



# Sacrificial template synthesis of high surface area metal oxides. Example: An excellent structured Fenton-like catalyst



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## ABSTRACT

Standard sacrificial template synthesis allows metal oxide nanotubes to be produced from ZnO nanowires. In spite of their high interest in several technological fields, the low surface area of these nanotubes is a drawback for most applications. Here we report for the first time the sacrificial template synthesis of stainless steel wire-mesh (SSWM) supported metal oxides of high technological interest (CuO, CeO<sub>2</sub>, α-Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) with specific surface area values (84–275 m<sup>2</sup> g<sup>-1</sup>) that are at least one order of magnitude higher than that of metal oxide nanotubes. The key to achieving this outstanding result was the use of a novel template (SSWM-supported ZnO nanosheets) with a large proportion of polar surfaces. As an example of application of these materials, a structured reactor with a highly active SSWM-supported α-Fe<sub>2</sub>O<sub>3</sub> catalyst was successfully tested for the continuous Fenton-like degradation of aqueous Methylene blue.

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## 1. Introduction

Metal oxides of high surface area are used in many applications such as heterogeneous catalysis, wastewater conditioning, the electrochemical storage of energy, sensing, etc [1–5]. There is a great need to develop versatile low temperature synthesis methods for the preparation of nanosized metal oxides with an elevated specific surface area and a high yield on the external surface of flexible metallic supports that will allow microdevices with excellent heat transfer and electrical conductivity properties to be built. Among these supports stainless steel wire meshes (SSWM) of micrometric dimensions have been recently used with great success for supporting high surface area cobalt and zinc oxides [6,7]. In this work, a low temperature method for obtaining nanosized metal oxides supported on SSWM is presented. To demonstrate the potential of this invention, one of the obtained materials (SSWM-supported α-Fe<sub>2</sub>O<sub>3</sub>) was successfully employed as a structured catalyst for the continuous degradation of aqueous methylene blue via the heterogeneous Fenton-like reaction with hydrogen peroxide [8,9].

## 2. Experimental

### 2.1. Preparation method

The support was SSWM [with a wire diameter of 30 μm and a screen opening of 40 μm] provided by CISA. The SSWM-supported ZnO was synthesized as described in [7]. In summary, Zinc acetate dehydrate was dissolved together with urea in deionized water. Concentrations of Zn<sup>2+</sup> and urea in the aqueous solutions were adjusted to 0.05 and 1.0 M, respectively. The pH of the solution was adjusted to 4.88 by using acetic acid. The wire mesh was placed in a Teflon autoclave (100 mL) filled with the growth solution. The autoclave was sealed and hydrothermal ZnO growth proceeded at 80 °C for 23 h in a constant-temperature water bath. The ZnO coated-wire mesh was then taken out of the solution, thoroughly washed with deionized water and vacuum-dried at 60 °C. Finally the sample was calcined at 200 °C for 0.5 h in air.

To fabricate the copper, cerium and titanium oxides by means of the *basic synthesis method*, the as-synthesized SSWM-supported ZnO templates were immersed in plastic flasks containing 50 mL water solutions of metallic salts. For the preparation of TiO<sub>2</sub> boric acid was added to the solution at a H<sub>3</sub>BO<sub>3</sub>/K<sub>2</sub>TiF<sub>6</sub> molar ratio of 3/1. The closed flasks were subjected to shaking at RT in an orbital shaker for different durations of time in order to obtain different degrees of metal substitution. To synthesize the iron oxides by the *dropwise synthesis method*, water solutions (50 mL) of iron(III) nitrate or iron(II) sulphate were slowly pumped with a syringe pump into plastic flasks containing 50 mL of water and the SSWM-supported ZnO templates, while the flasks were shaken in an orbital

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shaker at RT. Afterwards, the samples were taken out of the flasks and washed with deionized water, vacuum-dried at 60 °C for 30 min and calcined in air at 250 °C (in the case of copper, cerium, iron (ex-Fe<sup>2+</sup>) and titanium oxides) or at 275 °C (in the case of iron (ex-Fe<sup>3+</sup>) oxide) for 2 h. The calcination temperatures were selected after TGA analyses of the different samples.

## 2.2. Material characterization

The chemical composition of the metal oxides was evaluated by means of atomic absorption spectroscopy. The morphology of the samples was studied by scanning electron microscopy (SEM, FEI Quanta FEG 650 model) and transmission electron microscopy (TEM, JEM-2100F). The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The BET specific surface area of the samples was evaluated by means of N<sub>2</sub> adsorption isotherms (–196 °C) obtained on a Micromeritics ASAP 2020 analyser. Raman spectra from 100 to 1400 cm<sup>–1</sup> were obtained at room temperature using a T64000 System (Horiba).

## 2.3. Heterogeneous Fenton-like reaction

Fenton-like degradation of methylene blue (MB) in aqueous solutions was performed with SSWM-supported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts in two modes; batch and continuous operation. All reactions were carried out in the dark to avoid the influence of light. No acid or base was added to adjust the pH value of the reaction solution. A batch reaction experiment was carried out in order to compare the catalytic activity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder obtained in this work (scratched from the wire mesh-supported material) with that of yolk-shell structured Fe<sub>2</sub>O<sub>3</sub>@mesoporous SiO<sub>2</sub> particles reported by Cui et al. [10]. The reaction was performed in a magnetically stirred reactor at room temperature, at the same reaction conditions used by Cui et al. [10] (0.5 g L<sup>–1</sup>  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 50 mg L<sup>–1</sup> MB, 18 g L<sup>–1</sup> H<sub>2</sub>O<sub>2</sub>). Liquid samples were taken for measurement at given reaction times and centrifuged to remove the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. The visible absorption peaks of the analyzed samples were recorded in the 400–800 nm range by means of a UV–Vis spectrometer (Shimadzu UV-2401PC). The concentration of MB was evaluated from calibration curves using the absorbance at 664 nm.

For the continuous operation mode, a SSWM-supported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst with dimensions of 2.5 cm  $\times$  5 cm (36 mg  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was rolled around a stainless steel wire and inserted into a silicone tube with an internal diameter of 4 mm (Fig. 8). A 50 mL solution containing 50 mg L<sup>–1</sup> MB and 18 g L<sup>–1</sup> H<sub>2</sub>O<sub>2</sub> was introduced into a syringe coated with a black tape (not shown in Fig. 2). The MB/H<sub>2</sub>O<sub>2</sub> solution was then slowly injected by means of a syringe pump into the silicone tube containing the SSWM-supported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fig. 2). Experiments at different residence times (pumping rates) were performed. For a given experiment the concentration of the exit solution was analyzed every 5 mL and found to be quite stable during the entire experiment. The final degree of MB degradation was expressed as the average value of all measurements ( $\langle C/C_0 \rangle$ ).

## 3. Results and discussion

### 3.1. Sacrificial template synthesis of high surface area metal oxides

Of the many synthesis methods described in the scientific and patent literature, mainly for making unsupported metal oxides, hard templating methods are known to be among the most effective in producing high surface area metal oxides in powder form [11,12]. However, these methods involve several synthesis steps, including the removal of the template by oxidation or dissolution. Sacrificial

template-accelerated hydrolysis (STAH) is a novel hard exotemplating technique [13] that consists in the formation of metal oxide nanotubes via the hydrolysis of metal ions in the vicinity of ZnO nanowires, generally supported on ITO. Hydrolysis is favoured by the removal of protons due to the simultaneous dissolution of the ZnO scaffold, which is the distinctive characteristic of this technique. Thus, its main advantage over other classical hard templating approaches is that there is no need for a template removal step. Initially used for the synthesis of Fe<sub>2</sub>O<sub>3</sub> nanostructures with a high lithium-ion storage capacity [13–15] STAH has also been applied in the preparation of platinum and palladium nanotubes for electrocatalysis and chemical sensing [16,17], NiO-based electrodes [18,19], CeO<sub>2</sub> nanotubes [20], and active electrocatalysts consisting of mixtures of noble metal nanotubes [21]. The common feature of all these publications is that the ZnO template is made up of nanowires or nanorods and the metal oxides obtained are in the form of nanotubes, with the exception of the ZnO- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets described by Qin et al. [14], which have a higher specific surface area (27 m<sup>2</sup> g<sup>–1</sup>) than nanotube-based materials. The values of the specific surface area and yields of these nanotubes have not been reported in any of the revised papers though their geometrical characteristics (e.g. nanotube diameters of hundreds of nanometers) suggest that their associated specific surface areas and yields are low.

As an example of a nanotube-precursor template, Fig. 1a shows a SEM image of a SSWM-supported ZnO sample. The synthesis of this sample has been described in a previous work [22] (denoted there as S0-Bai). It consists of typical hexagonal prisms of large size, very low specific surface area and with a small proportion of polar planes (top of the prisms). Fig. 1b shows the prisms after they have been immersed in an aqueous solution of iron(III) nitrate. As can be seen, the iron oxide only forms on the external (non-polar) surface of the prisms (as detected by EDX) whereas their inner cores are hollowed out by the etching action of the protons released via the hydrolysis of Fe<sup>3+</sup> on the top (polar) surface of the prisms. A scheme of this mechanism is shown in Fig. 1. This is a similar mechanism to that proposed by Feng et al. [20].

We discovered that the main difference between the ZnO template used to produce moderate surface area ZnO- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets [14] and that displayed in Fig. 1a or those used in the works describing the production of nanotubes is to be found in their polarity. The XRD pattern of the ZnO in the ZnO- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets has a (100)/(002) intensity ratio higher than 1 (Fig. 3 in [14]), which indicates that the ZnO crystals have a greater proportion of polar surfaces [23] than the typical ZnO nanowires employed in other works (e.g. [13]). The latter present a low (100)/(002) intensity ratio ( $I_{100}/I_{002} \ll 1$ ), which evidences the exposure of a large proportion of non-polar surfaces [22,23]. It follows from this that metal oxide nanotubes are only produced from non-polar ZnO nanowires. It should also be noted that when Fe<sup>3+</sup> is used as precursor (a strongly acidic cation) the STAH reaction occurs readily at ambient conditions over the non-polar ZnO nanowires [13–15], whereas when much less acidic cations are used, such as Ni<sup>2+</sup> [18] or Ce<sup>3+</sup> [20] more drastic conditions are needed to produce the nanotubes. Only when the more polar ZnO is used it is possible to obtain ZnO- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets at ambient conditions with mildly acidic cations (Fe<sup>2+</sup>) [14], although up to now there has been no report in the literature on the synthesis of pure metal oxides with polar ZnO. This suggests that, contrary to what Feng et al. affirm [20], the nucleation of metal oxides is not prevented on the polar faces by an electrostatic effect, but by the increased rate of dissolution of the polar faces due to the high acidity of the metallic cations (Fe<sup>3+</sup>). On the other hand, when the metallic cations are less acidic, as in [14], the polar surfaces can be partially substituted by metal oxides.

From this deduction, the following questions naturally arise. Would a highly polar ZnO template be completely dissolved by the

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