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Controllable synthesis of nanostructured metal oxide and oxyhydroxide materials via electrochemical methods

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Highlights

- Electrochemical methods allow the control over the particle size and shape of metal oxide and oxyhydroxide materials
- (Photo)catalytic properties depend on the structural geometry, size and crystallinity of the metal oxide and oxyhydroxide nanoparticles.
- Various synthesis methods result in different nanostructure forms, namely thin films or dispersed nanoparticles.

Summary

The synthesis of metal oxide and metal oxyhydroxide nanomaterials is a very active area of research that has an enormous impact on the development and progress of new technologies. This review summarizes the most relevant and recent work on the electrochemical synthesis of metal oxides and oxyhydroxide nanostructures. It also provides the personal, critical view of the authors regarding the advantages and challenges of the methods upon potential commercialization.

Introduction

Metal oxides and metal oxyhydroxide nanoparticles play a central role in many areas of chemistry, physics, biology and materials science due to their vast number of applications such as catalysis, electronics, photonics, drug delivery, optics, sensing, environmental remediation, and energy storage/conversion applications.[1-8]

Such nanostructures, however, exhibit different physiochemical properties depending on the particle size, the structural geometries and level of crystallinity. Metal oxide and metal oxyhydroxide nanoparticles of the same material but different structure or particle size might show different optical, thermal, electrical and chemical properties. In particular it is well known that the size and surface structure play an important role in the photoelectrocatalytic processes.[9, 10] Therefore, special attention should be paid to the selection of the synthesis method, taking into account the close connection between the chosen pathway and the size/shape/crystallinity of resulting oxide and oxyhydroxide nanostructures.

Many chemical and physical synthetic pathways have been explored for the preparation of metal oxide nanomaterials and more recently metal oxyhydroxide nanomaterials with exercisable control over size, shape and composition of mixed metal oxides.[11-16] The most utilised approaches are sol-gel and hydro/solvo-thermal methods, which have been found to be extremely versatile when it comes to the scope of products.[17-20] Nevertheless, the utilization of the organic solvents/surfactants increases the cost, complexity, and likelihood of surface contamination by adsorbing species. In addition, such methods quite often require the implementation of high temperatures reaching over 1000 °C which result in the sintering of the nanostructures with lower of control over the size and shape of the resulting nanomaterials. These two methods, although very useful in the preparation of single metal oxide particles, do not provide many opportunities to prepare mixed metal oxide nanomaterials, an emerging class of materials with outstanding properties. Mixed metal oxides can be prepared via a microemulsion method,[21, 22] which also provides tools to control size, shape, and composition. However, emulsion formation requires the use of surfactants – molecules that are prone to adsorb on the surface of particles and decrease their activity due to the blocking of active sites.

Electrochemical routes have been shown to be powerful methods for synthesis of metal oxides and oxyhydroxides nanostructures and more recent improvements in the methodologies have demonstrated the potential to control the composition and/or morphological features in the absence of adsorbing capping agents.[23-26]

The purpose of this short review is to highlight some of new electrochemical methods of synthesis of metal oxides and oxyhydroxide nanomaterials. It does not aim to cover all the methods of synthesis but to provide a personal view of notable methods that, given their advantages, could potentially be commercialized. Specifically, we cover three synthetic routes, namely electrochemical deposition (both cathodic and anodic), cathodic corrosion, and galvanic exchange reactions. In addition, we will briefly discuss the impact of the morphology and size of the metal oxides and metal oxyhydroxide nanoparticles prepared by these routes in their (photo)catalytic activity.

Electrodeposition of nanostructured thin-film metal oxides

The generation of conductive metal oxides and oxyhydroxides via electrodeposition (ED) has long been shown to be a useful synthetic route. ED is a highly versatile technique that: allows for deposition under fixed potential or voltammetric conditions; operates at ambient/low temperatures; has great potential for industrial scale-up due to simplistic setup and mechanism; can be easily modified by variation of the substrate, operating potentials and/or electrolyte constituents.

Early examples of the ED of oxyhydroxides involved the anodic deposition of aqueous solution species, most commonly containing transition metal 2+ cations (M^{2+}), onto conductive metal substrates under potentiostatic control to generate oxide thin films for (photo)electrocatalysis applications.[27, 28] Cathodic ED is facilitated by pH changes local to the working electrode (WE) due to the hydrogen evolution reaction (HER) increasing the

concentration of hydroxide ions, which subsequently react with M^{2+} to precipitate and deposit metal hydroxide species, $M(OH)_2$, as thin films which can be further oxidised to the desired metal oxide.[29-32] Homogeneous cathodic deposition of the (oxyhydr-)oxide is only achieved provided that the reduction potential of M^{2+}/M^0 is sufficiently more negative than that of H^+/H_2 , otherwise the metallic form, M^0 , would be formed before the formation of the $M(OH)_2$ complex in the presence of liberated OH^- . Other reduction pathways such as nitrate and nitrite reduction have been used as precursors for the generation of OH^- during the cathodic ED of metal oxides and oxyhydroxides.[23, 27, 29-31]

ED of mixed oxides has been of particular interest in recent years due to their enhanced stability and activity. Sayeed and O'Mullane demonstrated the use of cathodic ED to synthesise single, binary and ternary oxides of Fe, Co and Ni utilising the hydrogen evolution reaction (HER) as the avenue for OH^- generation and equimolar concentrations of the metal salts.[29] Compositional analysis of the electrodeposited films, both before and after oxygen evolution reaction activity evaluation, highlighted the less favourable deposition of $Fe(OH)_2$ under cathodic conditions compared to the other metals due to lower observed Fe content. Under anodic deposition conditions, Fe deposition is more favourable, again hindering the transfer of stoichiometry from equimolar electrolytes to the resulting thin film. Hu et al. addressed this issue by replacing Fe^{2+} with Fe^{3+} in the deposition solution, leading to in-situ generation of Fe^{2+} by reduction at the CE, thereby counteracting preferential Fe deposition under anodic deposition conditions.[23]

The physical and electrochemical properties of the deposited oxyhydroxides is strongly dependent on the substrate and the additives used for its ED as demonstrated by Lin et al. The authors used a 3D porous Ni foam as substrate for the co-precipitation and deposition of Ni and Co and NiCo mixed oxyhydroxides (Figure 1A(i)).[30] The combination of a 3D substrate and introduction of oxygen vacancies in the crystalline structure via

oxidation/reduction steps using temperature annealing and reduction with (NaBH_4), resulted in an increase of the catalytic activity due to the increase of the surface area and active sites. Similar synthetic routes were employed to co-deposit $\text{La}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ to yield LaFeO_3 after annealing,[31] however, none of these studies have shown evidence for control of oxide size, shape or morphology. Improvement of the methodology to allow further control of the porous size and surface structure expose would be highly relevant in the development of this type of catalyst.

Investigations into the controllable synthesis of nanostructured copper oxide (Cu_xO) have been of particular interest in recent years due to the various applications in which these materials have found use including the upraising investigation of the conversion of CO_2 into fuel.[33-37] Li et al. conducted a comprehensive study on the nanostructures of Cu_2O formed by surfactant-assisted ED and observed that cubic structures are formed in the absence of the sodium dodecyl sulfate (SDS) surfactant, while increasing the SDS concentration served to reduce the cubic nature of the deposited oxide film, generating flower-like structures and, finally, amorphous nanostructures under identical electrochemical conditions.[38] While the presence of the surfactant in the reaction media seems to be relevant in the control of the surface structure and particle size of the nanostructures, the adsorption of organic molecules on the surface of the nanostructures might be a disadvantage in the utilization of this materials for catalysis due to the decrease of the available active sites.

The preparation of oxide nanostructure thin films can be achieved by underpotential deposition of metals under an oxygen atmosphere or electrodeposition/electrooxidation of the surface.[32, 39, 40] Demir et al. demonstrated the capabilities of this method to prepare Cu_2O and/or CuO over Au surfaces.[24] As can be seen in Figure 1A(ii-iv), the concentration of O_2 influenced not only the composition and termination of the copper oxides but also the structure of the nanostructures. The Cu nanostructure deposited with low oxygen (O_2) flow

rate resulted in the formation of cubic Cu_2O (Figure 1A(ii)) while those films deposited under a high O_2 flow rate displayed flower-like, dendritic CuO nanostructures (Figure 1A(iii)). Variation of the O_2 flow rate during deposition, increasing from the lower to the higher rate after 30 min, facilitated the formation dendritic CuO atop cubic Cu_2O , evidenced by Figure 1A(iv), demonstrating the tunability of the process. The authors also showed the versatility of the method by preparing the Cu_xO nanostructures onto ITO substrates, indicating that the process is not substrate dependent.

Pritzker et al. employed AC ED onto deposit Cu_2O thin films onto FTO substrates and demonstrated how the parameters of the square waveform such as frequency can be used to tune the nanostructure of Cu_2O deposits (Figure 1B).[25] The authors demonstrated that morphological changes – cubic to spherical/amorphous nanostructures – could be obtained by varying: the frequency, the amplitude and the duty cycle of the squarewave, the pH of the solution and the Cu^{2+} concentration. However, in all cases it appears that changes in the square wave parameters served to change the equilibrium between the two morphologies, i.e. only fluctuations between cubic and spherical particles are observed. Even though this work has shown the capabilities of the method to prepare Cu_2O nanostructures with defined nanostructure, further studies are needed to demonstrate its versatility in preparing a wider range of materials and fine control over the structure and size of the nanomaterials as a function of the pH, temperature and more importantly, the underlying substrate.

The cathodic ED has been also used to prepare other highly ordered, crystalline, uniform hierarchical metal oxide nanostructures such as ZnO nanostructures (Figure 1A(v-vi)).[41, 42] These hierarchical nanostructures were shown to possess improved activity towards the electrochemical oxidation and sensing of hydrazine molecules compared to non-hierarchical ZnO , with the observed improvement in sensing ability attributable to the significant increase in the electrochemical surface area.[42]

Template-assisted ED is another route that has been shown to generate metal oxide nanostructures by depositing the oxyhydroxide material into well-defined pore channels. Use of porous templates was pioneered in the 1990s,[43-45] with reports on the ED of metal oxides onto porous templates emerging at the turn of the 21st century.[46-49] Anodized aluminium oxide (AAO) templates, commonly used materials generated by the anodization of metallic aluminium, can be tuned to generate a variety of pore sizes, from a myriad of electrolyte, applied potential and temperature systems.[50] The anodization of metals to generate porous metal oxide nanostructures, i.e. nanotubes, has also been exploited for different metals, particularly for self-ordered TiO₂ nanotube arrays (TNTAs) since this type of material is useful for several applications; a comprehensive review of TNTAs can be found in reference [51]. Most commonly, a 2-step anodization procedure is employed to generate the TNTAs (Figure 1C), with homogeneous tube spacing and pore sizes observed at the end of synthesis (Figure 1C(i-ii)). TiO₂ has long been known to be an active material for photoelectrochemical water splitting,[52, 53] with the anatase form being more active than rutile or brookite, reported to be due to the presence of an indirect band gap which leads to a relative increase in the lifetime of photogenerated charge carriers compared to rutile/brookite systems, which have direct band gaps that facilitate a higher rate of charge carrier recombination.[54] In the direct band gap materials, the electron wave vectors of the valence band maximum and conduction band minimum are equivalent, resulting in direct recombination with photo-generated holes. The non-equivalence of these two electron wave vectors in direct band gap materials requires a transfer of momentum to occur before recombination. Thus, the effective lifetime of the charge carriers is increased in indirect band gap semiconductors.

Conversion of detached amorphous TNTAs to anatase by annealing at high temperature would present the possibility of a flow-through water splitting system. However, the

annealing process introduces defects, namely bending and cracks, disrupting the tubular channels. Schmuki and co-workers have addressed this issue in a series of reports published in the last 2 years. They found that the inclusion of lactic acid in the anodization electrolyte allowed for defect-free, TNTAs to be formed after annealing of the detached amorphous membrane at temperatures $>450\text{ }^{\circ}\text{C}$, generating crystalline anatase phases.[55] Further investigations revealed that the anodization of Ti in organic electrolytes generates core-shell structure, where a carbon-rich core is formed within the TiO_x -rich shell, but the inner core could be removed via a chemical dissolution step.[56] The effects of anodization potential and anodization time(Figure 1C), electrolyte, H_2O content and temperature on the resultant TNTAs has been also investigated. [55-59] It was found that the applied voltage and electrolyte temperatures were the most significant parameters in the production of spaced TNTAs at a fast rate.

Schmuki et al. have also extended the versatility of anodization to generate conductive core-shell nanotubes of TiO_2 , and also $\text{MoO}_x\text{-MoS}_2$; the first demonstration of the formation of self-ordered MoO_3 arrays.[58, 59] Self-ordered anodization offers an electrochemical pathway toward the generation of high surface area oxide materials that can be tuned to produce, single-walled, double-walled, tube-in-tube and core-shell nanostructures, with the potential to be used in many applications.

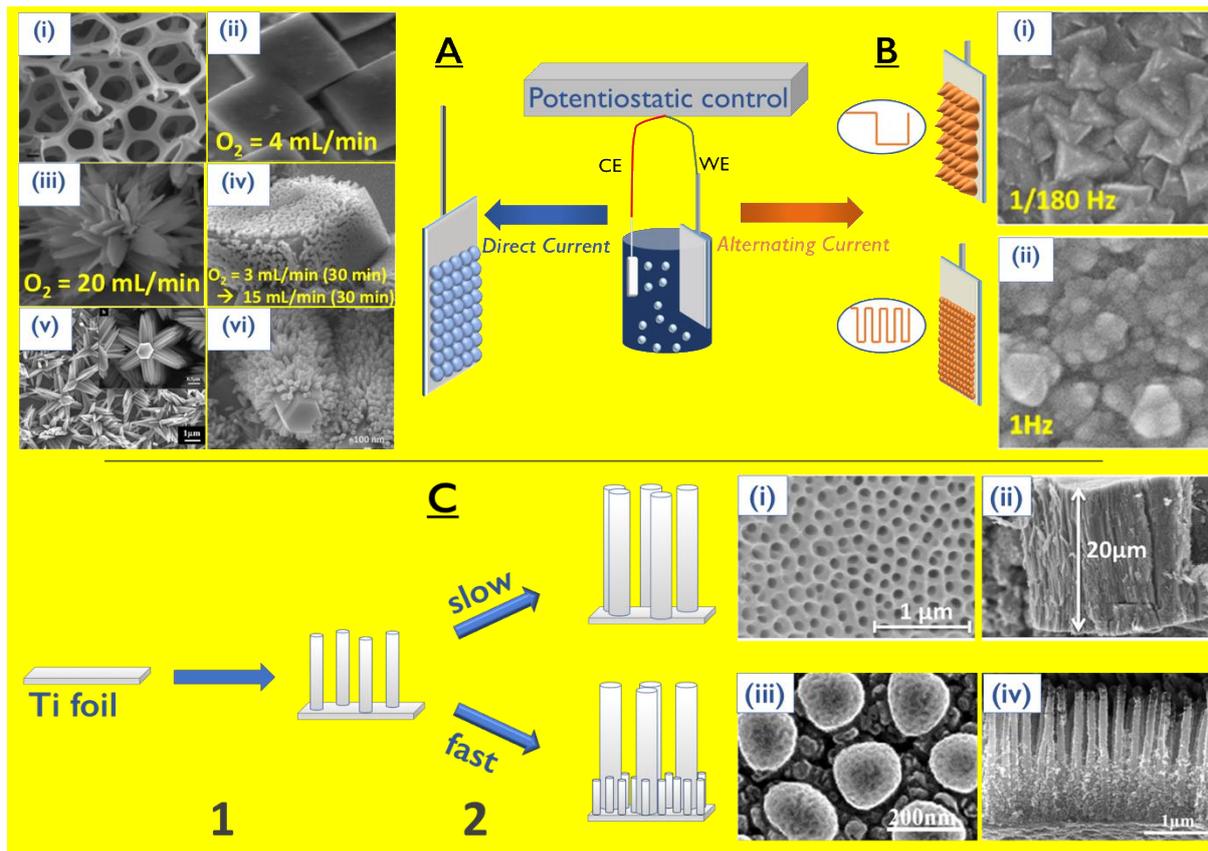


Figure 1: Schematic illustration of a 2-electrode setup for electrochemical deposition of aqueous species onto a conductive substrate under (A) applied direct current and (B) applied alternating current. Representative SEM images of: (A)(i) NiCo₂O₄ electrodeposited onto a 3D porous Ni foam substrate, adapted from Ref. [30] with permission from Wiley; (ii-iv) nanostructure of cubic, flower-like and flower-like covered cubes of Cu_xO produced via under potential deposition under various O₂ flow rates (annotated), adapted with permission from Ref. [24]. Copyright (2017) American Chemical Society; (v) hierarchical ZnO nanoneedle-on-nanoneedle structures with 6-fold symmetry, adapted with permission from Ref. [41]. Copyright (2007) American Chemical Society; (vi) hierarchical hexagonal nanorod-on-nanorod ZnO structures, adapted from Ref. [42] with permission from Elsevier; (B)(i-ii) the change in Cu₂O nanostructure due to changes in the applied square waveform frequency, adapted from Ref. [25] with permission from Elsevier. (C) Schematic illustration and accompanying SEM images of 2-step anodization processes applied to a Ti foil to generate self-ordered TiO₂ nanotubes (TNTAs); (i) top-view and (ii) side-view of TiO₂ membrane generated via a “slow” second anodization process, adapted from Ref. [58] with permission from Elsevier (iii) bottom-view and (iv) side-view of spaced TNTAs generated via a “fast” secondary anodization step, adapted from Ref. [57] with permission from Elsevier.

Electrochemical synthesis of metal oxide nanoparticles via cathodic corrosion

Many examples of the electrochemical synthesis of nanostructured metal oxides often involve the deposition of a thin film on a substrate, as either the main step or an inclusive step. Here we present cathodic corrosion as an alternative electrochemical method, in that, the nanostructures are produced as suspended particles rather than a thin film.[60, 61] Cathodic corrosion is a powerful tool for the facile electrochemical synthesis of metallic and alloy nanoparticles (NPs). The method involves the application of strong cathodic alternating current to electrochemically etch the WE in a conductive electrolyte. During cathodic corrosion, highly reactive intermediate anionic metal species are formed. These anionic intermediates are not stable and subsequently react via chemical oxidation, facilitated by aqueous oxygen species, to form metal nanoparticles. These metal clusters/nanoparticles can further oxidize, forming metal oxide nanoparticles. Early studies demonstrated the capabilities of the cathodic corrosion method to produce suspensions of crystalline core-shell Sn-SnO₂ nanoparticles as lithium-ion battery anode materials and amorphous TiO₂ nanowires as supports for Au nanocatalyst.[62-64] Recently, Rodriguez's group reported a more extensive description of the synthesis of TiO₂ nanowires, crystalline BiVO₄ nano-stars and crystalline H₂WO₄ nanorods using the cathodic corrosion method at room temperature, in the absence of organic solvents or surfactants (Figure 2).[26] The authors demonstrated for the first time that the size and shape of the oxide nanostructures can be controlled by variation of the applied square wave frequency as highlighted by the SEM/TEM images (Figure 2A-B). Early results have also shown that the particles size of the oxide nanoparticles increases with the concentration of the electrolyte in the same fashion as was reported for metal nanoparticles.[65] Preliminary data show that TiO₂ nanowires can be prepared in 10 M NaOH,[64] while small round TiO₂ nanoparticles can be obtained under similar conditions of applied voltage and frequency, but by reducing the concentration of the electrolyte to 2 M

(Figure 2C). Such differences on size and shape are highly relevant on the photoelectrochemical activity of the oxides towards water splitting.[26]

Similar pulse potential methods for the electrochemical synthesis of metal oxide NPs have been reported. Such methods compromise the reduction of the electrodes and oxidation of the electro-generated species by use of identical-sized working and counter electrodes. In terms of particle shape and size control, the produced ZnO nanorods suffered from poor size and shape homogeneity, whilst the TiO₂ lacked well-defined nanostructure, even in the presence of a capping agent.[66] Similarly, the as-produced Co oxyhydroxide material suffered from poor nanostructure homogeneity.[67]

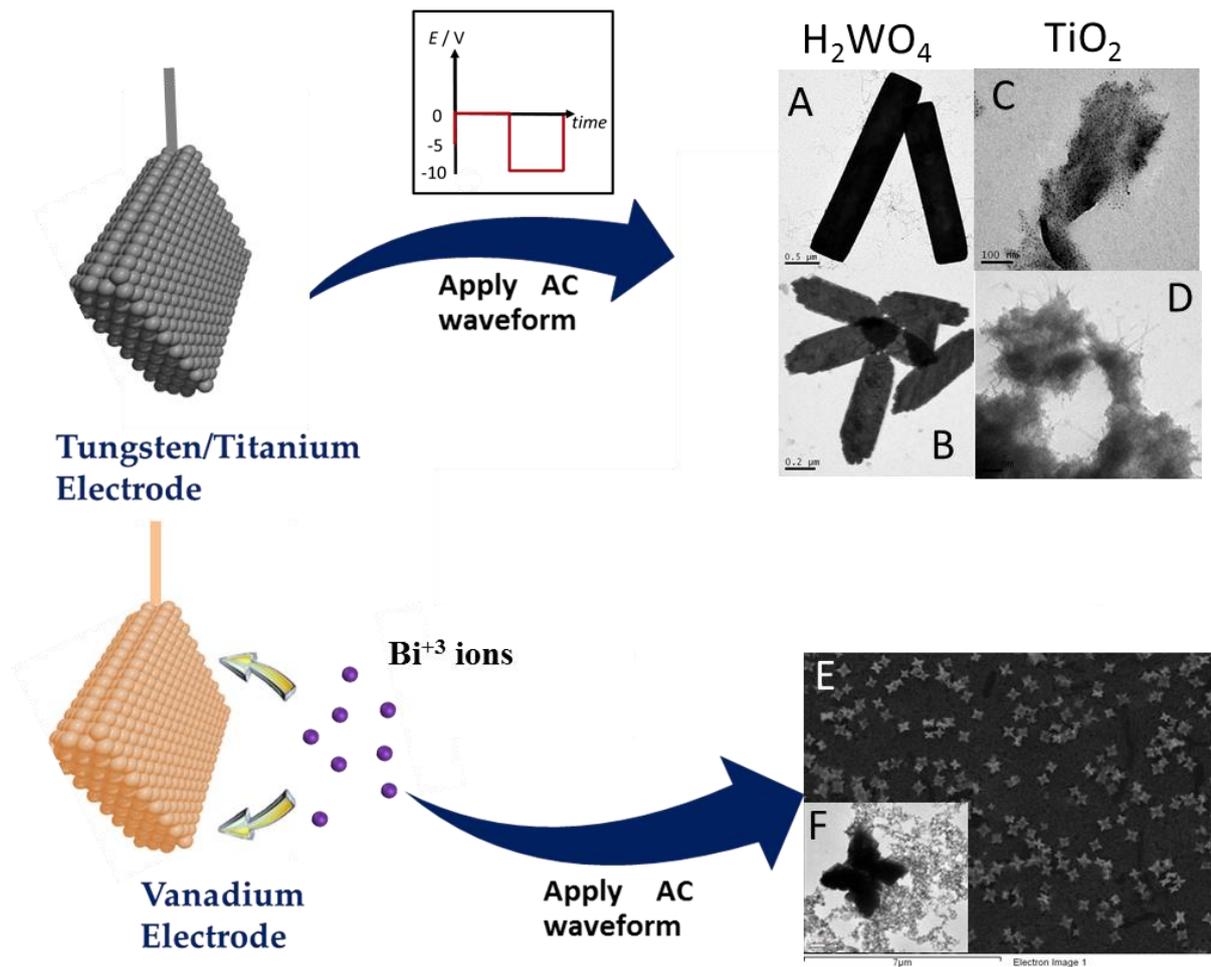


Figure 2: Schematic illustration of the formation of metal oxide nanoparticles via cathodic corrosion; pure metallic electrodes are electrochemically etched to produce a suspension of metal oxide nanoparticles, with controllable size and shape. TEM images of H₂WO₄ nanorods synthesized by application of a square waveform at (A) 100 Hz and (B) 1000 Hz, respectively. (C-D) TEM images demonstrating the effect of electrolyte concentration and applied potential on the morphology of TiO₂ nanowires synthesized via cathodic corrosion in (C) 2 M NaOH and (D) 10 M NaOH. (E) SEM and (F) TEM images of BiVO₄ nano-stars synthesized via cathodic corrosion. Adapted with permission from Ref. [26]. Copyright (2017) American Chemical Society.

Synthesis of nanostructured metal oxides by galvanic exchange

The majority of electrosynthetic pathways towards the formation of metallic oxides involve a substantial driving force to push the reaction to a state far from equilibrium. As an alternative to this, Oh et al.[68] have proposed an elegant way to prepare metal oxide nanostructures via the galvanic replacement reaction (GRR). GRR is a spontaneously occurring process at the open circuit potential (OCP) which is driven by a difference in electrochemical potentials between an oxide-confined metal and a free metal ion. As in a typical Galvani cell, this thermodynamic bias is diminished by a tendency of the system to reach equilibrium conditions, and eventually – a substitution of a cation in the oxide lattice.

Although this synthetic strategy has not been extensively studied, it has already brought a few advances to the field. First of all, the formation of core@shell nanoparticles is relatively straight-forward as it involves the addition of a foreign metal, which subsequently substitutes the outermost layers of the native metal within the oxide lattice (Figure 3A).[69-71] Additionally, it has been shown that the ratio between core and shell thickness can be modulated while maintaining the particle diameter.[70] However, the main drawback is the lack of homogeneity in the deeper layers due to diffusional limitations of the metal in the solid. In addition, the morphology of prepared nanoparticles was not well defined due to the so-called Kirkendall effect that gives origin to hollow structures (Figure 3B).[71, 72]

The formation of hollow structures via the Kirkendall effect has attracted substantial attention.[73-75] Many different hollow nano-forms including rattles, boxes, bowls, spheres, and particles of various shapes have been reported using GRR; Figure 3C(i-iv) shows the progressive change of the shape of the nanostructures during the synthesis of the nanobox.[69, 76, 77].

The GRR has been also employed in the preparation of exfoliated 2D layered metal oxide nanosheets. The authors reported the galvanic replacement reaction of exfoliated MnO₂ nanosheets by Fe²⁺ or Sn²⁺ ions resulting in highly anisotropic Fe or Sn oxide nanosheets. [78] These resulting materials are very relevant for lithium ion batteries and have potential as catalyst for oxygen evolution reaction.

Further improvements of the GRR methodology includes a fine control of the shape and structure of the particles. In this case, GRR has been implemented to metal oxide nanoparticles with well-defined shape as a sacrificial-template to grow particles of other metal oxides (Figure 3D).[77] The importance of particle shape control has been extensively described in the literature with a particular interest in electrocatalysis.[79] Therefore, some attention has been paid to the factors determining the shape of particles of metal oxides[76] and oxyhydroxides[80] applicable in the field of energy conversion.

The early stages of galvanic replacement reactions in metal oxide structures raise a promise of a facile way to prepare these structures with a certain degree of control over the size, shape and composition. Nevertheless, the GRR approach is yet applicable to a very few types of metal oxides of the highest reactivity. Moreover, the relatively slow kinetics require the use of moderately elevated temperature, what may be considered as a drawback when compared to the classical electrochemical methods. Finally, a clear understanding of the galvanic exchange process within metal oxides is needed in order to rationally explore the scope of the method.[81-83]

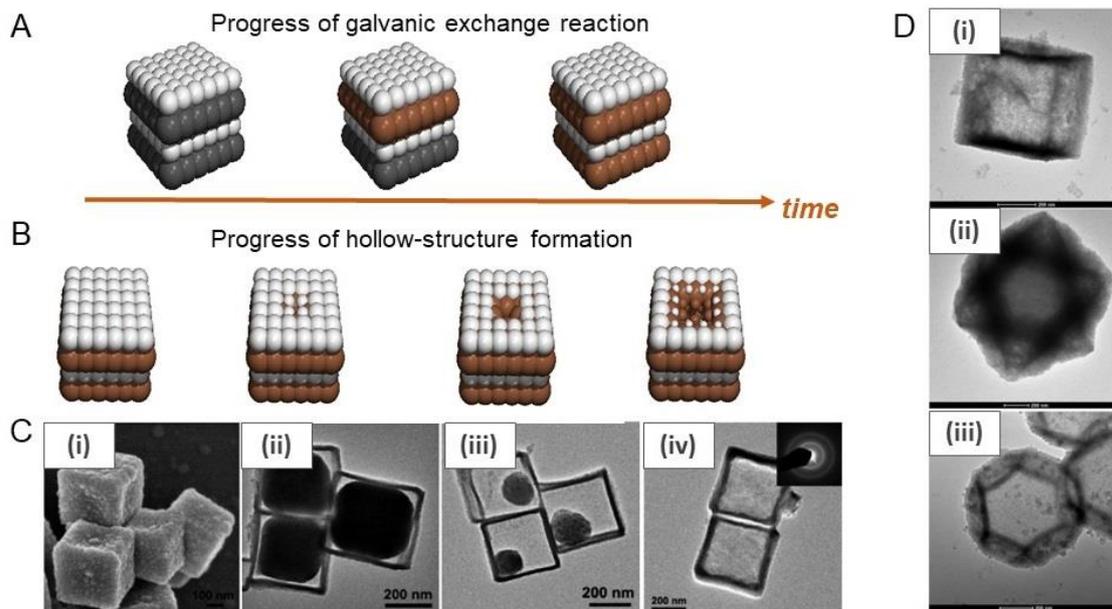


Figure 3: (A) Schematic representation of the galvanic exchange reaction and (B) hollow-structure formation where grey spheres represent the native metal; white – oxygen; brown – incoming metal. (C)(i) SEM and (ii-iv) TEM study of the evolution of $\text{Cu}_2\text{O}@Fe(\text{OH})_x$ over time to form a nanobox. Adapted with permission from Ref. [69]. Copyright (2010) American Chemical Society. (D) High-resolution TEM images of (i) cubic (ii) octahedral and (iii) dodecahedral NiO particles grown on a sacrificial Cu_2O substrate. Adapted from Ref. [77] with permission from Elsevier.

Conclusions

With this review, we have made an effort to highlight the more recent contributions and progress in the area of electrochemical methods for synthesis of metal oxide and oxyhydroxide nanoparticles. Each of the methods clearly present a number of advantages and disadvantages based on: the versatility of the materials can be prepared with said method, the control over the structure and morphology, the time and cost of the method, scalability for industrial applications and, of course, the application, i.e. whether the final nanostructure is an electrodeposited thin film or a dispersion of nanoparticles.

In the search for new nanostructured materials with enhanced (photo)catalytic properties, desired composition and structural characteristics, electrochemical methods are indeed powerful tools and the new advances in the control of the structure and size are very encouraging. The electrochemical synthesis of the metal oxides and oxyhydroxides is ecologically friendly and the preparation quite often is inexpensive, providing a more efficient route for the generation of a variety of highly active materials.

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