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Editor's Choice

Effects of Buffer on the Structure and Catalytic Activity of Palladium Nanomaterials Formed by Biomineralization

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Effects of a buffer on the structure and catalytic activity of Pd nanostructures obtained from biomineralization were evaluated. Significant structural differences attributed to the buffer were observed. In addition, the Pd nanostructures prepared in buffered solutions had enhanced catalytic activity in the reduction of aminonitrophenol isomers. Our findings emphasize that the buffer selection is critical for biomineralization. Moreover, these findings indicate that the buffer can be possibly used to control the structure and activity of Pd nanomaterials, which is a very simple and cost-effective way compared with other methods.

Metal nanostructures have found increased interest in a wide variety of applications, especially in catalysis because of the improved performance over their bulk counterparts.[1] Palladium nanostructures are highly sought after because Pd is known to catalyze diverse class of reactions ranging from C–C bond formation to functional group reduction.[2] Various methods are available to synthesize metallic nanostructures that include the use of polymer templates, stabilizers, and surfactants.[3] Among these methods, biomineralization is an emerging technique of inorganic nanomaterial synthesis that relies on biomineralization peptides (BMPep) for the regulation of the nanostructure.[4] Biomineralization has been applied to form nanostructures of different metals such as Pd, Ag, Au, Ti, Pt, among others by using various metal-specific BMPep.[5] However, the interplay among several factors involved in biomineralization still remains largely unknown. Although it has been established that the sequence of the BMPep affects the structure and catalytic activity of the resulting nanomaterial,[6] the effect of other synthetic parameters on the biomineralized product has not been thoroughly examined. Buffers are very important components of biomineralization because of the sensitivity of the overall properties of the BMPep with the pH. Because several buffers with different properties are available at identical pH ranges, we determined the effect of a buffer on the resulting Pd nanostructure produced through biomineralization. In this study, a 12-residue BMPep (TSNAVHPTLRHL-amide) was used to direct the formation of Pd nanostructures. This BMPep, termed as Pd4, was discovered through a phage display assay.[7] This sequence is well studied and frequently utilized for Pd biomineralization. However, previous studies that used this BMPep conducted biomineralization only in water.[6–9] In addition, we examined the effect of these buffer-related structural changes on the catalytic activity of the Pd nanostructures. Analyzing how this parameter affects the properties of the biomineralized products is very important because biomineralization will be better understood, which can potentially lead to the formation of improved materials.

The Pd4 BMPep was synthesized as a peptide amide using an automated peptide synthesizer employing Fmoc strategy. Its identity was confirmed by MALDI-TOF MS after purification by HPLC. Biomineralization was conducted with a 40 μM BMPep in Milli-Q water or 2.5 mM buffered solution at pH 7.4. Two buffers were used in this study, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) and tris(hydroxymethyl)aminomethane (Tris). HEPES and Tris are very common buffers, which are often used in biological experiments. Their respective buffering range overlaps, and their chemical structures are different from one another. A fivefold equivalence of $K_2[PdCl_4]$ (200 μM) was then added into the BMPep solution; after 45 min, a fourfold excess of $NaBH_4$ (800 μM) was added. Reduction was allowed to proceed for 90 min. Structural characterization was performed using a scanning transmission electron microscope (Hitachi HD-2000) operating at an acceleration voltage of 200 kV. Sample preparation involves placing the purified, resuspended materials on a carbon-coated copper grid. UV–vis measurements (Jasco V-630 spectrophotometer) of the biomineralization products were conducted in a glass cuvette after background subtraction.

Structural differences that can be attributed to the effect of the presence of a buffer were clearly observed for the Pd4 biomineralization products. In the absence of any buffer, disordered and aggregated particles were formed using the Pd4 BMPep (Figures 1A and 1B). The average particle size was 27.2 ± 10 nm, with a broad size distribution (Figure 2A). The surface of the materials was uneven and irregular (Figure 1C). On the other hand, conducting biomineralization in a Tris-buffered medium yielded fused particles (Figures 1D and 1E). The particle size distribution was narrow wherein the size was found to be 30.5 ± 4 nm (Figure 2B). The appearance of the particles is very different from the structures obtained under unbuffered conditions. The particle surface depicts a smooth spherical characteristic (Figure 1F). For the HEPES-buffered biomineralization, large, spherical, and fused particles were formed (Figures 1G and 1H). The fused particles resembled solid chains, which were 75.3 ± 9 nm in size (Figure 2C). The size distribution is not as narrow relative to that of the particles from Tris-buffered biomineralization. The surface of the materials is smooth and even (Figure 1I). These particles are very different from the structures obtained under the previous two conditions with respect to size and shape. The UV–vis spectra of the Pd nanostructures from buffered and unbuffered biomineralization (Figure 3) exhibited the typical spectra for nanosized Pd, as expected. The continuous absorption along the visible and near-UV regions coincides with the calculated spectrum of Pd nanostructures by using the Mie theory.[10]

The observed different Pd nanostructures indicate that the presence of the buffers influenced the peptide-mediated Pd biomineralization. It is reported that the Pd4 BMPep produces Pd nanostructures through a capping mechanism.[8] Under the unbuffered condition, the pH of the solution dropped to

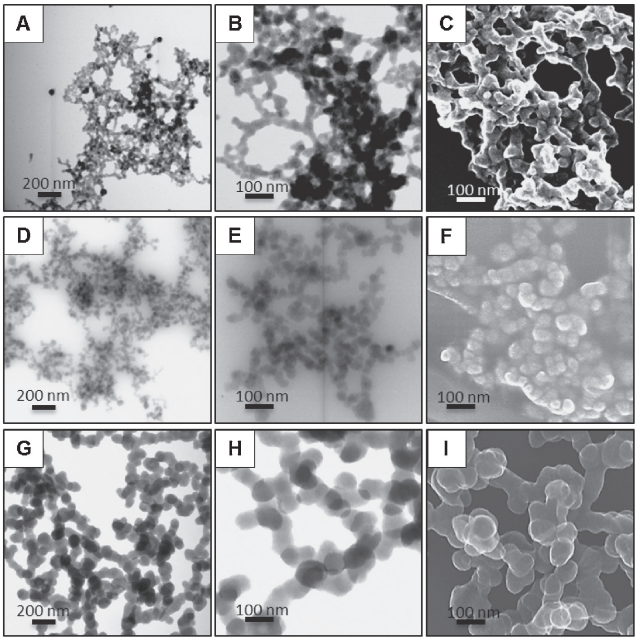

Figure 1. BF-STEM images of Pd nanostructures produced using the Pd4 BMPep. **A**), **B**) No buffer; **D**), **E**) Tris; **G**), **H**) HEPES. Surface morphology of the Pd nanostructures produced using the Pd4 BMPep as seen from the SE-STEM images. **C**) No buffer; **F**) Tris; **I**) HEPES.

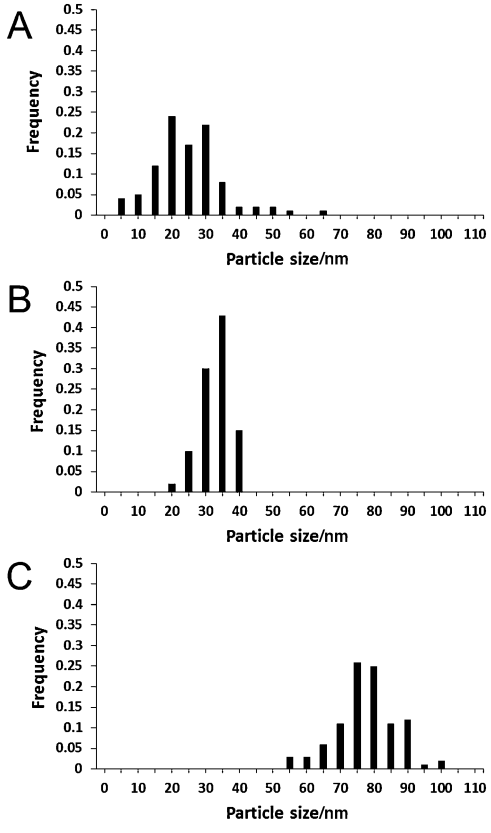

Figure 2. Size distribution histogram of 100 particles. Histogram increment is 5 nm. **A**) No buffer; **B**) Tris; **C**) HEPES.

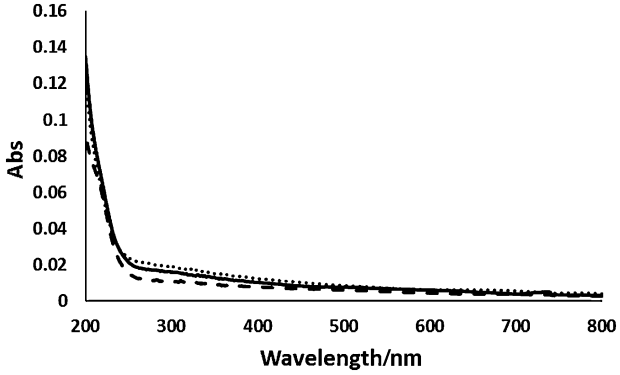

Figure 3. UV–vis spectra of the Pd nanostructures obtained from biomineralization using the Pd4 BMPep. Solid line: No buffer; dotted line: Tris; dashed line: HEPES.

approximately 4 upon the dissolution of the BMPep. The interaction of peptides with metals is pH-dependent. This is because of the dependence of the protonation states of the side chains, which can also affect peptide conformations.[11] Hence, a fluctuating environment pH can lead to a nonuniform binding of the BMPep onto the growing nanostructure surface. This explains the random and aggregated appearance of the nanostructures produced from unbuffered biomineralization, in addition to the very broad size distribution. Under buffered conditions, the pH of the system is maintained all throughout biomineralization or changes are minimized. This leads to a more uniform adsorption behavior of the BMPep toward the growing material. The buffer can also participate in the stabilization of the nanoparticle. This is possible through the three hydroxy moieties and a primary amine of Tris, which can bind to the surface of Pd.[12] In addition to a hydroxy group, HEPES has a sulfonic acid moiety that can bind with metal surfaces such as Pd.[13–15] The variation in the nanostructure produced under different buffer conditions possibly emanates from the difference in the pH of the system as well as in the structure, number, and type of the binding groups of the buffer. In addition, the bound buffer on the particle surface can influence the binding behavior of the BMPep on the growing particle.[16] It can be thus expected that the Pd4 binding is different between the two types of buffers used. Taken together, the results indicate that maintaining the pH during biomineralization is critical. In addition, the data suggest that using different types of buffer can yield biomineralization products with varying structures. Therefore, buffer selection is also very important for biomineralization.

Because the nanostructures obtained in the presence of the buffer had varying shapes and sizes, it can be thus expected that differences in activity will be observed. The catalytic activity of the materials was determined using the reduction of aminonitrophenol as the model reaction. The substrates used were the isomers 2-amino-4-nitrophenol ($\lambda_{max} = 443$ nm) and 4-amino-2-nitrophenol ($\lambda_{max} = 481$ nm) in which $NaBH_4$ serves as the reducing agent. In the absence of a metal catalyst, the reduction of the substrates to 2,4-diaminophenol does not occur. The reaction is monitored by time-resolved UV–vis measurements. In a typical experiment, 10 μL of a 5 mM substrate dissolved in ethanol was added in an aqueous solution containing 10 mM

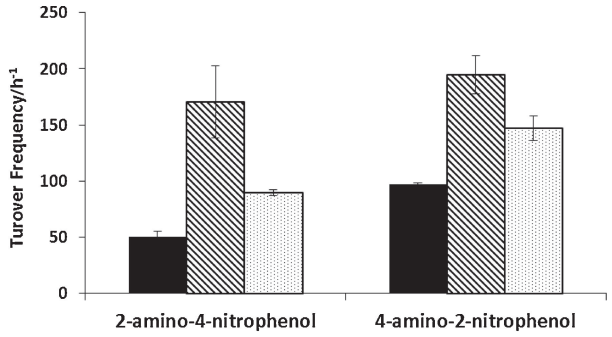

Figure 4. Turnover frequency of the Pd nanostructures formed from biomineralization using the Pd4 BMPep. Reaction is the reduction of aminonitrophenol isomers. [Substrate] = 50 μM, [Pd] = 1 mol %, [$NaBH_4$] = 10 mM, 25 °C, triplicate analyses. Solid fill: No buffer; diagonal striped pattern: Tris; dotted pattern: HEPES.

$NaBH_4$. Upon the addition of the Pd nanomaterials corresponding to 1 mol % Pd, UV–vis measurements were immediately recorded in a glass cuvette. The Pd nanomaterials prepared under the buffered conditions exhibited higher turnover frequency (TOF) compared to the materials prepared under the unbuffered condition (Figure 4). The materials prepared from unbuffered biomineralization were the least active because the structure is mainly aggregated. Aggregation leads to catalyst deactivation because less amount of active surface is exposed and available for reaction.[17] The high reactivity of the nanoparticles from Tris-buffered biomineralization for both substrates can be accounted for their size. Smaller particles have higher surface area compared with larger particles. The surface, corner, and edge areas of the nanoparticles are the reactive sites.[18] Therefore, if a particle has a higher surface area, more of these sites are exposed, which translates into higher activity. This explains why the nanoparticles from HEPES-buffered biomineralization are more active than the aggregated materials from unbuffered biomineralization, but less active than the materials derived under Tris conditions. All of the nanomaterials exhibited slight preference toward 4-amino-2-nitrophenol on the basis of higher TOF for this substrate. It is reasonable to assume that the binding of 4-amino-2-nitrophenol onto the catalyst surface is more favored over 2-amino-4-nitrophenol. Such an assumption is plausible because the reduction of nitroarenes follows an adsorption–reaction–desorption mechanism.[19] The nitro moiety must be adsorbed onto the catalyst surface after which the reaction takes place. Upon reduction, the product desorbs from the surface. The collective catalytic data indicate that the buffer-related structural differences of the biomineralization products are significant enough to affect their catalytic activity as well. Our results demonstrate that the buffer type can be used as a tunable parameter to modulate the structure and catalytic activity of the nanomaterials produced through biomineralization. This step is very simple and easy to carry out. For Pd4 BMPep-mediated biomineralization, catalytic enhancement was observed when amino acid residue substitutions were conducted.[6,9] Performing biomineralization in buffered solutions is far easier and more cost-effective than synthesizing different Pd4 BMPep analogs. However, further studies are still required to fully elucidate the precise mechanism behind the effect of the buffer on Pd biomineralization, as well as how the differences of nanostructure and buffer type influence the catalytic properties.

In summary, we have shown that the presence of a buffer affects the size and shape of the resulting nanostructures produced from biomineralization. This in turn affects the catalytic activity of the nanomaterial. The buffer possibly exerts its influence over the nanostructure formation by changing the binding behavior of the BMPep on the particle surface or by participating in the nanoparticle stabilization. Our findings emphasize that maintaining the pH during biomineralization, as well as buffer selection, is critical. Moreover, we have shown that the buffer can be possibly used to control the structure and activity of Pd nanomaterials, which is a very simple and cost-effective way compared with other methods.

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