



# Magnetically-actuated mesoporous nanowires for enhanced heterogeneous catalysis



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## ARTICLE INFO

### Article history:

Received 15 May 2017

Received in revised form 20 May 2017

Accepted 24 May 2017

Available online 26 May 2017

### Keywords:

Mesoporous magnetic nanowires

Magnetically-actuated catalysis

Water remediation

Hydrogen production

Catalyst recyclability

## ABSTRACT

We study the optimization of the catalytic properties of entirely magnetic Co–Pt compact and mesoporous nanowires of different diameters (25–200 nm) by using magnetic actuation. The nanowires are a single-entity, robust, magnetic-catalyst with a huge catalytically-active surface area. We show that apart from conventional parameters, like the size and morphology of the nanowires, other factors can be optimized to enhance their catalytic activity. In particular, given the magnetic character of the nanowires, rotating magnetic fields are a very powerful approach to boost the performance of the catalyst. In particular, the magnetic field induces them to act as nano-stirrers, improving the local flow of material towards the active sites of the catalyst. We demonstrate the versatility of the procedure by optimizing (i) the degradation of different types of pollutants (4-nitrophenol and methylene blue) and (ii) hydrogen production. For example, by using as little as 0.1 mg mL<sup>-1</sup> of 25 nm wide Co–Pt mesoporous nanowires (with ~3 nm pore size) as catalysts, kinetic normalized constants  $k_{nor}$  as high as 20,667 and 21,750 s<sup>-1</sup> g<sup>-1</sup> for 4-nitrophenol and methylene blue reduction, respectively, are obtained. In addition, activity values for hydrogen production from borohydride are as high as 25.0 L H<sub>2</sub> g<sup>-1</sup> min<sup>-1</sup>, even at room temperature. These values outperform any current state-of-the-art proposed catalysis strategies for water remediation reactions by at least 10-times and are superior to most advanced approaches to generate hydrogen from borohydride. The recyclability of the nanowires together with the simplicity of the synthetic method makes this approach (using not only Co–Pt, but also other mesoporous magnetic catalysts) very appealing for very diverse types of catalytic applications.

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## 1. Introduction

It is well-known that catalysis plays a crucial role in our everyday life and it is one of the pillars of modern chemistry. Most

industrial chemical processes (e.g., energy, pharmaceutical, food or material production industries) are based on catalytic processes [1–3]. Similarly, catalysis plays a strategic role in many environmental and energy issues such as air pollution control (e.g., car exhausts), wastewater remediation or hydrogen production [4–7]. Thus, any improvement on the performance of catalytic processes could result in a huge economic and social impact. Consequently, many different types of processes such as microwave-, plasma-, ultrasound-, electric field-, acoustic-, light- or temperature-assisted catalysis, among others, are continuously emerging as promising strategies to enhance these type of reactions [8–11]. Another aspect which is being actively explored to improve heterogeneous catalysis is to increase the surface area of

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the catalyst, using for example nanostructured materials [12,13]. In particular, mesoporous materials, which possess an extraordinarily large specific surface area, have attracted great attention for heterogeneous catalysis in liquid media [14,15]. Additionally, of all the variables involved in heterogeneously catalysed reactions, effective mass transfer is fundamental to enhance the reaction rate, magnetic stirring bars or mechanical stirrers are usually used to promote the mass transportation efficiency [16,17]. However, delicate catalysts might be damaged under vigorous mechanical stirring or catalysts involving magnetic materials may get stuck to the magnetic stirring bars [18].

Strikingly, an aspect that has been somewhat underexploited in catalysis is magnetic actuation on the catalyst itself. In fact, during the 90s and early 2000s it was shown that magnetic fields could actually control the mass transport in some chemical reactions [19]. In recent years, the important role of magnetic materials in the control of magnetic field induced convection has been established [20,21]. Other attractive aspects of magnetic fields in catalysis are their influence on the oxidation process of magnetic ions or their effect on the electronic structure of the catalysts [22,23]. Although lately there has been an increase of the use of magnetic materials in catalytic processes, usually the magnetic counterpart does not play an active role in the catalysis, but it is rather used as a simple means to recover the catalyst to recycle and reuse it [24–26]. An appealing aspect of magnetic materials in catalysis, that has been proposed recently, is the concept of magnetically-actuated remote micro-stirrers [27–31]. The use of these magnetic stirrers has been shown to improve diverse types of catalytic processes by favouring the local flow of matter. However, again, in these catalysts the magnetic counterpart does not play an active role in the reaction [27–31]. Moreover, these micro-stirrers are often composites (with both magnetic and catalytic moieties and usually other components), which could make them rather fragile. Moreover, often they require complex synthesis procedures, often involving many steps, making them less attractive for large scale production [27,31].

It is important to highlight that catalysts based on magnetic ions (e.g., Fe, Co or Ni) have also started to attract a great deal of attention, although not necessarily due to their magnetic nature but due to their transition-metal character. Namely, they have been proposed as suitable candidates to partially substitute the expensive noble-metal catalysts (e.g., Pt, Au or Pd) by inexpensive alternatives, which in general improve the catalytic performance [32–35]. In particular, the partial substitution of Pt by Co has been shown to result in excellent alternatives for many different types of processes [36–39].

Here we demonstrate that easily-synthesized mesoporous Co–Pt magnetic nanowires (NWs) can be used as effective magnetically-actuated micro-stirrers to boost diverse types of catalytic reactions (e.g., for 4-nitrophenol and methylene blue degradation or hydrolysis of alkaline sodium borohydride for hydrogen production). These mesoporous NWs constitute a sturdy, *all-in-one* catalyst (i.e., a strongly catalytically active magnetic material) with a large active area, which can be easily manipulated by magnetic fields. The role of different parameters in the improved catalytic performance is investigated, such as the magnetic field rotation speed, the NW morphology and diameter and the reaction geometry. The results show that narrow mesoporous NWs magnetically actuated at high rotation speeds in planar reaction geometry is the optimum combination to achieve outstanding performances in both types of reactions. Magnetically-actuated mesoporous NWs surpass all the state-of-the-art catalysts proposed for nitrophenol and methylene blue degradation by at least a factor 10. For hydrogen production, the mesoporous NWs have similar or better performance than more complex and costly catalysts used currently.

**Table 1**  
Electrochemical media selected for synthesising Co–Pt NWs.

Electrochemical media	W/wt.%	S/wt.%	IL/wt.%
Aqueous solution (W)	100	–	–
Ionic Liquid-in-water microemulsion (IL/W)	83.8	15.1	1.1

## 2. Experimental

### 2.1. Electrochemical media

The electrochemical media (Table 1) used for synthesising compact or mesoporous NWs were (i) an aqueous solution (W) of 2.5 mM  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Carlo Erba, >98.0%) + 1.2 mM  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 98%) + 0.1 M  $\text{NH}_4\text{Cl}$  (Fluka, 99.5%) +  $10 \text{ g L}^{-1} \text{ H}_3\text{BO}_3$  (Merck, >98%) and (ii) an ionic liquid-in-water (IL/W) microemulsion, respectively. IL/W microemulsions were prepared by mixing the adequate proportion of each component [W – aqueous solution –, S – Surfactant, *p*-octyl poly (ethyleneglycol) phenyl ether a.k.a. Triton X-100 (Acros Organics, 98%) –, and IL – Ionic Liquid, 1-butyl-3-methylimidazolium hexafluorophosphate a.k.a. bmimPF<sub>6</sub> (Solvionic, 99%) –] during 5 min under magnetic stirring (300 rpm) and argon bubbling, leading to a transparent, isotropic, and thermodynamically stable microemulsion [40,41]. All solutions were prepared using deionized water (Millipore Q-System) with a resistivity of 18.2 MΩ cm.

### 2.2. Electrochemical synthesis

The shape-controlled electrodeposition of compact or mesoporous (double-template electrodeposition) Co–Pt NWs was carried out using a microcomputer-controlled potentiostat/galvanostat Autolab with a PGSTAT30 equipment and the GPES software. Commercial polycarbonate (PC) membranes (Millipore Company) with nominal pore sizes of 100 or 200 nm and alumina membranes (*SmartPor Membranes GmbH*) with a nominal pore size of 25 nm were used as working electrodes. The pores of the membranes act as templates for the shape-controlled growth of nanostructured wires, where aqueous or IL/W microemulsion media lead to either compact or mesoporous NWs. The use of microemulsions allows the formation of a three-dimensionally interconnected network of open mesopores along the entire NWs [15,40,41]. However, in order to use the membranes as a working electrode a conductive layer on one side is necessary. Therefore, vacuum evaporation was used to coat the membrane on one side with around a 100 nm-thick gold layer. The electrodeposition process was performed at 25 °C, using a three-electrode electrochemical system – polycarbonate/Alumina membranes, Pt spiral, and Ag/AgCl/KCl (3 M) electrodes, as a working, counter and reference electrodes, respectively –, in potentiostatic mode (at –1.0 V). The electrochemical media was de-aerated by argon bubbling before each experiment and maintained under argon atmosphere during it.

After the deposition, the samples were dried and weighted several times until a constant weight in vacuum conditions was attained in order to determine the total mass of synthesized NWs. Then, the NWs were released from the membrane first removing the Au layer using a saturated solution of  $\text{I}_2/\text{I}^-$  and subsequently dissolving polycarbonate or alumina membrane with either chloroform (x10) or NaOH (1 M), and then washing with ethanol (x5) and water (x5) under flashing ultrasound stirring.

### 2.3. Materials characterization

The morphology of the Co–Pt NWs was examined by using transmission electron microscopy (Jeol 2100) and the elemental

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