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Using Prussian blue analogue nanoparticles confined into ordered mesoporous silica monoliths as precursors of oxides

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ABSTRACT

Powdered Prussian blue analogues (PBAs) and PBAs confined in ordered mesoporous silica monoliths were used as oxide precursors through thermal treatment under an oxidizing atmosphere. The study focuses on the transformation of the alkali cation-free **CoCo** PBA of chemical formula $K_{0.1}Co^{II}_4[Co^{III}(CN)_6]_{2.7}\cdot 20\,H_2O$. The compounds were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), IR spectroscopy and small-angle X-ray scattering (SAXS), and the magnetic properties of the calcined samples were investigated. In both cases, powdered and confined PBAs, the coordination polymers are transformed into well-crystallized Co_3O_4 spinel oxide. In the case of the confined PBA, isolated Co_3O_4 single crystals confined within the ordered mesoporosity of the monoliths were evidenced by HRTEM. A preliminary study shows an effect of particle size and confinement on the magnetic properties of the confined oxide particles.

RÉSUMÉ

Mots clés :
Analogues du bleu de Prusse
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Nanoparticules
Silice mésoporeuse

De l'analogue du bleu de Prusse (ABP) sous forme de poudre et de l'ABP confiné dans des monolithes de silice mésoporeuse ont été utilisés comme précurseurs d'oxydes par traitement thermique sous atmosphère oxydante. L'étude porte sur la transformation de l'ABP **CoCo** sans cation alcalin ayant pour formule chimique $K_{0,1}Co^{II}_4[Co^{III}(CN)_6]_{2,7}\cdot 20\,H_2O$. Les composés ont été caractérisés par microscopie électronique à transmission (MET), diffraction des rayons X (DRX), spectroscopie IR et diffraction des rayons X aux petits angles (SAXS), et les propriétés magnétiques des produits de la calcination ont été examinées. Dans les deux cas, les ABPs en poudre et les ABPs confinés sont transformés en structure spinelle Co_3O_4 bien cristallisée. Dans le cas de l'ABP confiné, des monocristaux isolés de Co_3O_4 confinés à l'intérieur de la mésoporosité bien ordonnée des monolithes ont été mis en évidence par MET haute résolution. Une première étude montre un effet de la réduction en taille des particules et du confinement sur les propriétés magnétiques des particules d'oxyde confinées.

1. Introduction

Currently metal oxides have a large range of functional applications and are technologically interesting in many fields: data storage, microelectronic, energy conversions, catalysts, sensors [1–5]. Most of the applications require oxides at the nanometer scale. A large variety of elaboration

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processes have been developed to produce these metal oxides at the nanoscale as precipitation and decomposition of metal salts, electrochemical methods, reverse micelles as nanoreactors for the oxide formation and sol–gel techniques [6–12]. Another way consists in the use of a hard template, such as the porosity of ordered mesoporous silica for the oxide formation [13–15]. However, in the case of mixed oxide, the classical synthetic methods bring together several precursors of the oxide in solution, making difficult the control of the stoichiometry of the final product.

Whereas PBAs have most often been used as precursors of alloys [16–19], some examples concerning the thermal treatment of PBAs to obtain mixed oxides are reported in the literature: FeCo [20], ZnFe [21], ZnCu [22] or TiFe [23]. Indeed, Prussian blue analogues (PBA) are good candidates for the elaboration of mixed oxides with controlled stoichiometry by thermal decomposition in oxidative atmosphere [22,24–26]. Actually PBA are constituted of a perfect organization of transition metal ions A and B in an ordered network with metal ions homogeneously mixed at the atomic scale. Indeed, the ambidentate cyanide ligands act as asymmetric bridges between the metals A and B, thus forming three-dimensional sequences –A–NC–B–CN–A– [27,28]. A high number of possible combinations of A and B ions originates from the extremely versatile chemistry of these systems. Then, a thermal treatment under oxidative atmosphere should allow the transformation of PBA with perfectly controlled stoichiometry into the corresponding monometallic or mixed oxide by the decomposition of the CN bond. This method is expected to adjust very precisely the chemical composition and the metals organization in the oxide at the molecular level by the control of stoichiometry of the PBA. Hence, this approach could lead to the formation of mixed oxides with a perfect control of the structure and the composition giving particles with adjusted properties.

The physical properties of the functional objects also depend on their size and shape, the control of these parameters and the study of their effect on the properties are a prerequisite for future applications. Several methods have been proposed to confine PBAs particles into mesostructured silica matrix: layer-by-layer growth in the functionalized porosity [19,29], direct reaction between the PBA precursors in the organic phase of the hybrid material [30–32]. We developed another method consisting of two steps:

- elaboration of a Co^{2+}-containing mesoporous silica monolith;
- formation of the PBA particles by a simple impregnation step [26,33,34].

This method combines two advantages:

- the one-step precipitation of the PBA particles;
- the control of the morphology of the PBA particles by the well-defined porosity.

In this preliminary work, a monometallic **CoCo** PBA precursor was chosen as Co oxide precursor in order to avoid phase demixing that can occur in bimetallic compounds (Supplementary data, Fig. S1). Powdered **CoCo** PBA freely precipitated in aqueous solution, and **CoCo** PBA confined into 2D-hexagonal mesoporous silica monoliths were heated under oxidative atmosphere. The products of the thermal treatment were studied and compared.

2. Experimental

2.1. Synthesis of powdered CoCo PBA (**CoCo**)

The alkali cation-free powdered CoCo PBA was prepared by adding 400 mL of an aqueous solution of potassium hexacyanocobaltate(III) (2.5 mmol L^{-1}, 332 mg) to 100 mL of a pink aqueous solution of Co(II) nitrate (50 mmol L^{-1}, 1.455 g) under vigorous stirring. The addition rate was regulated to last 3 h. The pink powder was centrifuged, washed three times with distilled water, and allowed to dry in air at room temperature. This sample is called **CoCo** in the following.

The synthesis method for the elaboration of the **CoCo** PBA/SiO_2 nanocomposite has been adapted from a synthesis procedure previously developed by the authors [26,33,34].

2.2. Synthesis of 2D-hexagonal Co^{2+}-containing ordered mesoporous silica monoliths

2D-Hexagonal mesostructured silica monoliths were synthesized using tetramethyl orthosilicate (TMOS) as the silica source and an amphiphilic triblock copolymer poly(ethylene glycol)-block-poly-(propylene glycol)-block-poly(ethylene glycol) with $M_n = 5750$ (Pluronic P123) as the structuring agent. Then, 2.4 g of P123 were added to 4 g of TMOS (3.9 mL) in a 30-mL polypropylene vial and the solution was stirred in a water-bath at 50 °C until the polymer had completely dissolved. After cooling to room temperature, 2 mL of a pink aqueous acidic cobalt(II) nitrate hexahydrate solution (0.137 mol L^{-1}, 80 mg) with pH = 1.4 were quickly added to the stirred silicate–block copolymer clear solution and stirred during 2 min 30 s. Then, the pink solution was divided in four vials, which were sealed and placed for one hour in a water thermostated bath at 23 °C without stirring. After removing the vial lid, the sol gelled to give after one week, a pink glassy silica-copolymer monolith containing Co^{2+} ions in octahedral (Oh) symmetry.

In order to liberate the porosity, the monoliths were heated up to 500 °C. During the thermal treatment, the monolith's color changed from pink to blue due to the thermohydrolysis of the Oh Co^{2+} complexes, giving hydroxylated tetrahedral (Td) species unreactive towards hexacyanocobaltate(III) [34]. Monoliths were stored in an oven at 80 °C.

2.3. Synthesis of **CoCo** Prussian blue analogue–silica-nanocomposites (**Mono CoCo**)

The blue monolith was impregnated using the double-solvent method [13,35,36]. The synthesis of the **CoCo** PBA/SiO_2 nanocomposite consists of two steps:

- the monoliths were immersed in 3 mL of hexane;