in length. The HRTEM in Fig. 4c and f confirms that the SnO$_2$ nanowires are single crystals in nature and grow preferentially along [0 0 1] direction. Such a result confirms the conclusion from XRD analysis that in a certain range a higher NaOH concentration favors the crystal growth of SnO$_2$ nanoparticles. On consideration that XRD analysis cannot provide information of particle growth in [0 0 1] direction clearly, SEM observation can show the morphology and particle size of SnO$_2$ more precisely in three dimensions. Additionally, defects could be clearly observed in the lattice of the nanowire (Fig. 4f), showing traces of combination between adjacent particles. Similar phenomenon has been found in the growth of ZnO nanowires, and the OA mechanism was introduced to explain this growth behavior [17]. It indicates that a

multi-step OA growth mechanism probably exits in the formation process of SnO$_2$ nanowires.

Based on the above analysis, we proposed a two-steps strategy for recycling of SnO$_2$ nanowires from the electroplating sludge (Scheme 1). First, a selective and rapid growth of amorphous Sn phase into acid-insoluble SnO$_2$ crystallites is achieved by introducing NaOH as a mineralizer. Subsequently, the extraction of valuable SnO$_2$ is realized via an acid treatment to dissolve amorphous Fe compound and Ca₅(PO₄)₃(OH) into solution. Thus, valuable SnO$_2$ nanowires and Fe(NO$_3$)$_3$ solution can be ultimately separated and recycled, respectively. It should be noted that, after hydrothermal treatment, the NaOH solution containing with 12% dissolved SnO$_2$, as well as acidized solution containing HNO$_3$ and Fe(NO$_3$)$_3$, can be recycled and reused in next cycle of disposal.

The pilot-scale experiment was further conducted with this strategy. It is proved that the recycling of 90 g SnO$_2$ from 2.3 kg sludge can be successfully achieved. Nano-SnO$_2$ is an extremely expensive industrial material universally used as opacifier and white colorant in ceramic glazes or as polish powder and electrode material in glass, and has potential applications in lithium-ion batteries [18], gas sensors [19], or solar cells [20]. Consequently, profit might be obtained with treatment of the sludge, in spite that an investment should be paid in early stage. Therefore, the industry will find it more acceptable to adopt the strategy in real system.

## 4. Discussions

Our previous work has proved that the growth of nano-SnO$_2$ in water is very slowly and the particle size is no more than 5 nm even by coarsening at 230 °C for hundreds of hours [21]. In comparison, the present work shows that an addition of 0.4 M NaOH solution could help in the fast formation of SnO$_2$ nanowires with length over 200 nm. The contrast implies an important role of NaOH in accelerating the nucleation and crystal growth of SnO$_2$. Based on previous growth kinetic studies, as illustrated in Scheme 2, we speculate that the alkaline condition could facilitate both the OR and
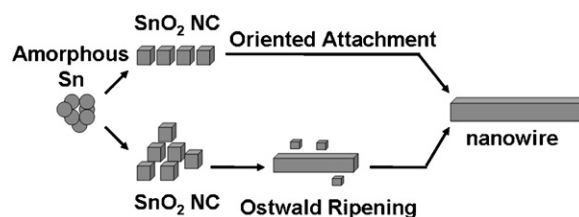


**Scheme 2.** Illustration of the growth and formation of large-scale SnO$_2$ nanowires via OA and OR mechanism, respectively. SnO$_2$ NC stands for SnO$_2$ nanocrystalline.
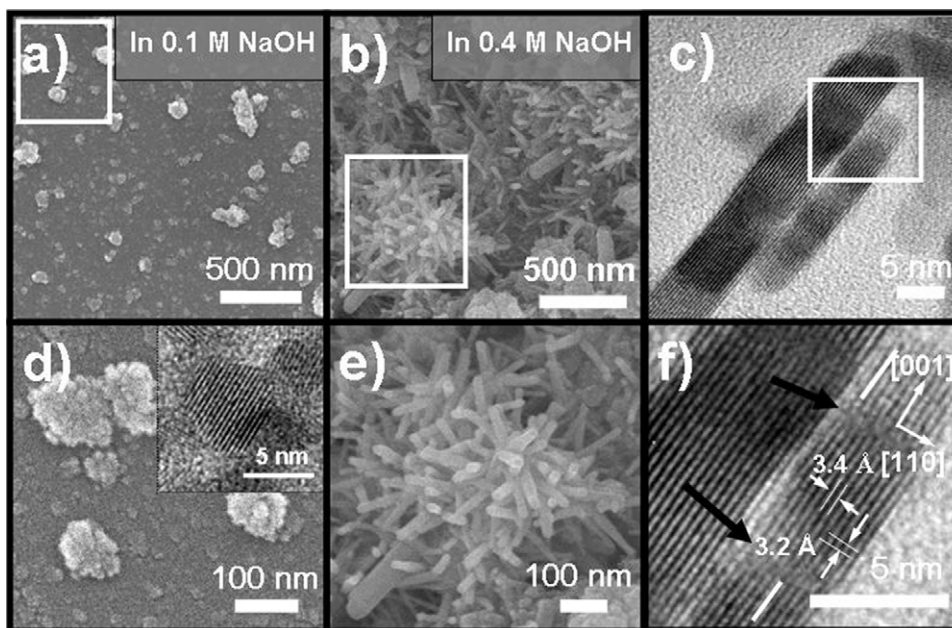
**Fig. 4.** SEM images of the SnO$_2$ recycled from the sludge coarsened (a) in 0.1 M NaOH solution, (b) in 0.4 M NaOH solution at 230 °C for 48 h, followed with an acid treatment. (c) HRTEM image showing details about crystal growth of SnO$_2$ nanowires in 0.4 M NaOH system. (d–f) Enlarged images of the white square part of (a–c), respectively. Insert in (d) shows HRTEM image of a typical 5 nm-SnO$_2$ nanocrystal. The parallelism of lattice fringes in (f) shows the crystallographic axes of particles in this area are basically parallel.

OA growth of SnO$_2$. First, the addition of NaOH could speed up the dissolution of SnO$_2$ as shown in Fig. 2c. Since OR growth involves the growth of larger particles at the expense of smaller ones via a dissolution–precipitation process [22], the onset of nucleation and subsequent OR growth of SnO$_2$ particles becomes more easily in NaOH solution. On the other hand, theoretically the diffusion rate of large-scale SnO$_2$ nanoparticles could be greater in alkaline solution than in water environment, owing to an increasing in the viscosity ($\eta$) of the alkaline liquid phase [23]. This solution could favor the multi-step OA growth of large-scale particles [23], where two crystallographically oriented nanoparticles combined together to form a larger one [24], leading to the formation of particles with anisotropic shapes [17]. Correspondingly, it was found that SnO$_2$ nanowires were formed during the mineralization process of sludge, and the multi-step OA growth mechanism probably participated in this process. As a result, NaOH as mineralizer promotes a fast growth of SnO$_2$, which could be regarded as a critical factor for treating the electroplating sludge.

In view that SnO$_2$ is amphoteric, previously Cao et al. also reported a simpler method to isolate 70% Sn in electroplating sludge from other sparsely soluble solids by dissolving Sn under alkaline condition, which generates Na$_2$SnO$_3$ solution [14]. Nevertheless, the method may have difficulties that, (a) the separation of Na$_2$SnO$_3$ solution from highly suspended amorphous Fe solid could be quite difficult by centrifugation or filtration method, and residual amorphous Fe compound still need the post-processing. (b) Results shown in Fig. 2 have revealed that, only ~12% Sn dissolved in 0.1 M NaOH solution at 230 °C for 48 h. Thus to reach the dissolution and recycling of Sn as much as possible, the longer process time and higher energy cost may be necessary. In comparison, the strategy by transforming the sludge into valuable nanoproduct via a fast crystal growth in this work seems more efficient. It means a higher return in spite of some energy costs in the early stage. Moreover, microwave can also be used in industrial scale to save the energy consumption during the realizaiton of the fast growth and recycling of nano-SnO$_2$.

Besides the electroplating sludge, in fact, issues on managing metals sludge containing amorphous/nanophase MOH are

universal in industry, as precipitation of metal ions via alkalization treatment is the most conventional method of wastewater treatment. Taking previous Cr$^{VI}$-adsorbed 20 nm-Mg(OH)$_2$ [11] and electroplating sludge in this work as study cases, it well shows that one of the most effective approaches to treat sludge containing ultra-fine MOH is to make nanoparticles grow into large ones. Differ from the release of adsorbed Cr$^{VI}$ ions into solution via a rapid transformation of nano-Mg(OH)$_2$ into bulk material [11], here we further shows that, a fast growth of SnO$_2$ can promote a change in acid solubility of Sn phase in electroplating sludge. The change makes the separation of Sn phase from other acid-soluble compositions of sludge feasible via an acid treatment. Enlightened by above results, as normally the growth of MOH is slow under ambient condition, an artificial addition of suitable mineralizer is necessary to speed up the select crystal growth of specific phase in sludge. Notably, in such way the hazardous electroplating sludge can be transformed into valuable SnO$_2$ nanowires. Moreover, both the mineralizer and Fe(NO$_3$)$_3$ solution can also be recyclable in this process. In a word, the strategy proposed here could provide a good example for disposing, cleaning up, and adequately making use of industrial sludge containing amorphous/nanophase MOH in industry.

## 5. Conclusion

In conclusion, a strategy to recycle SnO$_2$ nano-wires from tin-plate electroplating sludge was proposed in this work. By a selective control of the crystallization and growth of SnO$_2$ with an addition of NaOH as a mineralizer, the amorphous Sn compound fast transformed into acid-insoluble SnO$_2$ nanowires. Valuable SnO$_2$ nanowires thus were obtained via a subsequent acid treatment. The key role of NaOH in speeding up both the OA and OR growth of SnO$_2$ was discussed, and the introduced fast growth was regarded as a critical factor to implementing the treatment of sludge. We hope a strategy developed in this way could have a potential ability to the recycling of valuable metals from industrial sludge containing amorphous/nanophase MOH in other areas.

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