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Facile Synthesis of Catalytic AuPd Nanoparticles within Capillary Microreactors Using Polyelectrolyte Multilayers for the Direct Synthesis of H2O2

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Supporting Information

ABSTRACT: Microreactors present innovative solutions for problems pertaining to conventional reactors and therefore have seen successful application in several industrial processes. Yet, its application in heterogeneously catalyzed gas–liquid reactions has been challenging, mainly due to the lack of an easy and flexible methodology for catalyst incorporation inside these reactors. Herein, we report a facile technique for obtaining small (<2 nm) and well-distributed catalytic nanoparticles on the walls of silica-coated capillaries, that act as micro(channel) reactors. These particles are formed in situ on the reactor walls using polyelectrolyte multilayers (PEMs), built by layer-by-layer self-assembly. Manipulating the PEMs’ synthesis condition gives easy control over metal loading, without compromising on particle size. Both monometallic (Au and Pd) and bimetallic (AuPd) nanoparticles were successfully obtained using this technique. Finally, these catalytic microreactors were found to exhibit exceptional activity for the direct synthesis of hydrogen peroxide from H2 and O2.

KEYWORDS: Polyelectrolyte multilayers (PEMs), AuPd catalyst, hydrogen peroxide, direct synthesis, bimetallic catalysts, microreactor

Bimetallic nanoparticles, composed typically of metals like Au, Pd, Pt, Ag, Ni, Cu, and so forth, have attracted significant research interest due to their superior properties, compared to their monometallic counterparts. 1−3 As a result, these materials have found extensive applications in numerous fields, particularly in catalysis. 4−6 Alloying of the two constituent metals in a bimetallic system leads to changes in their electronic and geometric properties, giving rise to synergistic effects that are often reflected in terms of enhanced activity and selectivity in catalytic reactions. 7−10 The direct synthesis of hydrogen peroxide (H2O2) from hydrogen and oxygen is one of the various catalytic reactions where bimetallic nanoparticles have shown tremendous potential. 11,12 This synthesis is highly coveted as it provides a greener, one step alternative to the traditional anthraquinone auto-oxidation process, which is a complex, multistep process with significant waste generation. 13−15 Extensive research has shown that the most active catalysts for this reaction are Pd based, 16 and more recently bimetallic catalysts like Au−Pd, Pt−Pd, and Sn−Pd have come to the forefront for their superior performance. 17−20

An inherent drawback encountered in the direct synthesis route is the explosive nature of the reactant mixture, the flammability limit of H2 in O2 being 4−94%. Use of such dilute mixtures required for safe operation limits the maximum attainable H2O2 yields. A potential solution to this constraint is the use of novel reactor concepts like membrane reactors 21 and microreactors. 22 In microreactors, extensively reduced dimensions not only ensure safe operation even for explosive H2/O2 mixtures but also lead to enhanced heat and mass transfer, which is extremely beneficial for this multiphase (gas–liquid–solid) reaction. 22 Here, microreactors can be realized as micropacked beds 23−25 and microchannel reactors 26−28 with the catalysts used as powder and as wash coat layer, respectively. In our previous studies, we demonstrated successfully the direct synthesis of H2O2 in explosive (H2, O2, 50 vol % each) conditions using a wall-coated microchannel/capillary (320 μm ID) with embedded colloidal AuPd nanoparticles. 27,28 Continuous and stable operation was observed and peroxide concentration as high as 5.5 wt % was achieved by optimizing the operating conditions. 29 Nevertheless, one of the major bottlenecks of the process was recognized to be the deposition of the AuPd nanoparticles on the reactor walls. The colloidal particles were prepared ex situ by an elaborate two-phase synthesis process and the long solvent evaporation time from the capillary made the entire procedure overly delicate and time-consuming.

This Letter reports a facile and fast technique for the deposition of the active phase, where the metal nanoparticles (Au, Pd, and AuPd) are formed in situ on the reactor walls, previously coated with polyelectrolyte multilayers (PEMs).

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PEMs are formed by a layer by layer (LBL) self-assembly technique, first introduced by Decher.\(^{30,31}\) It is the alternating deposition of oppositely charged polyelectrolytes on a substrate, thus giving rise to multilayers of thin films. PEMs can be fabricated on surfaces having different shapes, sizes, and geometries,\(^{32,33}\) where the film properties can be easily controlled by changing the assembly conditions\(^{34,35}\) (like pH, electrolyte type, and concentration). This technique has found application in various fields including antireflective coatings, biological applications, drug delivery, and formation of nanoparticles for membrane and catalytic applications.\(^{36–40}\) In particular, the synthesis and in situ formation of nanoparticles using PEMs has been studied extensively by the groups of Stroeve and Rubner, among others.\(^{41}\)

Although highly versatile, the application of this method in catalyst synthesis has been limited, with only a few studies reported in literature.\(^{38–40,47,48}\) Moreover, the use of PEMs for the in situ synthesis of nanoparticles to form wall coated catalytic microreactors has not been demonstrated before. Since PEMs can be easily fabricated on surfaces having different shapes and sizes, it is an ideal technique to be applied in microreactors. In this study, PEMs were first assembled on the micro reactor walls, which provide ideal charged surfaces for the controlled deposition of the metal precursors, which subsequently form highly dispersed nanoparticles. The catalytic microreactors, thus synthesized, were then applied to test their performance in the direct synthesis of \(\text{H}_2\text{O}_2\).

Figure 1 shows the overall scheme of the PEMs formation technique, followed by metal deposition and characterization. Fused silica, 320 \(\mu\)m ID capillaries of 1–1.5m length with a silica precoat layer (CP-silicaPLOT, Agilent), were first pretreated by flushing with ammonium nitrate solution (1 M), followed by drying at 120 °C for 12 h and calcination at 300 °C for 2 h in a static air oven. The LbL-method was implemented for obtaining PEMs by flushing solutions of poly(acrylic acid) (PAA) and polyethylene imine (PEI) alternatively through these microchannels by means of a syringe pump. PAA (35 wt% in \(\text{H}_2\text{O}\), Sigma-Aldrich) was prepared as a 10 mg/mL solution and PEI (50 wt% in \(\text{H}_2\text{O}\), Sigma-Aldrich) as a 2 mg/mL solution with DI water. Both solutions were treated with hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) to adjust the pH to 4 and 9 for PAA and PEI, respectively. Each fluid was fed through the capillary at 4 mL/h for 20 min with an intermittent rinse with DI water. Consecutive repetition of the same procedure resulted in the formation of multiple layers, such that one flushing with PAA followed by PEI led to formation of one layer of polyelectrolyte. Thus, capillaries with one, two, and three layers each were prepared and were denoted as 1LbL, 2LbL, and 3LbL, respectively. The formation of PEMs on the silica layer is clearly evidenced in the SEM image of Figure 1b. Moreover, the layer thickness was observed to increase with the number of cycles (Figure S2).

After formation of PEMs, metal deposition was carried out by passing solutions of \(\text{HAuCl}_4\) (Aldrich, 30 wt% in HCl) and \(\text{K}_2\text{PdCl}_4\) (Sigma, 99.99%) as precursors. For AuPd deposition, a solution was prepared using these precursors in DI water, according to the desired loading of 5 wt% total metal (\(\text{Au/Pd} = 1:2\) molar ratio),\(^9,19\) based on the amount of silica precoat in the capillary and the empty volume. For example, in case of the AuPd capillary a 10 mL solution having concentration of 5.7 mg\(\text{metal}/\text{mL}\) (\(\text{Au/Pd} = 1:2\) molar ratio) was prepared. For the metal deposition, the capillary was completely filled with this solution using a syringe pump at 15 mL/h and kept undisturbed for about 10 min. After this time, the excess solution was removed by flushing the capillaries at 15 mL/h. As soon as this solution was passed, the capillary appeared dark, indicating successful reduction and hence metal incorporation. The reduction was carried out until no more visible color change in the capillary was observed, which was about 10 min. The detailed procedure for PEMs formation and metal deposition, along with photos are provided in the Supporting Information.
loading was also 5 wt % and they were prepared in a similar manner as mentioned above. Finally, the capillaries were dried at 120 °C for 12 h and calcined at 380 °C for 4 h. The capillaries thus obtained, were named x/yLbL, where x denotes the metal(s) deposited and y stands for the number of PEMs. The following capillaries were synthesized in this manner: AuPd/1LbL, AuPd/2LbL, AuPd/3LbL, Au/2LbL, and Pd/2LbL. In addition, a powder sample named AuPd/SiO2_2LbL was prepared in the same manner, using Davisil 643 as support. This was done to perform additional characterization like thermogravimetric analysis (TGA) and UV–vis spectroscopy (UV–vis), which were not possible with the capillary samples. Moreover, the successful preparation of the powder catalyst exhibited the flexibility of this method for metal deposition on conventional supports with the advantage of tuning the metal loading and particle size.

The formation of metal nanoparticles was confirmed by Transmission Electron Microscopy (TEM), as shown in Figure 2. It can be seen that the metal nanoparticles are well distributed throughout the support surface with a uniform particle size distribution. The density of particles is clearly more in the 3LbL sample, compared to the 2LbL, indicating a higher metal loading in the former, which follows from an increased number of sites for ion exchange. It can also be observed that the method is successful in yielding very small particles ~1 nm in size. Increase in the number of PEMs and hence the metal loading, did not lead to particle agglomeration. This was also observed in case of the monometallic (Au/2LbL and Pd/2LbL) capillaries, where ~1–2 nm sized particles were observed (Supporting Information). Such precise control over particle size is relevant as it plays an important role in determining activity and selectivity in most catalytic reactions, making the control of particle size an ongoing challenge in catalysis research.49–51 Moreover, recent studies have shown that single sites and nanoclusters (NPs with size <2 nm) are the most active sites in catalytic processes.52–56 Along with the TEM images we also see the selected area electron diffraction (SAED) patterns as insets in Figure 2a,b that show well-defined diffraction rings and face-centered cubic diffraction features (the diffraction rings represent the (111), (200), (220), and (311) planes). The existence of a single set of rings indicates successful alloying of Au and Pd and excludes phase segregation. A further confirmation that the particles are bimetallic and do not constitute a mixture of separate Au and Pd nanoparticles was done by carrying out UV–vis spectroscopy (Supporting Information, Figure S3). More in depth characterization to reveal the nanoparticle structure (core–shell/alloy, existence of defects, and so forth) is being carried out and will be reported in a future publication.

To have a more quantitative picture about the control of metal loading with different number of PEMs, inductively coupled plasma-optical emission spectroscopy (ICP-OES) was employed to determine the exact metal loading in all the capillaries. As observed in Table 1, as the number of PEMs increased the total weight loading of metal also increased. Introduction of each layer increased the loading by approximately 2.6 times and three layers of PEMs (3LbL) proved sufficient to approach the target loading of 5 wt %. This
exponential increase in metal deposition is most likely due to an exponential growth of the PEMs, which is one of the growth modes (the other being linear) of PEMs and depends on the assembly conditions.42 Along with the metal content and nanoparticle size (as discussed in the previous section), it is also important to obtain the targeted Au/Pd ratio, as this can further affect the Au–Pd interaction and finally the catalytic activity. As observed, the real Au/Pd ratio ranges from 0.7 to 0.9, which is not far from the target of 0.92 and is not affected with change in the number of PEMs (and hence metal loading). Hence, we see that this method of metal deposition allows easy tuning of the amount of metal incorporation. The scope of achieving high metal loadings is desired, as it increases the operational window of micro reactor technology.

Finally, the catalytic activity of these capillaries was tested for the direct synthesis of H₂O₂ using concentrated H₂−O₂ mixtures. The detailed experimental setup, reaction conditions, and expressions for evaluating catalytic activity (conversion, selectivity, and rate of formation of H₂O₂) can be found in the Supporting Information. Briefly, the gas phase consisted of a 1:1 mixture of H₂ and O₂ and the liquid phase consisted of solvent with promoters. The H₂ conversion was determined by an online gas chromatograph, while the amount of peroxide formed was quantified by titration with standard cerium(IV) sulfate solution.

Figure 3 shows the peroxide formed with time on stream for AuPd/2LbL, along with H₂ conversion and H₂O₂ selectivity. A steady peroxide yield of ~1 wt % is reached after 2 h of reaction, where the average selectivity and H₂ conversion are 67% and 42%, respectively. The average is calculated between 180 and 300 min of reaction. To compare the performance of different capillaries, we use the term productivity, defined by molH₂O₂/kgcat/h, as this allows comparison of capillaries with different lengths. This is shown in Figure 4, where we see that the 2LbL capillary is more active in peroxide formation, than the 1LbL, whereas the latter has higher peroxide selectivity. The higher activity can be correlated to the higher metal loading in the 2LbL capillary, whereas the loss in selectivity can be attributed to an increase in the total sites (due to increase in loading) for hydrogenation and decomposition of the formed peroxide.12 Surprisingly, the Au/2LbL capillary also produced substantial amount of peroxide with productivity slightly higher than 1LbL and selectivity similar to 2LbL. This is rather contrary to values reported in literature where activity of Au catalysts for peroxide was substantially lower than the bimetallic counterpart.57 A probable explanation for this behavior may be attributed to the very small Au nanoparticles achieved using this synthesis technique, compared to the ones used in literature for this reaction. The catalytic behavior of Au is strongly dependent on particle size with small changes leading to significant effect on the catalytic activity.58−60 The Pd/2LbL capillary was also found to be active for peroxide formation, but its yield decreased drastically with time on stream (from 0.9 to 0.07 wt % in 3 h, Figure S6). This can be attributed to Pd leaching from this capillary, as verified by ICP-OES of liquid samples collected during reaction. This is a common occurrence in Pd catalysts and is another reason for alloying with Au, as it inhibits Pd leaching.51,62 Accordingly, the Au and AuPd capillaries did not exhibit metal leaching (within limits of detection) during reaction (Table S3). In summary, the performance of the AuPd capillary was most superior, followed by Au and finally Pd.

Finally, we compare the performance of the capillary microreactors developed in this study with values in literature, as enumerated in Table 2. It must be noted that apart from using catalysts prepared by different synthesis methods, the reaction conditions (including promoters added in the liquid phase) and reactor types were quite different from each other and hence a direct comparison is not encouraged. Extensive studies have been performed by the group of Hutchings11,12,18 in the development of AuPd catalysts for direct synthesis of

| Table 1. Effect of Layers on Metal Loadings*4 |
|---|---|---|---|---|
| sample | Au (wt %) | Pd (wt %) | total metal (wt %) | Au/Pd w/w (real) |
| AuPd/1LbL | 0.30 | 0.37 | 0.68 | 0.81 |
| AuPd/2LbL | 0.73 | 1.01 | 1.84 | 0.70 |
| AuPd/3LbL | 2.22 | 2.48 | 4.88 | 0.96 |

“Determined by ICP-OES.

Figure 3. Time-on-stream formation of hydrogen peroxide in a AuPd/2LbL capillary (1.1 m in length); reaction conditions: total gas flow rate = 5 mL/min (H₂/O₂ = 1:1), liquid flow rate = 0.1 mL/min, reaction temperature = 42 °C, and total pressure = 20 bar.

Figure 4. Conversion, selectivity, and H₂O₂ productivity of different capillaries at total gas flow rate = 5 mL/min (H₂/O₂ = 1:1), liquid flow rate = 0.1 mL/min, reaction temperature = 42 °C, and total pressure = 20 bar.
H₂O₂, and three of the most active ones are enlisted as the first three entries (Table 2). Although they are tested at dilute conditions, the total pressure is higher (40 bar) and reaction temperature is substantially lower, compared to our study. Entry 4 shows a Pd catalyst on titanate nanotubes that showed exceptional activity in relatively mild conditions. Another Pd catalyst is shown in entry 5, this time synthesized using the polyelectrolyte PAH, that exhibits high productivity, although quite high O₂ partial pressures were used. The only catalyst tested at nearly similar conditions as ours, is shown in entry 6, where micropacked bed made it possible to conduct the reaction with concentrated H₂/O₂ mixtures. We see that our microchannel catalyst shows much higher productivity, especially if expressed per kg catalyst. Overall, we see that the application of microreactor (that ensured safe use of concentrated mixture and better heat and mass transfer) coupled with an active catalyst, resulted in highly superior performance, as compared to literature.

In summary, metal nanoparticles, Au, Pd, and AuPd, were successfully synthesized inside the walls of microchannel capillaries using PEMs. PEMs that were incorporated inside the capillary prior to metal deposition by a layer-by-layer technique, formed a charged surface that was ideal for metal ion adsorption. The metals were reduced using NaBH₄ and calcination in the final step ensured removal of the PEMs, yielding metal nanoparticles that were <2 nm in size with homogeneous distribution. The metal loading could be easily controlled by varying the number of multilayers. The capillaries synthesized using this technique showed exceptional catalytic performance for the direct synthesis of H₂O₂. Given the flexibility and facility of the synthesis technique described in this study, it can be easily extended to a variety of substrates, where controlled metal nanoparticle incorporation is desired, for catalytic or other applications.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b03589.

Detailed experimental method for catalyst preparation, description of characterization methods used, experimental setup for catalytic activity measurement, SEM and TEM images, ICP-OES data, UV–vis spectra, TGA and catalytic activity results (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

REFERENCES


Table 2. Catalytic Performance of Various Catalysts in the Direct Synthesis of H₂O₂

<table>
<thead>
<tr>
<th>catalyst</th>
<th>reactant mixture</th>
<th>reactor type/temperature/ pressure</th>
<th>productivity (mol/kgcat/h)</th>
<th>productivity (mol/kgcatO₂/h)</th>
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<td>1. AuPd/C</td>
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<td>batch/2 °C/40 bar</td>
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<td>2. AuPd/SiO₂</td>
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<td>2160</td>
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<tr>
<td>3. AuPd/TiO₂</td>
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<td></td>
<td>100</td>
<td>10000</td>
<td>19</td>
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<tr>
<td>4. AuPd/titanate-nanotubes</td>
<td>H₂/O₂/Ar = 5:10:85</td>
<td>batch/5 °C/20 bar</td>
<td>175</td>
<td>11670</td>
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<tr>
<td>5. Pd/PAH-K2621</td>
<td>N₂/H₂/O₂ = 50:3:47</td>
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<td>6. Pd/C</td>
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<td>7. AuPd/2LbL</td>
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<td>this work</td>
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