

Synthesis of Pd-coated FeCo@Fe/C core-shell nanoparticles: microwave-induced 'top-down' nanostructuring and decoration†

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We report a novel microwave-induced fast and efficient synthesis of sub-10 nm sized palladium-decorated FeCo@Fe core-shell nanoparticles (ca. 3–7 nm) from a large-sized FeCo@Fe (0.21–1.5 μm) precursor, suggesting 'top-down' nanosizing. The high electrochemical surface area, tolerance to methanol during oxygen reduction reaction, and the excellent stability of FeCo@Fe@Pd in alkaline electrolytes indicate that this nanomaterial may find future applications in Pd-based catalysis and/or alkaline fuel cells.

The need for the replacement of the expensive platinum-based catalysts in fuel cells has continued to drive the search for an alternative and equally efficient electrocatalyst. Palladium-based nanocatalysts have been considered as viable alternatives to platinum, especially in direct alkaline alcohol fuel cells (DAAFCs).^{1,2} Palladium is naturally more abundant than platinum, and exhibits better electrochemical properties towards alcohol oxidation and oxygen reduction reaction (ORR) in alkaline media.^{3–6} The electrocatalytic activity of bulk polycrystalline Pd for ORR is poor compared to Pt, which prevents it from being used directly in fuel cells. Therefore, to improve the electrocatalytic activities of Pd-based catalysts, efforts should be directed towards nanostructuring (to increase the electrochemical surface area) and alloying with non-noble metals. Importantly, considering that non-noble metals are sufficiently stable in alkaline electrolytes, the integration of Pd with non-noble metals (as alloys or core-shell nanostructures) promises to remarkably reduce the cost of the membrane electrode assemblies (MEAs) and boost the widespread usage and commercialization of the DAAFCs.^{7,8}

Core-shell nanostructures have emerged as efficient electrocatalysts for fuel cells.^{9,10} Some of the reasons for coating the core or core-shell nanoparticles with precious metals such as

Pd include the ability to increase the functionality, enhance the stability, and reduce the consumption of precious materials. It should be noted that core-shell nanoparticles with sizes less than 10 nm are within the range relevant to be used as catalysts in practical applications and multi-metallic core-shell nanostructures with sizes less than 10 nm are rarely reported in the literature due to the intrinsic challenges in the synthesis.¹¹ In this communication, we report the synthesis of sub-10 nm Pd-coated FeCo@Fe/C core-shell nanoparticles from large-sized (>210 nm) FeCo@Fe/C core-shell particles *via* a rapid and simple microwave-assisted method. The synthesis procedure is summarized in Fig. 1. The precursor FeCo@Fe/C was synthesised by annealing under H₂/Ar conditions at 300–500 °C. A rapid solvothermal microwave reaction in the presence of a palladium(II) salt and ethylene glycol (as a solvent and a reductant) was then performed to obtain the Pd-coated FeCo@Fe/C core-shell nanocatalysts.

HRTEM analysis showed that the size of FeCo@Fe/C ranged between 0.21 and 1.5 μm (exemplified in Fig. 2a), while that of FeCo@Fe@Pd (Fig. 2b) is mainly in the 3–7 nm range, further confirmed by the HAADF-STEM image (Fig. S1, ESI†). Elemental analysis gave the expected stoichiometry as used in the synthesis (Fe/Co ratio: 2 : 1). TEM and XRD confirmed the crystal structure to be a bcc structure. This is in agreement with that of the Fe_{100-x}Co_x alloy, which exhibits a body-centered cubic structure when $x < 70$ at ~730 °C and a face-centered cubic structure at higher temperature.

Scanning Transmission Electron Microscopy (STEM) was conducted by making use of a high angle annular dark field (HAADF) detector. STEM-EDS revealed that Co is concentrated in the center, while the shell is predominantly Fe (see Fig. 3(a)). STEM-EDS confirmed the structure revealing the clear lines of Fe in the outer sphere relative to that of Co with an approximately 7.14 nm Fe-shell coat on Co. This fast formation of the sub-10 nm sized FeCo@Fe@Pd core-shell-shell *via* microwave irradiation, a 'top-down' nanostructuring process, is very interesting as it has never been observed for any noble metal based catalyst.

The microwave-enhanced chemistry is hinged upon the efficiency of interaction of molecules with the electromagnetic waves. Unlike the traditional heating process, the temperature

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† Electronic supplementary information (ESI) available: Experimental details; HRTEM particle size distribution; electrochemical stability of FeCo@Fe@Pd/C in 1 M KOH. See DOI: 10.1039/c3cc38672d

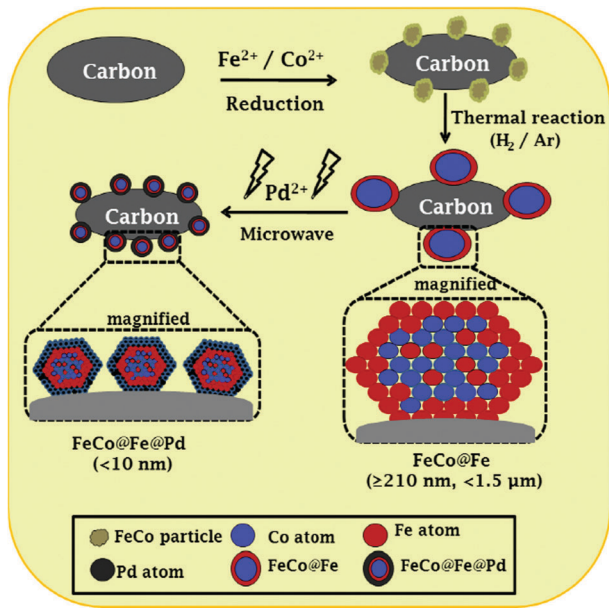


Fig. 1 Schematic representation of the microwave-assisted synthesis of sub-10 nm FeCo@Fe@Pd via large-sized FeCo@Fe/C core-shell soft magnetic material.

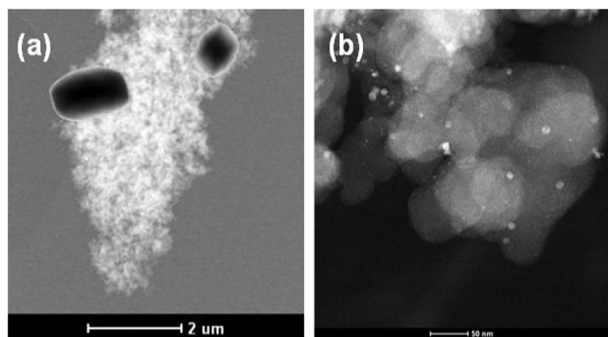


Fig. 2 HRTEM images of (a) FeCo@Fe/C and (b) FeCo@Fe@Pd/C.

of the surrounding in the microwave heating process is colder than that of the target sample (*i.e.*, 'in-core' heating, generated from within the sample). Although the mechanism of microwave-matter interaction is not perfectly understood, it is thought to occur *via* two physical phenomena: the electric (E) and magnetic (H) field vectors.^{12,13} FeCo@Fe is a soft magnetic material with good microwave-absorbing properties. The microwave solvent used in this study, ethylene glycol (EG), gives the highest 'loss tangent' ($\tan \delta > 0.5$; *i.e.*, the ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature) compared to other common solvents such as alcohol, water, DMSO or DMF. The excellent microwave-absorbing properties of EG and FeCo@Fe may explain the fast nanostructuring of this soft magnetic material followed by Pd coating. While preparing this manuscript, we found a report in the press where microwave irradiation reduced the size of AgCl from 0.2–1 μm to 100 nm.¹⁴ Of course, the synthetic conditions and the materials investigated as well as the results obtained by these workers¹⁵ are quite different

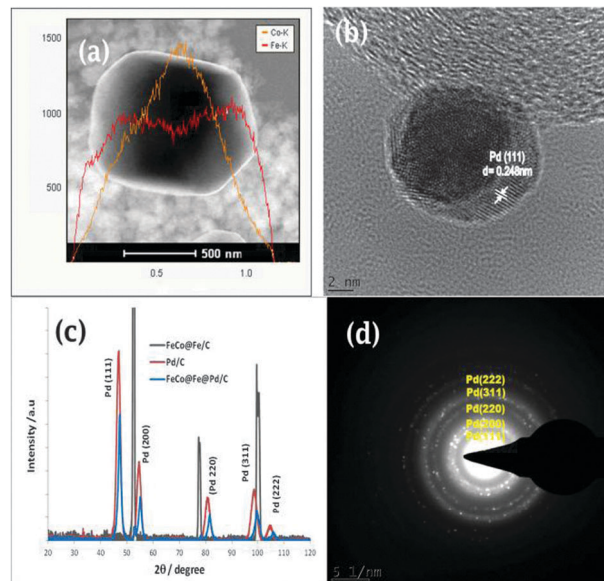


Fig. 3 (a) HAADF-STEM image of FeCo@Fe/C; (b) high magnification HRTEM of a single particle FeCo@Fe@Pd/C; (c) XRD patterns of Pd/C compared to FeCo@Fe/C and FeCo@Fe@Pd/C; and (d) SAED pattern of FeCo@Fe@Pd/C.

from our present study. One of the unique results of our work is the nanostructuring to <10 nm catalytic particles.

The core-shell preference (*i.e.*, the relative enrichment of a shell by one metal over another) in transition metals is closely linked to the (i) cohesive energy and/or (ii) atomic size, quantified by the Wigner-Seitz (WS) radius. A transition metal with larger cohesive energy and a smaller WS radius prefers to be in the core region. Thus, cohesive energies of 4.5 eV and 4.3 eV and WS radii of 1.4 Å and 1.47 Å for Co and Fe, respectively, imply that Co is the core in the FeCo alloy. Also, an alloy with a Fe-enriched surface combined with Pd having a cohesive energy of 3.5 eV and a WS radius of 1.55 Å will have Fe in the core region.^{15,16} This explains the structure of FeCo@Fe/C and FeCo@Fe@Pd/C described in this work. The XRD patterns of FeCo@Fe/C and FeCo@Fe@Pd/C are shown in Fig. 3c. The diffraction pattern of FeCo@Fe/C can be indexed to the body-centered cubic (bcc) structure (space group $Pm\bar{3}m$) (JCPDS card: No. 03-065-6829). The intense peaks of the spectrum indicate the crystallinity and large-sized alloy. FeCo@Fe@Pd/C and Pd/C both display diffraction peaks at 2θ (hkl) values of 46.9° (111), 54.7° (200), 81.1° (220) and 99.4° (311) corresponding to a typical face-centered structure of Pd. The shift in the diffraction lines of Pd in FeCo@Fe@Pd/C to higher 2θ positions compared to those of Pd/C reflects a lattice contraction as a result of the substitution of the Pd lattice by the FeCo alloy. The lattice strain effect has already been observed on Pd alloys with the Pd-rich surface incorporated with smaller atoms.^{17–19} The lattice resolved HRTEM image and the corresponding SAED pattern of the core shell can be seen in Fig. 3d.

The interplanar distances from the lattice fringes of the FeCo@Fe@Pd/C nanoparticles lie between 0.231 and 0.248 nm which correspond to the (111) plane of the Pd alloy, in close agreement with the *d*-spacing of 0.225 nm obtained from the

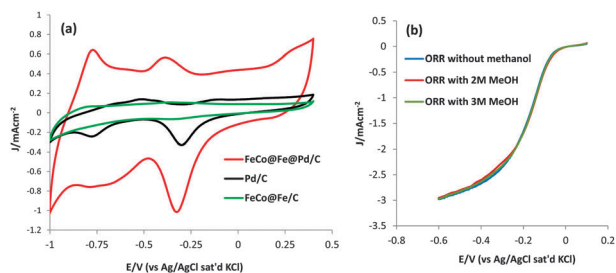


Fig. 4 (a) Cyclic voltammetric evolutions of Pd/C, FeCo@Fe/C and FeCo@Fe@Pd/C in 0.1 M KOH; (b) linear sweep voltammograms obtained at 1600 rpm in oxygen-saturated 0.1 M KOH in the absence and presence of 2 and 3 M methanol.

XRD data. A well-defined Pd icosahedron has an interplanar distance of about 0.230 nm between its (111) planes.^{20,21}

To gain some insights into the electrochemistry of the core-shell nanocatalyst for its potential application in alkaline fuel cells, we carried out experiments in 0.1 M KOH. The cyclic voltammograms of FeCo@Fe/C, FeCo@Fe@Pd/C and Pd/C in nitrogen-saturated 0.1 M KOH alkaline medium (Fig. 4a) showed a high electrochemical surface area (ECSA) for FeCo@Fe@Pd/C ($314.80 \text{ cm}^2 \text{ mg}^{-1}$) compared to Pd/C ($29.47 \text{ cm}^2 \text{ mg}^{-1}$). Unlike FeCo@Fe, both FeCo@Fe@Pd/C and Pd/C showed the characteristic features of Pd. Preliminary ORR study showed that FeCo@Fe@Pd/C gave about twice the current density of Pd/C (Fig. 2, ESI[†]). Gladly too, the linear sweep voltammograms obtained for the ORR test (conducted at 1600 rpm) at FeCo@Fe@Pd/C remained unchanged even in the presence of high concentrations (2–3 M) of methanol (Fig. 4b), a clear indication of tolerance to methanol. Furthermore, FeCo@Fe@Pd showed excellent electrochemical stability as confirmed by stable voltammograms even upon 100 repetitive cycling (Fig. S3, ESI[†]). The excellent electrochemical properties of FeCo@Fe@Pd/C clearly indicate that this nanomaterial may potentially be applied in Pd-based catalysis and/or in DAAFCs. Further investigations to explore such applications, including other optimization experiments, are being explored in our laboratory and will be reported elsewhere.

In conclusion, a unique new microwave-assisted synthetic strategy has been developed for fast and efficient synthesis of

sub-10 nm sized palladium-decorated FeCo@Fe core-shell nanoparticles (*ca.* 3–7 nm) from a large-sized soft magnetic material FeCo@Fe (0.21–1.5 μm) precursor. This method involves fast and efficient ‘top-down’ nanostructuring and coating with precious metal. The excellent electrochemical and electrocatalytic properties of FeCo@Fe@Pd in alkaline medium promise to find potential applications in Pd-based catalysis and/or alkaline fuel cells. This work has the potential to be applied to a plethora of nano-alloys for several applications.

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