

# Palladium Nanowires Synthesized in Hexagonal Mesophases: Application in Ethanol Electrooxidation

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Palladium nanowires (of length a few tens of nanometers) are synthesized in a hexagonal mesophase formed by a quaternary system (Pd-doped water, surfactant, cosurfactant, and oil) by electron beam irradiation. The mesophases can be doped by high concentrations of palladium (0.1 M) without any disturbance of the structure of the mesophases which allows the quantitative synthesis of 1D Pd nanostructures. We found an increase in the average length of the nanowires with the amount of cosurfactant (pentanol) that assists the reduction/growth processes. The electrocatalytic oxidation of ethanol was selected as a test reaction in alkaline medium where Pd is known to be among the best electrode materials. We found that the Pd nanowires exhibit both a very important electrocatalytic activity for ethanol oxidation and a very high stability.

## 1. Introduction

Palladium plays a crucial role in catalysis and is involved in many industrial applications, especially for the formation of C–C bonds in organic reactions such as Heck, Suzuki, and Stille coupling<sup>1–5</sup> as well as for the hydrogenation of polyunsaturated hydrocarbons.<sup>6,7</sup> Palladium displays as well a remarkable performance in H<sub>2</sub> storage and sensing.<sup>8</sup> It has been shown recently that palladium is promising for direct alcohol fuel cells application, as it is very active for ethanol electrooxidation in basic media, and that its electroactivity is even higher than that of platinum.<sup>9–12</sup>

Direct alcohol fuel cells have attracted much attention as power sources for portable electronic devices and fuel-cell vehicles.<sup>13</sup> A lot of research is focused on platinum-based catalysts for methanol oxidation.<sup>14</sup> Indeed, several advantages are attached to ethanol oxidation on Pd. First, this alcohol is less toxic than methanol and can be produced in large quantities from agricultural products, and second, palladium is much cheaper than platinum and is 50 times more abundant on earth.

As catalytic and electrocatalytic activities strongly depend on the size and shape of the metal nanoparticles,<sup>7,15–19</sup> an accurate control of these parameters is an important step in their preparation. It has indeed been demonstrated that this control helps to drastically increase the performances of the

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- (1) Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, 2, 2385.
- (2) Reetz, M. T.; Westermann, E. *Angew. Chem., Int. Ed.* **2000**, 39, 165.
- (3) Astruc, D. *Inorg. Chem.* **2007**, 46, 1884.
- (4) Franze'n, R. *Can. J. Chem.* **2000**, 78, 957.
- (5) Son, S. U.; Jang, Y.; Park, J.; Na, H. B.; Park, H. M.; Yun, H. J.; Lee, J.; Hyeon, T. *J. Am. Chem. Soc.* **2004**, 126, 5026.
- (6) Redjala, T.; Remita, H.; Apostolescu, G.; Mostafavi, M.; Thomazeau, C.; Uzio, D. *Oil Gas Sci. Technol.* **2006**, 61, 789.
- (7) Berhault, G.; Bisson, L.; Thomazeau, C.; Verdon, C.; Uzio, D. *Appl. Catal., A* **2007**, 327, 32.
- (8) (a) Tobiska, P.; Hugon, O.; Trouillet, A.; Gagnaire, H. *Sens. Actuators A* **2001**, 74, 168. (b) Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. *Science* **2001**, 293, 2227. (c) Langhammer, C.; Zoric, I.; Kasemo, B. *Nano Lett.* **2007**, 7, 3122.
- (9) Gupta, S. S.; Datta, J. *J. Power Sources* **2005**, 145, 124.

- (10) Liu, J.; Ye, J.; Xu, C.; Jiang, S. P.; Tong, Y. *Electrochim. Commun.* **2007**, 9, 2334.
- (11) Xu, C.; Wang, H.; Shen, P. K.; Jiang, S. P. *Adv. Mater.* **2007**, 19, 4256.
- (12) Mackiewicz, N.; Surendran, G.; Remita, H.; Keita, B.; Zhang, G.; Nadjo, L.; Hagège, A.; Doris, E.; Mioskowski, C. *J. Am. Chem. Soc.* **2008**, 130, 8110.
- (13) Lamy, C.; Belgisir, E. M.; Léger, J.-M. *J. Appl. Electrochem.* **2001**, 31, 799.
- (14) Arico, A. S.; Srinivasan, S.; Antonucci, V. *Fuel Cells* **2001**, 1, 133.
- (15) Fukuoka, A.; Avaki, H.; Sakamoto, Y.; Inagaki, S.; Fukushima, Y.; Ichikawa, M. *Inorg. Chim. Acta* **2003**, 350, 371.
- (16) Fukuoka, A.; Higashimoto, N.; Sakamoto, Y.; Inagaki, S.; Fukushima, Y.; Ichikawa, M. *Microporous Mesoporous Mater.* **2001**, 48, 171.
- (17) Sasaki, M.; Osada, M.; Higashimoto, N.; Yamamoto, T.; Fukuoka, A.; Ichikawa, M. *J. Mol. Catal. A: Chem.* **1999**, 141, 223.
- (18) Narayanan, R.; El-Sayed, M. A. *Nano Lett.* **2004**, 4, 1343.
- (19) Wang, C.; Daimon, H.; Lee, Y.; Kim, J.; Sun, S. *J. Am. Chem. Soc.* **2007**, 129, 6974.

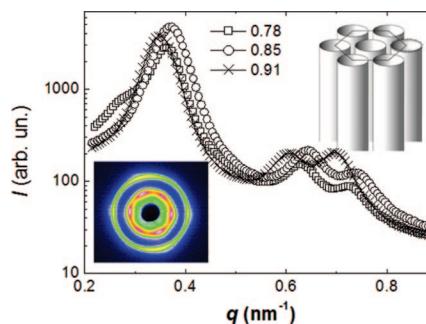
nanoparticles.<sup>20,21</sup> Herein, we report the radiolytic synthesis of palladium nanowires in soft templates by electron beam irradiation and we show that these nanowires are promising electrocatalysts for ethanol oxidation.

Specific hard templates such as mesostructured silica can be used to obtain nanomaterials with high aspect ratio such as metal nanowires. Ichikawa et al. synthesized platinum and palladium nanowires using mesoporous silica as templates.<sup>15–17</sup> These Pd nanowires have shown higher turnover frequencies in the oxidation reaction than those of nanoparticles. The authors attributed this difference to the electronic states of the surface atoms owing to the morphology of the nanowire and to the metal–support interaction.<sup>15</sup> Arrays of palladium nanostructures have also been obtained using cubic and hexagonal mesoporous silica matrixes as templates.<sup>22,23</sup> Ball-shaped palladium nanocatalysts illustrate perfectly the shape effect because they exhibit a remarkable selectivity for the cleavage of benzylethers.<sup>24</sup> These results have demonstrated that the hard template approach is an effective route to synthesize metals, semiconductors, and polymer nanowires; however, most templates are tedious to produce and their dissolution in corrosive media is required to extract the nanomaterials synthesized within. We note on the other hand that only a few template-free syntheses of Pd nanowires have been reported in the literature.<sup>25–28</sup>

In parallel, surfactant mesophases have proved to be useful and versatile soft templates for the synthesis of nanostructured materials. This has first been demonstrated by Attard et al., who showed that direct hexagonal liquid crystals, which are made with a ternary mixture (nonionic surfactant, metal salts, and water) and consist of thin surfactant tubes arranged on a triangular lattice in salted water, can template the synthesis of bulk porous materials and porous metal films by electrodeposition.<sup>29</sup> This approach for synthesizing mesoporous metals has been recently reviewed by Y. Yamauchi and K. Kuroda.<sup>30</sup>

We have recently shown that giant direct hexagonal mesophases made by a quaternary system (water, surfactant, cosurfactant, and oil) can be used as nanoreactors to synthesize nanostructured materials (metals, polymers, ox-

- (20) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, 272, 1924.
- (21) Xiong, Y.; Xia, Y. *Adv. Mater.* **2007**, 19, 3385.
- (22) Steinhart, M.; Jia, Z.; Schaper, A. K.; Wehrspohn, R. B.; Gösele, U.; Wendorff, J. H. *Adv. Mater.* **2003**, 15, 706.
- (23) Kang, H.; Jun, Y.-W.; Park, J.-I.; Lee, K.-B.; Cheon, J. *Chem. Mater.* **2000**, 12, 3530.
- (24) Lee, H. Y.; Ryu, S.; Kang, H.; Jun, Y. W.; Cheon, J. *Chem. Comm.* **2006**, 1325.
- (25) Teng, X.; Wang, Q.; Liu, P.; Han, W.; Frenkel, A. I.; Wen, W.; Marinkovic, N.; Hanson, J. C.; Rodriguez, J. A. *J. Am. Chem. Soc.* **2008**, 130, 1093.
- (26) Gao, S.; Zhang, H.; Wang, X.; Mai, W.; Peng, C.; Ge, L. *Nanotechnology* **2005**, 16, 1234.
- (27) Xie, J.; Zhang, Q.; Lee, J. Y.; Wang, D. I. C. *J. Phys. Chem. C* **2007**, 111, 17158.
- (28) Teng, X.; Han, W.-Q.; Ku, W.; Hücker, M. *Angew. Chem., Int. Ed.* **2008**, 47, 2055.
- (29) (a) Attard, G. S.; Göltner, C. G.; Corker, J. M.; Henke, S.; Templar, R. H. *Angew. Chem., Int. Ed.* **1997**, 36, 1315. (b) Attard, G. S.; Barlett, P. N.; Colemen, N. R. B.; Elliott, J. M.; Owen, J. R.; Wang, J. H. *Science* **1997**, 278, 838.
- (30) Yamauchi, Y.; Kuroda, K. *Chem.–Asian J.* **2008**, 3, 664.



**Figure 1.** SAXS spectra of Pd-doped hexagonal mesophases, with different molar ratios of cosurfactant over surfactant  $n_{\text{cosurf}}/n_{\text{surf}}$ . Top inset: scheme of a oil-swollen hexagonal phase. Bottom inset: two-dimensional diffraction pattern of a sample with  $n_{\text{cosurf}}/n_{\text{surf}} = 0.91$ , where the 6-fold symmetry is clearly seen.

ides) both in the aqueous and in the oil phases.<sup>31–34</sup> The mesophases consist in surfactant-stabilized oil-swollen tubes that are arranged on a triangular lattice in an aqueous medium (scheme inset of Figure 1).<sup>35</sup> These mesophases are very stable in a large pH domain and can be doped with a large amount of metal salts of various types.<sup>31</sup> The present report describes the use of this new class of mesophases as soft molds to synthesize palladium nanowires that exhibit a remarkable electrocatalytic activity for ethanol oxidation.

## 2. Experimental Section

The preparation of Pd doped mesophases is as follows: 1.03 g of cetyltrimethylammonium bromide (CTAB) (Sigma 99%) was first dissolved in 2 mL demineralized water with  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$  (Alfa Aesar 99.9%) (0.1 M), to give a transparent and viscous micellar solution. The subsequent addition, under stirring, of 2.98 mL of oil (cyclohexane) into the micellar solution led to a white unstable emulsion. The cosurfactant pentanol was then added to the mixture. Samples with various amounts of pentanol were prepared, 240–280  $\mu\text{L}$ , corresponding to cosurfactant over surfactant molar ratio in the range 0.78–0.91. The mixture was strongly vortexed for a few minutes. This led to a perfectly transparent and birefringent stable gel: a hexagonal mesophase. These mesophases were exposed to electron beam irradiation for fast radiolytic reduction. Electron beam irradiations were performed with a 20 kW and 10 MeV electron accelerator (LEONI Studer Hard Society, Switzerland). The dose 48 kGy was applied in 2 steps to limit the heating of the samples (the heating up is around 5° per 10 kGy).

X-ray scattering experiments were performed using an in-house setup with a rotating anode X-ray generator equipped with two parabolic mirrors giving a highly parallel beam of monochromatic  $\text{Cu K}\alpha$  radiation (wavelength  $\lambda = 0.154 \text{ nm}$ ). The scattered intensity was collected on a two-dimensional detector. The experimental data were corrected for the background scattering and the sample transmission. Measurements of the hexagonal mesophase were performed at a sample–detector distance  $D = 1 \text{ m}$ .

- (31) Pena dos Santos, E.; Tokumoto, M. S.; Surendran, G.; Remita, H.; Bourgault, C.; Dieudonné, P.; Prouzet, E.; Ramos, L. *Langmuir* **2005**, 21, 4362.
- (32) Surendran, G.; Pena dos Santos, E.; Tokumoto, M. S.; Remita, H.; Ramos, L.; Kooyman, P. J.; Santilly, C. S.; Bourgault, C.; Dieudonné, P.; Prouzet, E. *Chem. Mater.* **2005**, 17, 1505.
- (33) Surendran, G.; Apostolescu, G.; Tokumoto, M.; Prouzet, E.; Ramos, L.; Beaunier, P.; Kooyman, P. J.; Etcheberry, A.; Remita, H. *Small* **2005**, 1, 964.
- (34) Surendran, G.; Ramos, L.; Pansu, B.; Prouzet, E.; Audonnet, F.; Beaunier, P.; Remita, H. *Chem. Mater.* **2007**, 19, 5045.
- (35) Ramos, L.; Fabre, P. *Langmuir* **1997**, 13, 682.

After reduction, the nanomaterials were extracted in 2-propanol, centrifuged, and washed several times before being mounting on carbon-coated copper TEM grids for observations. Transmission electron microscopy (TEM) observations were performed with a JEOL JEM 100CX II transmission electron microscope operated at 100 kV. HRTEM images were taken on a JEOL JEM 2010 LaB<sub>6</sub> operated at 200 kV, image acquisition and analysis were performed using Gatan Digital Micrograph.

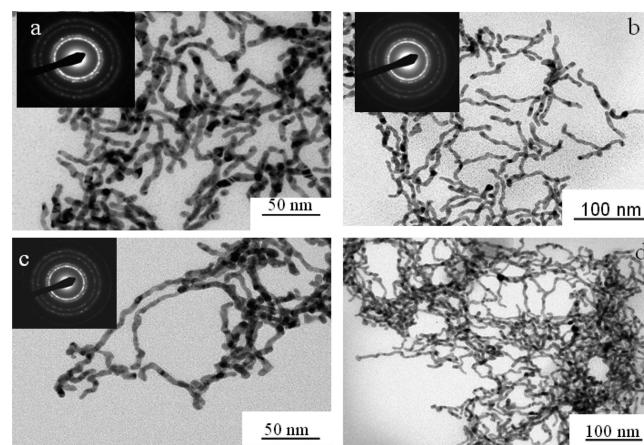
For nitrogen porosimetry, the Pd nanomaterials were dried in an oven under primary dynamic vacuum for a few hours at 60 °C to evaporate the solvent. The nitrogen gas adsorption isotherm was performed on a Belsorp-Mini (BelJapan Inc.), in a standard operating mode. The sample was preliminary degassed during 2 h at 35 °C under a primary dynamic vacuum.

For electrochemical experiments, the source, mounting, and polishing of the glassy carbon (GC, Le Carbone Lorraine, France) electrodes<sup>36</sup> and the fabrication technique of the modified electrodes<sup>37</sup> have been described previously. Typically, an electrode is fabricated by depositing 6  $\mu$ L of the Pd nanowire suspension in 2-propanol on the polished electrode surface, letting it dry in air, and then covering with 3  $\mu$ L of 5 wt% Nafion solution and letting it dry again in air. The electrochemical setup was an EG & G 273 A driven by a PC with the M270 software. Potentials were measured against a Hg/HgO reference electrode. The counter electrode was a platinum gauze of large surface area. Pure water from a RiOs 8 unit followed by a Millipore-Q Academic purification set was used throughout. The solutions were deaerated thoroughly for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The supporting electrolyte was 1 M KOH.

The Pd content deposited on the electrode was determined by inductively coupled plasma-mass spectrometry (ICP-MS) as follows: the solvent was first evaporated. Samples were mineralized using 5 mL of aqua regia and injected, after a 20 times dilution by ultrapure water, via a peristaltic pump at 0.1 mL min<sup>-1</sup> flow rate. Nebulization of samples was performed by means of a microconcentric nebulizer (Micromist). A 7500 ce ICP-MS (Agilent) was used as elemental detector. Detection of Pd was performed by selecting an abundant isotope free of interferences, i.e., <sup>105</sup>Pd.

### 3. Results and Discussion

The mesophases were composed of cetyltrimethylammonium bromide (CTAB) as surfactant, and tetraaminepalladium(II) chloride, Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>, as salt, pentanol as cosurfactant, and cyclohexane as oil. The concentration of metallic salt in water was set at 0.1 M. Hexagonal mesophases with increasing amount of cosurfactant were prepared keeping constant the molar ratios of oil over surfactant and of water over surfactant. The molar ratio of cosurfactant over surfactant,  $n_{\text{cosurf}}/n_{\text{surf}}$ , was varied between 0.78 and 0.91. The Pd-doped hexagonal phases were translucent and birefringent due to their anisotropic structure. Small-angle X-ray scattering (SAXS) experiments confirmed the *p6mm* hexagonal symmetry of the samples, as demonstrated by the occurrence of three Bragg peaks in the scattered intensity, whose positions are in the ratio 1:3<sup>1/2</sup>:2. The center-to-center distance between adjacent tubes, or lattice parameter,  $d_c = (4\pi)/(\sqrt{3}q_0)$ , where  $q_0$  is the position of the first peak, was



**Figure 2.** TEM images of palladium nanowires formed in hexagonal mesophases with different values for the cosurfactant over surfactant molar ratio: (a) 0.78, (b) 0.85 (c, d) 0.91.

about 20 nm for all samples ( $d_c = 20.0$  nm for  $n_{\text{cosurf}}/n_{\text{surf}} = 0.78$ ,  $d_c = 19.6$  nm for  $n_{\text{cosurf}}/n_{\text{surf}} = 0.85$ , and  $d_c = 20.5$  nm for  $n_{\text{cosurf}}/n_{\text{surf}} = 0.91$ ) and the diameter of the oil-swollen tubes was about 17 nm (Figure 1). Note that in the 2D diffraction pattern in the inset of Figure 1, a strong 6-fold symmetry is observed, which indicates that the sample probed by the X-ray beam is close to a monodomain.

The Pd-doped mesophases were used as nanoreactors to synthesize palladium nanowires. The samples were exposed to fast radiolytic reduction by electron beam irradiation during a few seconds. The hydrated electrons and the reducing radicals produced during the radiolysis of the solvent induced homogeneous reduction in the water phase.<sup>38</sup> The pentanol, used as a cosurfactant, contributed to Pd<sup>II</sup> reduction on the radiolysis-induced seeds. Compared to chemical reducing processes that follow a diffusion front, radiolysis presents the advantage of inducing a homogeneous nucleation and growth in the whole volume.

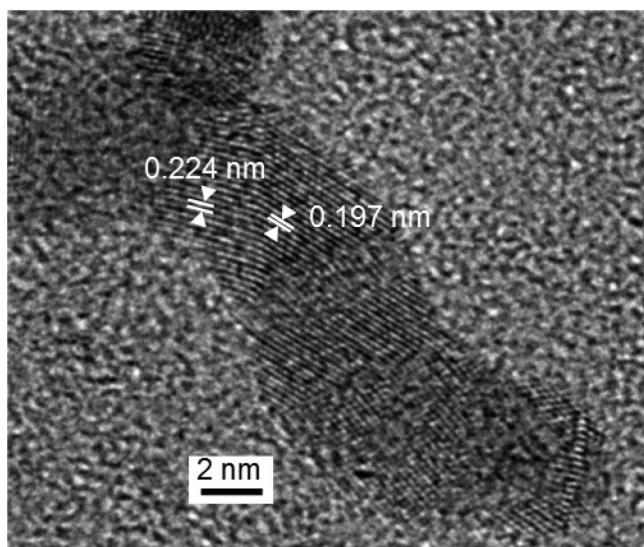
After a dose of 48 kGy, a homogeneous black gel was obtained. The mesophases were then destabilized by addition of 2-propanol and the Pd nanomaterials were extracted by centrifugation, and washed several times with 2-propanol.

The extracted Pd nanostructures were deposited on TEM grids. Transmission electron microscopy observations showed Pd nanowires with a diameter of 4 nm. This dimension is comparable to the thickness of the water channels in between the cylinders ( $\sim 3$  nm). The nanowires were a few tens of nanometers long (Figure 2). Note that a slow radiolytic reduction (20 h of  $\gamma$ -irradiation) of Pd confined in the same mesophase led to the formation of Pd nanoballs. Interestingly, this nanoball is a porous three-dimensional structure, constituted of three-dimensionally interconnected nanowires of diameter comparable to that of the nanowires synthesized here.<sup>39</sup>

We noticed that the average length of the Pd nanowires slightly increased with the amount of pentanol that was added as cosurfactant. We measured an average length of respec-

(36) Keita, B.; Nadjo, L. *J. Electroanal. Chem.* **1988**, *243*, 87.  
 (37) Keita, B.; Zhang, G.; Dolbecq, A.; Mialane, P.; Sécheresse, F.; Miserque, F.; Nadjo, L. *J. Phys. Chem. C* **2007**, *111*, 8145.

(38) Belloni, J.; Mostafavi, M.; Remita, H.; Marignier, J. L.; Delcourt, M. O. *New J. Chem.* **1998**, *22*, 1239.  
 (39) Surendran, G.; Ksar, F.; Ramos, L.; Keita, B.; Nadjo, L.; Prouzet, E.; Beaunier, P.; Audonnet, F.; Remita, H. *J. Phys. Chem. C* **2008**, *112*, 10740.



**Figure 3.** High-resolution TEM images of palladium nanowires formed in hexagonal mesophases with electron beam irradiation (dose 20 kGy).

tively 30–45 nm for  $n_{\text{cosurf}}/n_{\text{surf}} = 0.78$  (Figure 2a), 35–60 nm for  $n_{\text{cosurf}}/n_{\text{surf}} = 0.85$  (Figure 2 b) and 60–200 nm for  $n_{\text{cosurf}}/n_{\text{surf}} = 0.91$  (images c and d in Figure 2). Recently, we have synthesized platinum nanoparticles of different shapes by radiolytic reduction of Pt<sup>II</sup> dispersed in a micellar CTAB/cosurfactant solution and we have also shown that the nanoparticle morphology was very sensitive to the molar ratio of surfactant over cosurfactant.<sup>41</sup> Increasing the amount of alcohol would increase the reduction efficiency. Because these particles are confined in the mesophase, they can lengthen only along the main axis of the mesophase.

The selected area electron diffraction patterns confirmed the cubic structure of the Pd with predominant (111) and (200) diffraction rings, corresponding to the Pd interplanar distances of 0.225 and 0.194 nm. High-resolution TEM (HRTEM) micrographs showed the polycrystallinity of these nanowires. Twinning boundaries and stacking defaults were observed along the nanowires. All the HRTEM images showed the alternation of small domains with lattice planes corresponding to interplanar distances of 0.224 and 0.197 nm ( $\pm 0.002$  nm) consistent with the (111) and (200)  $d$ -spacing of cubic Pd (Figure 3).

Direct BET (Brunauer–Emmet–Teller) calculations<sup>42</sup> on the type II  $\text{N}_2$  adsorption isotherm gave a low specific surface area of  $12 \text{ m}^2 \text{ g}^{-1}$  (see Figure S1 in the Supporting Information) which is lower than that reported in the literature for palladium black ( $17\text{--}23 \text{ m}^2 \text{ g}^{-1}$ ).<sup>39</sup>

We validated the actual effect of the confinement on the nanowire formation, by carrying out electron beam irradiation either on emulsions formed by a ternary system (pentanol free) composed of water containing Pd, surfactant (CTAB) and oil or on micellar systems (oil free) composed of water containing Pd, surfactant (CTAB) and pentanol. In the first

case, individual spherical Pd nanoparticles of 5–6 nm were obtained, whereas in oil free micellar solutions nanoparticles of 6–7 nm assembled in necklaces were observed (Figure 4). These experiments confirm that both confinement and fast reduction are compulsory to obtain the Pd nanowires.

Further characterization of the Pd nanowires included the study of both their electrochemical behaviors and their electrocatalytic performances in the oxidation of ethanol in alkaline medium. In the following, results for the sample with the longest nanowires (samples prepared with  $n_{\text{cosurf}}/n_{\text{surf}} = 0.91$ ) are presented. In 1 M KOH, the voltammetric pattern associated with a Pd-nanowire-modified glassy carbon electrode (see Figure S2 in the Supporting Information) showed characteristic features close to those of a Pd electrode, thus confirming the presence of Pd in the zero oxidation state. Ethanol (EtOH) electrooxidation was selected as an electrocatalytic test because Pd has been demonstrated to be very active for this process in alkaline medium.<sup>10</sup> The generally accepted oxidation sequence for ethanol oxidation in alkaline media reads

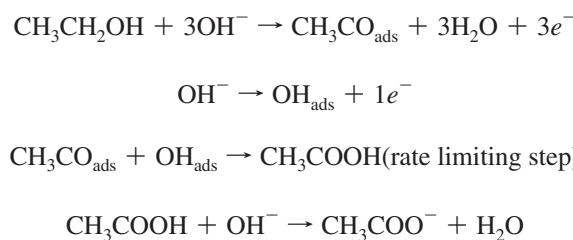


Figure 5 (solid line curve) shows the first voltammogram run with a Pd nanowire-modified electrode in 1 M KOH containing 1 M EtOH at a scan rate of  $50 \text{ mV s}^{-1}$ . This electrode was the same as that used for the characterization in pure 1 M KOH (see Figure S2 in the Supporting Information). It is worth noting that the whole pattern is reminiscent of that observed in the methanol electro-oxidation process on Pt-based electro-catalysts in acidic media.<sup>43</sup> In line with this analogy, the voltammetric pattern featuring the electrooxidation of alcohol is characterized by two well-defined current peaks, one on the forward and the other on the reverse potential scans. The forward scan peak current is related to the oxidation of freshly chemisorbed species issued from alcohol adsorption. The reverse scan peak represents the removal of carbonaceous species not completely oxidized in the forward scan. As a consequence, the ratio of the forward anodic peak current density ( $I_f$ ) to the reverse anodic peak current density ( $I_b$ ) quantifies the catalyst tolerance to carbonaceous species accumulation. High ( $I_f/I_b$ ) ratio indicates efficient oxidation of alcohol during the forward anodic scan, with little accumulation of carbonaceous residues. Finally, we note that in the present experiments, the values of  $I_f/I_b$  remain close to 1 or higher (see Table S1 in the Supporting Information), thus indicating a relatively important electrocatalytic activity of the electrode material toward ethanol oxidation during the forward anodic scan.

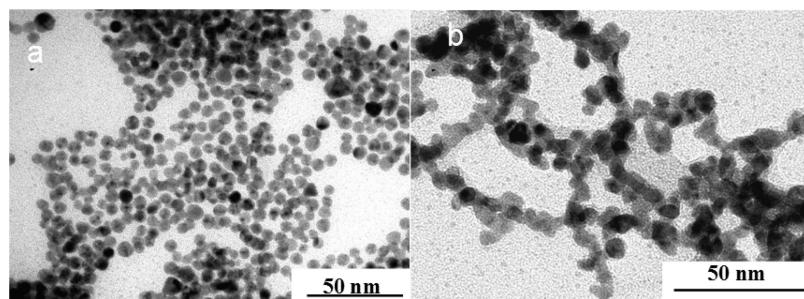
Comparisons between the electrode described in this work and the ones investigated in the literature during the oxidation

(40) Krishnaswamy, R.; Remita, H.; Impérator-Clerc, M.; Even, C.; Davidson, P.; Pansu, B. *Chem Phys Chem* **2006**, 7, 1510.

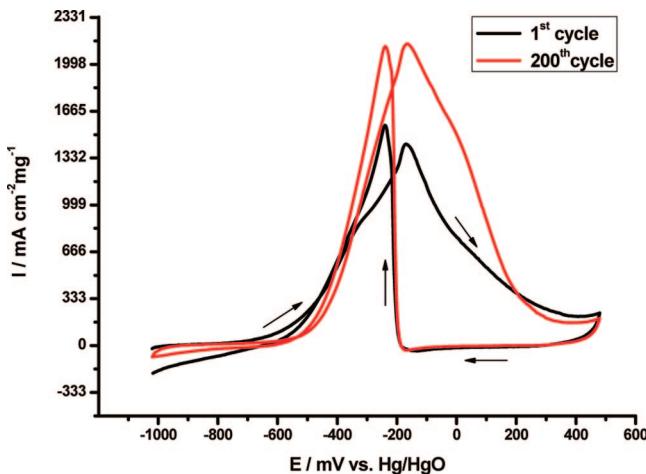
(41) Surendran, G.; Remita, H.; Pansu, B. To be submitted.

(42) Brunauer, S.; Emmet, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, 60, 309.

(43) Jiang, S. P.; Liu, Z.; Tang, H. L.; Pan, M. *Electrochim. Acta* **2006**, 51, 5721.

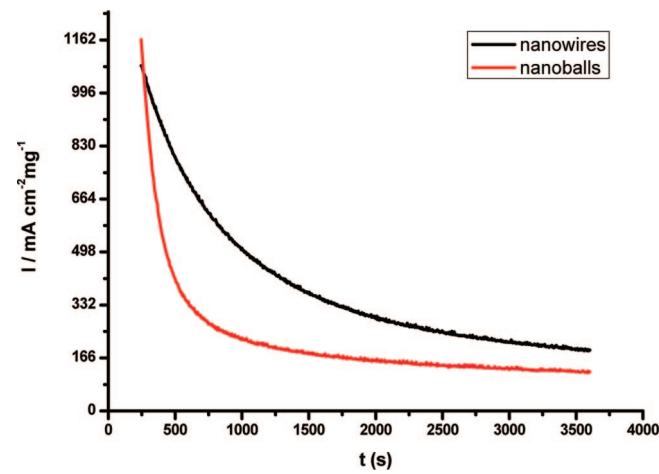


**Figure 4.** TEM images of palladium nanoparticles obtained by irradiation of micellar solutions formed by a ternary system containing CTAB, 0.1 M Pd<sup>II</sup> in water and (a) cyclohexane (pentanol-free sample) or (b) pentanol (cyclohexane-free sample).



**Figure 5.** Superposition of the first (black solid line curve) and the 200th (red solid line curve) cyclic voltammetric runs associated with the electrocatalytic oxidation of 1 M EtOH in 1 M KOH with continuous cycling of the electrode potential. The working electrode was a glassy carbon disk modified with the Pd nanowires synthesized as described in the text. The reference electrode was a Hg/HgO (1 M KOH) electrode. The scan rate was 50 mV s<sup>-1</sup>.

of ethanol are necessary to evaluate the performance of these Pd nanowires. The main features determined from the voltammogram include  $E_{\text{onset}}$ , the onset potential of the faradaic current, as well as  $E_f$  and  $E_b$ , the potentials corresponding to the maxima of the forward peak current and of the backward peak current, respectively. Values obtained from Figure 5 are  $E_{\text{onset}} = -664$  mV;  $E_f = -166$  mV;  $E_b = -278$  mV. The value  $E_{\text{onset}} = -664$  mV can be compared with the value of -620 mV previously measured with Pd nanowire arrays obtained by the anodic aluminum oxide template electro-deposition method.<sup>11</sup> The negative potential shift from -620 to -664 mV underscores the enhancement in the kinetics of ethanol oxidation with the Pd nanowires of the present work. The numerical values of the different potentials measured in the present work indicate a better electrocatalytic activity of the Pd nanowires than the Pd nanoballs obtained by our group ( $E_{\text{onset}} = -550$  mV;  $E_f = -151$  mV;  $E_b = -296$  mV).<sup>39</sup> Other related literature results were obtained recently at a scan rate of 5 mV s<sup>-1</sup> either with Pd fixed on Vulcan XC-72 (denoted Pd/C) or with Pd fixed on carbon microspheres (Pd/CMS).<sup>44</sup> For both types of material, a less negative value than that measured with the nanowires was also observed for the onset potential:



**Figure 6.** Chronoamperometric curves for ethanol electrooxidation at -0.230 V vs. Hg/HgO on a glassy carbon electrode modified with Pd nanowires (black curve) or Pd nanoballs (red curve). The solution was 1 M KOH + 1 M EtOH. The current axis was expanded to highlight the difference between the curves.

$E_{\text{onset}} = -520$  mV for Pd/C ( $E_f = -140$  mV;  $E_b = -250$  mV; estimated from the curve) and  $E_{\text{onset}} = -580$  mV for Pd/CMS ( $E_f = -140$  mV;  $E_b = -230$  mV; estimated from the curve). Clearly, the characteristics of the present Pd nanowire-modified electrode are more negative than the ones measured with other systems described in the literature, thus pointing out a higher electrocatalytic activity than these already remarkable recent literature achievements. Therefore, our measurements suggest that the Pd nanowires synthesized in soft hexagonal phases constitute a new class of material, which is very promising for use in direct ethanol fuel cells. However, beyond their intrinsic properties, these materials could be qualified for ethanol oxidation only if they demonstrate durability. To check this point, we carried out two series of potential cycling experiments (200 and 500 cycles, respectively) and a one-hour chronoamperometry. The same modified electrode was used throughout for this series of experiments. In addition, from one type of experiment to the next, the electrode was kept dry, which constitutes a complementary test of its durability in the atmosphere of the laboratory. Repetition of the same sequence of experiments with an independently prepared electrode gave the same trends as exposed in the following.

Figure 5 shows, in superposition to the first cyclic voltammogram (black solid line curve), the 200th cycle (red solid line curve) between -1020 mV and +480 mV vs Hg/HgO.

(44) Xu, C.; Cheng, L.; Shen, P.; Liu, Y. *Electrochim. Commun.* **2007**, *9*, 997.

HgO reference electrode. Table S1 in the Supporting Information gathers the main quantitative parameters measured from these two voltammograms and from those related to the series of 500 potential cycles. It also contains the voltammetric characteristics measured just prior and just following the chronoamperometry experiment. Strikingly, after a few potential cycles, the forward scan current peak density, measured at a scan rate of 50 mV s<sup>-1</sup>, rises and stabilizes, always remaining in the range of 2 A cm<sup>-2</sup> (mg<sup>-1</sup> of Pd). This current density is six times larger than that measured in analogous experimental conditions for a highly ordered Pd nanowire array synthesized by the anodized aluminum oxide template method,<sup>11</sup> thus indicating a substantial improvement in the present case. This current density compares very favorably with the best literature result (roughly 2 A cm<sup>-2</sup> (mg<sup>-1</sup> of Pd) obtained with Pd) fixed on carbon microspheres.<sup>43</sup> To the best of our knowledge, a larger current density, exceeding 3.5 A cm<sup>-2</sup> (mg<sup>-1</sup> of Pd) was published recently,<sup>12</sup> in the case of prior decoration of carbon nanotubes with Pd nanoparticles. Provisionally, it is planned to also combine the present Pd nanowires with carbon nanotubes in a forthcoming work. As concerns other characteristics, in short, no shift was observed either for the onset potential or the forward peak potential after the series of 200 potential cycles. In contrast, a substantial improvement of the catalytic process is apparent through an increase in both the forward and backward current densities accompanied by a more favorable ratio of these currents, which now reaches 1.38. Such improvement in modified electrode characteristics was described previously in the literature and attributed to some reorganization of the surface film. These characteristics remain constant and serve as initial conditions at the beginning of the chronoamperometry experiment. The potential was stepped from -1020 mV to -230 mV vs Hg/HgO. With the potential set to -230 mV vs Hg/HgO, the current intensity was monitored for at least one hour (Figure 6, black line). It is worth pointing out that directly comparable literature chronoamperometry experiments have lasted from 17 min<sup>44</sup> and up to 30 min.<sup>11</sup> In a previous work from our group, Pd nanoballs were shown to exhibit remarkable electrocatalytic behaviours for ethanol oxidation in 1 M KOH.<sup>39</sup> This material offers a basis for an enlightening comparison between the chronoamperogram recorded with an electrode modified with Pd nanowires (Figure 6, black line) and that run, in identical experimental conditions, with an electrode modified with Pd nanoballs, (Figure 6, red line). Qualitatively, the decrease of the current appears much steeper in the case of the Pd nanoball-modified electrode than for the Pd-nanowires. Quantitative measurements at three selected durations on the two chronoamperograms corresponding respectively to Pd nanoball- and Pd nanowire-modified electrodes confirm this appreciation. After 500 s monitoring, the current of Pd nanowire-modified electrode is twice as large as that of its nanoball analogue. Ratios of 2.3 and 1.6 are obtained, respectively, after 1000 and 3600 s. In short, Figure 6 shows the higher efficiency of the present Pd-nanowire modified electrode. After the electrode was kept dry overnight, the very first cyclic voltammogram in the

second series of potential cycling experiment exhibits a slight deterioration of voltammetric characteristics (see Table S1 in the Supporting Information). However, these characteristics improved very fast upon potential cycling. Finally, the subsequent 500 potential cycle series changes only slightly the onset potential. Altogether, these observations support the following conclusions: (i) the electrode recovers very fast from the slight deterioration of its characteristics after it was kept dry; (ii) the Pd-nanowire-modified electrode shows very good and stable characteristics after the first series of potential cycling experiment; (iii) the results suggest that the electrode might be considered as very active and durable in the present experimental conditions.

Although the reported results were obtained only with the samples that gave the longest average nanowires (nanowires obtained from a hexagonal phase with  $n_{\text{cosurf}}/n_{\text{surf}} = 0.91$ ), we have investigated the influence of the nanowires average length on their electrochemical activity and compared the longest nanowires to the shortest ones (nanowires obtained from a hexagonal phase with  $n_{\text{cosurf}}/n_{\text{surf}} = 0.78$ ). Even though no remarkable difference was observed as concerns the durability of the electrodes, the other parameters are definitely in favor of the longest nanowires: improvements of roughly 55, 135, and 115 mV are respectively obtained between the onset potentials, the forward and the backward peak potential locations. These observations also support the tentative explanation proposed by Ichikawa et al.,<sup>15</sup> in terms of the electronic states of the surface atoms because of the morphology of the nanowire.

#### 4. Conclusions

In summary, we have synthesized Pd nanowires (of length a few tens of nanometers) using hexagonal mesophases as templates. We have found an increase in the average length of the nanowires with the amount of cosurfactant (pentanol) that assists the reduction/growth processes. As the mesophases are doped by high concentrations of palladium (0.1 M), relatively large quantities of Pd nanowires are obtained. These Pd nanowires can be easily extracted from the mesophase by a simple addition of 2-propanol and applied onto electrodes by direct deposition. They show promise for use in direct ethanol fuel cells because they exhibit a very good electrocatalytic activity for ethanol oxidation and a high stability. These nanostructures might also find applications in catalysis and sensing. These aspects are currently under study.

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**Supporting Information Available:** Nitrogen isotherms, cyclic voltammogram, and main electrochemical characteristics of the Pd nanowires (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.