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# Core-shell Fe<sub>3</sub>O<sub>4</sub>@CoFe<sub>2</sub>O<sub>4</sub> nanoparticles as high-performance anode catalysts for enhanced oxygen evolution reaction

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#### Abstract

Water electrolysis is a promising and environmentally friendly means for renewable energy storage. Recent progress in the development of anion exchange membrane (AEM) opened new perspectives for high-performance anode catalysts based on transition metal oxides (TMOs) for the sluggish anodic oxygen evolution reaction (OER). Here, we report on core-shell nanoparticles ( $Fe_3O_4@CoFe_2O_4$ ) which allow combining an electrocatalytic shell ( $CoFe_2O_4$ ) with a conductive core ( $Fe_3O_4$ ). Such an original approach significantly minimizes critical Co content in the catalyst and avoid unstable conductive carbon black. The catalyst shows an exceptional OER activity per Co unit mass (2800 A/g<sub>cobalt</sub> at 1.65 V vs. RHE). Along with the core-shell structure, the size of the  $Fe_3O_4$  core is a critical parameter. A large conductive  $Fe_3O_4$  core is beneficial for the enhancement of OER.

Water electrolysis provides an environmentally friendly way to store renewable energies through the H<sub>2</sub> production. While proton exchange membrane water electrolysis is well suited to the renewable energy storage, it relies on the utilization of scarce and expensive Ir to accelerate the sluggish kinetics of the anodic oxygen evolution reaction (OER). Thanks to the recent progress in the development of anion-exchange membranes (AEM), transition metal oxides (TMOs) appear as promising substitutes for noble metals.<sup>1–4</sup> Various approaches were proposed to enhance their OER activity, notably varying the composition, particle size, defect concentration, or, recently, forming core-shell structures.<sup>5–9</sup>

Owing to their composition-dependent and widely tunable properties, TMOs with spinel structures became very attractive. While  $Co_3O_4$  and CoOOH thin films deposited on an Au(111) substrate were reported to significantly enhance the OER activity,<sup>10</sup> core-shell nanoparticles (NPs) combining a gold core and a TMO shell reached 10 000 A/g<sub>TM</sub> at 1.65 V *vs.* RHE. Such a high OER activity of TMOs may result from an electronic effect of gold that favors the oxidation of TM up to the 4+ state.<sup>11,12</sup> The use of core-shell nanoparticles might be an efficient way to reduce the amount of expensive and rare electrocatalysts by circumscribing them to a thin shell,<sup>13,14</sup> the exclusive use of cost-effective and abundant materials is the next challenge for the worldwide dissemination of water electrolysis.

TMO NPs are of significant interest since the catalytic activity can be greatly enhanced by adapting their size and shape, i.e. the active surface area. The valence of the metallic cations and their chemical environment are also critical to enhance the OER activity<sup>3,15,16</sup>. Beyond the fine control of these parameters, recent advances in nanoparticle synthesis in liquid media avoid aggregation which also favors high surface area, *i.e.* enhanced mass-weighted catalytic activity. Consequently, the challenge lies in controlling the formation and the chemical structure of NPs in order to systematically study their electrochemical properties.

Although most of TMOs are insulating, magnetite (Fe<sub>3</sub>O<sub>4</sub>) is conductive due to electron hopping between Fe (II) and Fe (III)<sup>17</sup>. Therefore, it may be considered as a promising support material to avoid carbon black, which is often added to circumvent the lack of conductivity of TMOs catalysts, but is unstable under the anode operation conditions. Furthermore, iron cations in TMO phases may result in synergetic effects with the surrounding atoms, thus enhancing the OER<sup>18,19</sup>. Hence, nanostructures combining Fe<sub>3</sub>O<sub>4</sub> as a conductive core and a TMO as catalyst shell would be promising high performance noble metal-free OER catalysts.

Here we report on an original approach to design a new type of carbon-free, noble-metal-free nanostructured material for the OER. The core-shell structure of  $Fe_3O_4@CoFe_2O_4NPs$  allows combining a conductive magnetite core and a catalytically active cobalt ferrite shell. Such a cost-effective material resulted in an excellent OER activity per unit mass of Co. The fine control of the core size and the shell thickness led us to investigate the influence of the core-shell structure on the OER activity which is markedly enhanced by a larger  $Fe_3O_4$  core.

Core-shell NPs were synthesized by the thermal decomposition of metal complexes in high-temperature-boiling solvents (around 300 °C) as we recently reported<sup>20</sup> (see SI for details). Two different approaches were applied: (i) The seed-mediated growth of a CoFe<sub>2</sub>O<sub>4</sub> shell onto the surface of pristine Fe<sub>3-δ</sub>O<sub>4</sub> nanoparticles which led to samples CS-1, CS-3, and CS-4. (ii) The diffusion of cobalt cations into vacancies at the surface of partially oxidized pristine Fe<sub>3-δ</sub>O<sub>4</sub> nanoparticles which led to sample CS-2.<sup>21</sup> The core size were varied by adjusting the experimental condition upon synthesis of Fe<sub>3-δ</sub>O<sub>4</sub> nanoparticles as we reported earlier.<sup>29</sup> The shell thickness was modified by adjusting the amount of Co and Fe metal complexes with a Co/Fe molar ratio of 0.5. An increase of the mount of Co and Fe complexes by 2.5 from CS3 and CS4 resulted in a volume increase of the shell by two times which agree with the larger size of pristine Fe<sub>3-δ</sub>O<sub>4</sub> nanoparticles used for CS4. For instance, an increase of the Conventional transmission electron microscopy (TEM) images showed faceted-spherical shapes and narrow size distributions both for pristine and for core-shell NPs (Figure 1). Granulometry measurements showed stable colloidal suspensions of non-aggregated NPs thanks to the efficient coating of oleic acid which was added in the reaction medium (Figure S2).



**Figure 1.** TEM micrographs of core-shell NPs: CS-1 (A), CS-2 (C), CS-3 (E), CS-4 (G) and the corresponding size distributions of the core-shell NPs and their pristine core NPs.

Energy-dispersive X-ray (EDX) spectroscopy confirmed the presence of Co between 12 and 19 at. % with respect to Fe in core-shell NPs (Table S1). For CS-1,2,3, these values are much higher than those corresponding to the size variation between pristine and core-shell NPs (Table S1) which is indicative of the diffusion of cobalt in the Fe<sub>3-8</sub>O<sub>4</sub> core as we have reported earlier.<sup>22</sup> X-ray diffraction (XRD) patterns recorded for core-shell NPs display peaks that are all indexed to the spinel crystal structure (Figure S3). Although Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> phases cannot be distinguished because of similar cell parameters (8.396 Å and 8.3919 Å, respectively),<sup>20</sup> cell parameters of core-shell NPs are relatively close to that of Fe<sub>3</sub>O<sub>4</sub> (Table S2). This is ascribed to the low extent of the surface oxidation of pristine nanoparticles which are protected by the CoFe<sub>2</sub>O<sub>4</sub> shell when exposed to air. The high crystallinity was confirmed by lattice fringes all-across core-shell NPs as observed in scanning transmission electron (STEM) micrographs recorded in the high angle annular dark field (HAADF) mode (Figure S4).

The local composition of these NPs was further investigated by electron energy-loss spectroscopy (EELS) analysis in STEM (Figure 2 and Figure S6). Spatially-resolved EELS maps show the homogeneous distribution of O in NPs. In contrast, the Co content is the highest at the edge while the Fe content is at its lowest. Cross-section profiles

show that the Co fraction reaches a maximum value of 15 - 20 % with respect to Fe and O on the edge while it quickly goes down to 5 % (CS-2 and CS-4) and 2 % (CS-3) in the center of the NP, in agreement with a much thinner shell than the core size. Considering stoichiometric  $CoFe_2O_4$  (14 % at. Co) and the resolution of the measurement (5 Å), Co is certainly distributed as a graded concentration ( $Co_{1+x}Fe_{2-x}O_4$ ) which decreases from the NP surface to the center. This result is supported by the variation of Co Content on a longer distance than the size variation calculated from TEM micrographs. A slight increase of O content can also be observed in the edge of nanoparticles which can be correlated to some cationic vacancies and surface defects as usually observed for such nanoparticles.

Complementary information on the average near-surface composition of NPs were obtained by performing X-ray photoelectron spectroscopy (XPS) measurements. The variation of the photon energy from 850 to 1350 eV allowed changing the inelastic mean free path of the photoelectron emission ( $\lambda$ ) from 0.6 to 1.3 nm depth. Considering that 68 % of the emitted photoelectrons arise from a thickness  $\lambda$  and 99 % emerge from 3  $\lambda$ ,<sup>23,24</sup> the Fe/Co ratio was calculated from the area of Co2p and Fe2p peaks which were recorded for CS-1 and CS-3 (Figure 2 G). While the Fe/Co molar ratio is close to stoichiometric CoFe<sub>2</sub>O<sub>4</sub> at short  $\lambda$ , the Fe content gradually increases with the photon energy. These results confirm that the Co content at the surface of core-shell NPs is much higher than expected for CoFe<sub>2</sub>O<sub>4</sub>. It may be ascribed to the decomposition of the Co stearate which happens at a higher temperature than the Fe stearate.<sup>25</sup> According to the La Mer theory, the iron oxide starts growing before cobalt oxide at the surface of pristine NPs. It results in a gradient of the Co concentration in the shell. Nevertheless, both decomposition temperatures (of the iron and cobalt stearate) are close enough to avoid phase segregation since no CoO phase was observed in the XRD patterns <sup>22</sup> (Figure S3).



**Figure 2.** Scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) images of CS-2 (A, B, C) and CS-3 (D, E, F). Spatially-resolved electron energy loss spectroscopy (EELS) analyses (B, E) showing the spatial distributions of oxygen O (red), iron Fe (green) and cobalt Co (blue). Quantitative cross-section profiles (C, F) recorded along the arrows depicted in B, E, respectively. The left *y*-scale refers to percentage s of Fe, Co and O atoms. Depth profiling analysis performed for different incident energy (G) on CS-1 and CS-3, the photon energy of the X-ray source was varied from 850 to 1350 eV in order to analyse Co2p and Fe2p peaks. Schematic illustration of the nanoparticle depth (H) probed as a function of the inelastic mean free path ( $\lambda$ ).

The electrochemical properties of core-shell NPs were studied in order to determine their OER activity. Cyclic voltammograms were recorded after deposition of a thin layer of NPs on a glassy carbon electrode. In order to accurately compare our results with the literature, current-potential curves were normalized in three different ways : to the mass of metal oxide, to the mass of cobalt, and to the NPs surface area (calculated from the TEM mean diameter), see Figure 3 A and S8. In contrast to pristine Fe<sub>3- $\delta$ </sub>O<sub>4</sub> NPs, core-shell NPs display an important OER activity at 1.65 V *vs.* the reversible hydrogen electrode (RHE). Hence, the OER activity of NPs unambiguously arises from the cobalt ferrite shell. This was confirmed by Tafel slopes which were extracted from the anodic scans of cyclic voltammograms

(Figure 3 B). All the core-shell NPs all display Tafel slopes of about 60 mV/decade which are much lower than those of non-active pristine NPs.<sup>15,26,27</sup>

Considering the low NP loading on the electrode, the Co mass- and surface-weighted OER activities were measured at a relatively high potential of 1.65 V vs. RHE (Figure 3C, D). The activity per metal oxide unit mass can be found in Figure S8. While all core-shell NPs exhibit an excellent OER activity, the largest CS-3 and CS-4 NPs display Co-mass weighted-activities (2300 and 2800  $A.g_{cobalt}^{-1}$ , respectively) which are twice those of CS-1 and CS-2 (about 1300 $A.g_{cobalt}^{-1}$ ). This trend is even clearer when considering the surface-weighted activity which is increased 3-4-fold. It is worth noting that the Co-weighted activity of the largest Fe<sub>3</sub>O<sub>4</sub>@CoFe<sub>2</sub>O<sub>4</sub> core-shell NPs (CS-4) greatly outperforms that of TMO catalysts, either with uniform or core-shell structures, which were reported in the literature (Table S3). Indeed only CoO<sub>x</sub>(OH)<sub>y</sub> NPs<sup>28</sup> and core-shell NPs with a gold core<sup>6,8</sup> (Au@CoFeO<sub>x</sub> and Au@NiCo<sub>2</sub>S<sub>4</sub>) display higher efficiency although they are mixed with unstable carbon black.



**Figure 3.** A) Cyclic voltammetry measurements performed on CS-1, CS-2, CS-3 and CS-4 deposited on a glassy carbon electrode (oxide loading below 1µg cm<sup>-2</sup>), in 0.1M NaOH, scan rate 10mV/s. The current has been divided by the oxide mass (B) Tafel slopes of these NPs (in mV/decade). Panels C and D show activity of these NPs at 1.65V *vs.* RHE per cobalt unit mass (C) and per cm<sup>2</sup> (D).

The difference in activity between CS-1 and CS-2 vs. CS-3 and CS-4 likely originates from the core size (7.5 - 9.1 vs. 12.7 - 13.6 nm). Indeed, the surface of Fe<sub>3-8</sub>O<sub>4</sub> NPs is usually oxidized thus generating an insulating layer assimilated to maghemite<sup>29</sup>. Therefore, a larger core is likely to be essential for efficient OER since it results in a higher fraction of conductive magnetite.<sup>30,31</sup> This hypothesis is supported by the low activity of Fe<sub>3</sub>O<sub>4</sub>@CoO, consisting of a 4.5 nm core as reported in Ref.<sup>32</sup> Furthermore, as mentioned in the literature on gold catalysts, we also presume some synergistic electronic effects between Fe and Co cations which may contribute to the OER activity. In this purpose, the OER will be nearly studied *in operando* by means of soft X-ray spectroscopy.

To sum up,  $Fe_3O_4@CoFe_2O_4$  core-shell NPs with a narrow size distribution and uniform shape were successfully synthesized through two alternative approaches (diffusion and crystal growth). They present excellent OER activities per unit mass of Co (from 1300 to 2800 A/g<sub>cobalt</sub>.) which greatly outperform the OER activities of transition metal oxide nanoparticles reported in the literature. Along with the core-shell structure, the size of the Fe<sub>3</sub>O<sub>4</sub> conductive core and the Co loading at the NP surface are critical parameters for efficient OER activity. Thus, TMO based core-shell nanostructures with fine control of the chemical structure is a viable approach for high performance alkaline OER electrocatalysts.

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#### Keywords

Nanoparticles, Oxygen Evolution Reaction, Cobalt, Core-shell, Catalyst

#### **Supplementary information**

Nanoparticle synthesis, TEM images, XRD patterns, cyclic voltammetry, impedance measurements, EELS and STEM HAADF micrographs

#### Notes

The authors declare no competing financial interests.

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