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Screening of Oligopeptides that Recognize Inorganic Crystalline Facets of Metal Nanoparticles

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Abstract

Peptides that possess specific affinity to distinct crystal facets have been reported previously. However, their adsorption behavior in terms of the crystal sizes and shapes is less exploited. Herein, we isolate several phage clones that show the strong affinity to {100} of Pd at a neutral pH from the M13 phage library, and among them the phages that have shape selectivity to the cubic structure are identified by eliminating ones that bind randomly shaped Pd nanoparticles (NPs). Since Pd nanocube-binding phages are eluted by lowering pH values in the biopanning process, the selected phages (and their binding peptides displayed on protein pIII) can be released from Pd surfaces through pH changes. We used this feature to modulate the capping density of selected peptides on NPs. For example, when less peptides are capped on Pd nanocubes by lowering the pH values, the shape of the nanocubes is deformed and some evolve into a concave shape, indicating that Pd atoms are released from the less protected {100} facet selectively due to the higher surface energy. This type of crystalline facet-recognizing peptides can be applied for smart capping agents that not only bind target crystalline planes, but also modify their coverage on the specific surfaces with pH changes. The peptide-capping agents could be useful to fabricate NPs with characteristic shapes through etching and adsorption of atoms on specific crystalline planes of seed nanocrystals.

Keywords

crystal growth; nanostructures; palladium; peptides; phage display

1 Introduction

Molecular recognitions, such as streptavidin—biotin, barnase—barstar, and lectin—carbohydrates, play essential roles in numerous biological events. These specific interactions have been utilized in both diagnostic and therapeutic areas.^[1] Recent studies have shown that complex macroscale superstructures between biomolecules and inorganic nanostructures can be constructed based on bio-recognition *in vitro*, and these materials demonstrate excellent functionality, customizability, and mechanical stability.^[2] The next step in the field of biomolecule-assisted self-assembly is to add programmable properties. Recently, there has been significant progress in DNA bionano-technology, utilizing precise designs of 1D,

2D, and 3D nanostructures through spontaneous and sequence-specific DNA hybridization.^[3] However, to achieve shape reconfiguration and responsive nature by using DNA as scaffolds, the strong Watson—Crick base-pairing force could be a disadvantage when producing responsive materials with environmental stimuli.^[4] Peptides are another type of building species in nature that are specific, versatile, and robust. In addition, the interactions between the peptide and the target substrate can be rationally regulated according to external stimuli, such as temperature, light, and pH values. Therefore, peptides could be promising building blocks to construct self-assembled super-structures that have not only a hierarchical arrangement, but also an environmental responsive nature, leading to tunable functionality in these materials.^[2c,5]

Previously, many oligopeptides that could specifically recognize target substrates (e.g., noble metals,^[6] metal oxides,^[7] semiconductors,^[8] carbon nanotubes,^[9] graphene,^[10] polymers,^[11] peptide nanofibers,^[12] and small organic molecules^[13]) were isolated using cell-surface display and phage-display methods. Some of these peptides also showed the ability to mineralize or direct the crystal growth of target inorganic nanoparticles (NPs) in aqueous solution at room temperature.^[14] Recently, biomolecule-directed growth of shaped NPs has attracted interest, since biomolecules, such as oligopeptides, show distinct adsorptive patterns on crystal facets that depend on the sequences of amino acids. For example, two 7-mer peptides, T7 (TLTTLTN) and S7 (SSFPQPN), were found to be selectively bound to the {100} and {111} faces of Pt, respectively.^[15] Further investigation indicates that the capping of specific crystalline facets with recognition peptides is a powerful toolbox to manipulate the surface energy landscape of seed crystals. For example, a variety of differently shaped NPs, such as nanocubes, nanotetrahedra, and nanobipyramids, could be synthesized by thermodynamically depositing atoms on low-energy facets of seed nanocrystals, the surface of which was protected selectively by oligopeptides.^[15,16]

Herein, in addition to demonstrating the selection of oligopeptides for the precise recognition of distinct crystal facets, we are interested in investigating their adsorption behavior on target NPs with different sizes and shapes. The responsive property of these isolated facet-recognition oligopeptides to external stimuli is also examined. Our approach for this investigation is to isolate phage clones that are specifically bound to Pd nanocubes, the surface of which is dominated by {100} facets, by the M13 phage-display method. Then, we identify phage clones that are selective to recognize Pd nanocubes by eliminating those that show strong affinity to randomly shaped Pd NPs (i.e., eliminating those that have no specificity to the cubic shape). The binding efficiency of phage clones to Pd nanocubes of different sizes is also examined to verify whether the recognition is based on crystalline facets. In addition, the adsorption of catalytic oligopeptides free from viruses on Pd nanocubes is analyzed. Since Pd nano-cube-binding phages are eluted at low pH values in the biopanning process, the selected phages (and their binding peptides displayed on protein pIII) can be released from Pd surfaces through pH changes. We used this feature to modulate the capping density of selected peptides on NPs. For example, when fewer peptides are capped on Pd nanocubes by lowering the pH, the shape of the nano-cubes is deformed and some evolve into a concave shape, indicating that Pd atoms are released from the less protected {100} facet selectively on the basis of the surface energy landscape. This result indicates that it is possible to use biomolecules as “smart” capping agents to rationally

promote the shape control of metal NPs, following atomic etching/adsorption pathways under aqueous conditions at room temperature; this would be beneficial for a variety of areas, such as catalysis, electronics, and biomedicine, where the shapes of nanostructures have a significant impact on their performance.^[16a,17] The inherent pH response of peptides isolated by the phage-display method can be an excellent feature to produce environmentally responsive materials that possess tunable functions due to the shape reconfiguration property.^[2c]

2 Experimental Section

2.1 Synthesis of Pd NPs

All Pd NPs were prepared in aqueous solutions. For the synthesis of 12 nm Pd nanocubes, 30 mM Na₂PdCl₄ (600 μ L) and 500 mM NaOH (200 μ L) were added to 12.5 mM cetyltrimethylammonium bromide (CTAB; 10 mL) with stirring. After heating at 95 °C for 10 min, freshly prepared ascorbic acid solution (200 μ L, 500 mM) was rapidly injected. The reaction was allowed to proceed for 30 min. The product was separated by centrifugation and washed with H₂O. The as-prepared Pd seeds were stored in water at 4 °C.^[17a]

The 40 nm Pd nanocubes were prepared using a modified method of that reported by Shen et al.^[18] Specifically, CTAB (182 mg) and Na₂PdCl₄ (12 mg) were dissolved in H₂O (18.5 mL) in a 50 mL flask at 50 °C. Then, ascorbic acid (8.8 mg) was dissolved in H₂O (500 μ L), and injected into the flask. The reaction was allowed to proceed for 30 min at 50 °C under stirring. The as-prepared Pd nano-cubes were collected by centrifugation and washed with H₂O.

Randomly shaped Pd NPs were synthesized under the same conditions as those used for the 40 nm Pd nano-cubes, except the reaction temperature was 95 °C.

2.2 Peptide Selection

The Ph.D.-7 Phage Display Peptide Library Kit (New England Bio Labs, Beverly, MA) was used to select the facet recognition peptides (Figure 1a). First, 12 nm Pd nanocubes were deposited onto a carbon-based support and treated with UV/ozone (UVO, Bioforce Nanosciences) for 3 h to remove CTAB capped on the NPs.^[17b] After the Pd nanocubes were redispersed in Tris-buffered saline (TBS) buffer at a concentration of 2 mg mL⁻¹, the phage library (10¹¹ pfu) was added and incubated for 30 min at room temperature (Figure 1b and c). The non-bound phages were separated by centrifugation and washed with TBS containing 0.1% Tween 20 (TBST, 3 $\times$ 1 mL; Figure 1d). Next, the phages on the Pd nanocubes were eluted through incubation in 0.2 M glycine/HCl (pH 2.2) for 20 min. The eluted phages were amplified by infection into *Escherichia coli* strain ER2738 (Figure 1e), and then they were harvested by precipitation with polyethylene glycol (PEG). The amplified and purified phages were titered on Lysogen broth (LB) agar plates containing 5-bromo-4-chloro-3-indolyl- β -D-galactoside (X-gal) and isopropyl β -D-1-thiogalactopyranoside (IPTG). The biopanning cycles were repeated three times. For each cycle, we used freshly synthesized Pd nanocubes that were treated with UVO as the target.

The DNA products were then isolated from 20 independent blue plaques and sequenced on ABI Prism 3730xl DNA sequencers (Seq-Wright, Houston, TX).

2.3 Amounts of Bound Phage Clones on Pd Nanocubes

To compare the affinity of phages to Pd NPs, the relative amounts of phages displaying Pd-1, Pd-2, and Pd-3 were quantified by enzyme-linked immunosorbent assays (ELISAs; Figure 2).^[11b,c,e,12] The Ph.D.-7 Phage Library displaying 7-mer random peptides were used as a control. Typically, after all phage solutions were adjusted to 3.0×10^7 pfu μL^{-1} in TBS (50 pM, 180 μL), Pd NPs (20 μL , 2 mg mL^{-1} in TBS) was added through a vortex. After incubation for 30 min at room temperature (Figure 2a), Pd NPs bound with phages were separated by centrifugation and purified by washing with TBST (3×1 mL) (Figure 2b and c). Next, blocking buffer (200 μL , 2% non-fat dry milk in phosphate-buffered saline (PBS)) was added, and these NPs were incubated for another 1 h. After Pd NPs were separated by centrifugation, horseradish peroxidase conjugated anti-M13 bacteriophage antibody (200 μL ; HRP/Anti-M13, GE Healthcare) was added and samples were incubated for 1 h at room temperature (Figure 2d). The Pd NPs were collected with centrifugation and washed six times with PBS containing 0.05 % Tween 20. After 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)diammonium salt (ABTS; 200 μL) substrate solution was added, the relative amounts of bound phages (RAs) were analyzed by measuring the absorbance at 410 nm, which corresponded to the peak of the product.

For the study of the pH dependence of peptide capping on Pd nanocubes, Pd NPs bound with phages (Figure 2c) were incubated at pH 2.2 (0.2 M glycine/HCl) for 20 min, followed by centrifugation to remove released phages. Then, to analyze the relative amounts of phages retaining on Pd NPs, Pd NPs were added to the blocking buffer, as described above, and RAs were recorded by ELISA (Figure 2d).

2.4 Amounts of Virus-Free Peptides Bound on Pd Nanocubes

The adsorption of synthetic oligopeptide (virus free) onto the {100} facets of Pd was detected by using a quartz-crystal microbalance (QCM).^[11e] In this experiment, 12 nm Pd nanocubes bound by six identical {100} facets were deposited on 4.95 MHz silicon sensor tip (Q-sense, BiolinScientific Inc.). Then, the sensor tip could serve as the Pd {100} substrate.^[15] After UVO treatment, the tip was soaked in 2% sodium dodecylsulfate (SDS) solution followed by washing with H_2O to remove any impurities on the substrate. All synthetic oligopeptides were dissolved in TBS (2 mg mL^{-1}). The adsorption of these peptides was monitored with QCM at a flow rate of 30 $\mu\text{L min}^{-1}$. The amounts of bound oligopeptides were derived from the frequency decreases, according to Sauerbrey's equation.

3 Results and Discussion

3.1 Characterization of Pd NPs

The morphology of as-prepared Pd NPs was analyzed using TEM. The average size of Pd nanocubes is 12 nm with a size distribution of 10% (Figure 3a). The single-crystal characteristics of Pd nanocubes can be revealed by the high-resolution TEM (HRTEM) images. As shown in Figure S1 in the Supporting Information, a lattice spacing of 0.195 nm,

which corresponds to the {200} planes of face-centered cubic (fcc) Pd (JCPDS no. 05–0681), is observed; this suggests that Pd nanocubes are fully enclosed by {100} facets.^[17] The inset of Figure S1b in the Supporting Information is an indexed fast Fourier transform (FFT) pattern of Figure S1b, which also shows the single-crystalline characteristics of the nanocubes. In addition, the powder X-ray diffraction (PXRD) results show peaks at $2\theta = 40.09, 46.67, 68.15, 82.18,$ and 86.62° that represent the {111}, {200}, {220}, {311}, and {222} planes, respectively, which also confirms the formation of metallic Pd crystals, and there are no detectable impurity peaks in the PXRD pattern (Figure S1c).^[17] The Pd nanocubes shown in Figure 3b have an average size of 40 nm with a size distribution of 5 %. The monodispersity of these 40 nm Pd nanocubes is also detected in a TEM image of the ordered 2D arrays (Figure 3b, inset).

Figure 3c is a typical image of Pd NPs with random shapes. In this sample, various single-crystal and twinned structures are observed (Table S1 in the Supporting Information). For example, one of them has the fivefold symmetry of a twinned particle, as shown in a high-magnification TEM image in Figure S2a in the Supporting Information. The lattice spacing separated by 0.238 nm is ascribed to the forbidden $1/3\{422\}$ reflection, which indicates that the twinned particle is enclosed by {111} facets (Figure S2b in the Supporting Information).^[19] Similarly, a triangular nanoplate observed in this sample shows the forbidden $1/3\{422\}$ reflection in a HRTEM image (Figure S3 in the Supporting Information), which suggests that the top and bottom faces of the triangular nanoplate are bound with {111} planes. The Pd nanorods in this sample reveal two types of lattice fringes with lattice spacings of 0.195 (= {200}) and 0.225 nm (= {111}) (Figure S4 in the Supporting Information), which indicates that the side surfaces of Pd nanorods are enclosed by {110} facets.^[17b,20] For Pd nanocubes and nanobars in the samples, only {200} planes are observed, which suggests that these NPs are only enclosed by {100} facets (Figures S5 and S6 in the Supporting Information).^[17a,20b] Therefore, the randomly shaped sample of Pd NPs contains a variety of different types of facets, including {111} and {110} faces, and thus, it serves as a control to select phages that do not have specificity for binding the {100} face.

The CTAB capped on the Pd NPs can be removed by UVO treatment, as confirmed by FTIR spectroscopy. In the high-frequency region ($2800\text{--}3000\text{ cm}^{-1}$) of the spectrum of the CTAB crystal shown in Figure S7a in the Supporting Information, two intense bands at 2917 and 2849 cm^{-1} are assigned to the asymmetric ($\nu_{\text{asym}}(\text{C-CH}_2)$) and symmetric ($\nu_{\text{sym}}(\text{C-CH}_2)$) stretching vibrations of C–CH₂ in the methylene chain.^[17a] These bands shift to slightly higher frequencies (2920 and 2851 cm^{-1}) as CTAB is bound onto Pd nanocubes due to less packing of the methylene chains on the NP surface.^[17a] After UVO treatment for 3 h, the stretching bands are barely observed, which suggests that CTAB is eliminated. In the low-frequency region ($750\text{--}1350\text{ cm}^{-1}$) of the CTAB crystal spectrum (Figure S7b in the Supporting Information), peaks at $906, 963,$ and 965 cm^{-1} were assigned to C–N⁺ stretching bands.^[21] As CTAB is bound to Pd nanocubes, the intensities of these bands are decreased, while new bands at $1008, 1033, 1064, 1113,$ and 1167 cm^{-1} are appeared. These bands are assigned as stretching modes of [C–N⁺···Pd] of the polar head group, directly bound to Pd NP surfaces. Similar band changes were observed for CTAB-capped gold nanorods.^[21] After UVO treatment, the [C–N⁺···Pd] stretching bands disappear, supporting that CTAB is fully removed.

3.2 Affinity of Phage Clones to Pd NPs

After three rounds of biopanning with 12 nm Pd nano-cubes as the solid target, 14 different 7-mer peptides displayed on the phage clones were isolated (Table S2 in the Supporting Information). In this study, the same clones showing multiple appearances, namely, Pd-1, Pd-2, and Pd-3, were investigated. However, it should be noted that the affinity of phage clones to the target samples is not always necessarily proportional to the frequency of appearance, probably due to unfavorable virus amplification during biopanning.^[7a,11b,12] To quantify the adsorption behavior of the selected phage clones to Pd NPs, ELISA was performed. In these experiments, all phage solutions were set at 50 pM, and the relative bound amounts were represented by the absorbance at 410 nm.^[11b,12] When 12 nm Pd nanocubes are used as the solid substrate for the binding experiment the bound amounts of all selected clones to the substrate are at least 2.5 times greater than the one for the phage library (Figure 3d). Among selected phages, the Pd-1 clone shows the highest affinity. All phages are eluted from the Pd nanocube substrate at pH 2.2, and the drop of affinity for the Pd-1 phage by lowering the pH is most significant among the three phages. This observation indicates that the binding affinity of the Pd-1 clone to Pd nanocubes is most sensitive to pH changes.

To select phages that have the specificity for binding nanocubes, the binding affinity of Pd-1, Pd-2, and Pd-3 phages to Pd NPs with random shapes is compared: for any phages that show nonspecific high affinity to Pd NPs with random shapes, they tend to bind any Pd NPs, and thus, these phages do not possess binding specificity for the shape of the cube. When the randomly shaped Pd NPs shown in Figure 3c are used as target substrates and mixed with these phages, the Pd-2 clone shows the highest affinity to these irregular Pd NPs, as shown in Figure 3f. Therefore, both Pd-1 and Pd-3 clones are confirmed to be specific to {100} facets of Pd nanocubes, while the Pd-1 clone shows slightly higher specificity than that of the Pd-3 clone. The pH dependence of affinity is very similar between the Pd-1 and Pd-3 clones. Furthermore, in the case of using 40 nm Pd nanocubes as target substrates, all phage clones show similar adsorption behavior to that observed with 12 nm Pd nanocube as substrates (Figure 3e). This result suggests that the selected viruses displaying 7-mer peptides are not specific to particle size, but the crystalline facets because the facets of both 12 and 40 nm Pd nanocubes are dominated by {100} planes.

To further explore the affinity and specificity, the relative affinities were plotted against phage concentration (Figure S8 in the Supporting Information). Assuming Langmuir-type adsorption, the saturation relative bound amount ($RA_{\max}$) and apparent affinity constant (K_{app}) are derived by fitting the experimental data.^[11b,c,e,12] Table S3 in the Supporting Information shows $RA_{\max}$ and K_{app} values for all clones to Pd NPs with different sizes or shapes. Because $RA_{\max}$ is not a constant for phage clones, it would be unsuitable to use only K_{app} to evaluate the binding specificity in this study. However, it can be deduced from Figure S8 and Table S3 in the Supporting Information that the Pd-1 clone shows the best pH response to the {100} face of Pd, since both $RA_{\max}$ and K_{app} are dramatically decreased after acid treatment, while Pd-2 possesses a pH response to all types of crystalline planes. In addition, the particle size has no influence on the adsorption behavior.

3.3 Affinity of Virus-Free Oligopeptides to Pd NPs

To investigate the adsorption behavior of synthetic oligo-peptide (virus free) onto Pd nanocubes, QCM analysis was performed.^[11e] Figure 4 provides a comparison of the adsorption behavior of the Pd-1 peptide with the one for the 7-mer control peptide (DYFSSPC). In this experiment, the substrate was prepared by coating 12 nm Pd nanocubes on a silicon sensor tip. The bound amounts of peptides were determined by the decrease of the frequency, according to Sauerbrey's equation. As shown in Figure 4, the bound amount of Pd-1 peptide is 920 ng/cm², which is much greater than that in the control experiment, 130 ng/cm². A small number of the control peptides are still bound to the substrate; this could be due to nonspecific adsorption.^[7a,12] This result suggests that, even without the virus body, the Pd-1 peptide shows strong affinity to the {100} facets of Pd.

3.4 Shape Evolution Mediated by Oligopeptides

When surfaces of Pd NPs are protected by stable capping agents, the size and shape of the NPs are preserved.^[17a] For example, when 12 nm Pd nanocubes were coated with CTAB, there were no detectable size or shape changes after overnight incubation, both at pH 7.5 (TBS, 2 mg mL⁻¹; Figure S9a in the Supporting Information) and at pH 2.2 (glycine/HCl, 0.2 M; Figure 5a). This observation is reasonable because CTAB caps Pd nanocubes stably, and thus, the capped NP structure is not sensitive to pH. Our hypothesis is that the shape evolution of NPs can be triggered as the capping agent is released from the particle surfaces under external stimulus, such as pH changes. To demonstrate this, we investigated the shape evolution of Pd-1 peptide-capped Pd nanocubes (seeds) at pH 2.2 (glycine/HCl, 0.2 M) after replacing CTAB with the Pd-1 peptide on the seeds at pH 7.5 (TBS, 2 mg mL⁻¹). Since the surfaces of the Pd nanocubes are protected by the Pd-1 peptide at pH 7.5, the shape of the nanocubes is preserved under these conditions (Figure S9b in the Supporting Information). When the pH is lowered from 7.5 to 2.2, Pd-1 peptide is released from the Pd surfaces. Then, the deprotection of Pd facets generates a new surface energy landscape, which subsequently promotes atomic transfer from the high surface energy site to the lowest site. Under these conditions, NPs can no longer maintain the cubic shape, and the growth of large NPs at the expense of smaller ones can be observed after overnight incubation, as indicated in Figure 5b. Furthermore, the small NPs (< 12 nm) in Figure 5b always show concave profiles. These NPs should be formed by etching of the seed nanocrystals, whose edge-to-edge distance is about 12 nm (Figure 3a). In the HRTEM images shown in Figure 5c and Figure S10 in the Supporting Information, etching is dominant on the face centers of the {100} facets, which suggests that the Pd-1 peptides are likely to be released from these planes, where the deprotection of crystal facets tends to promote the desorption of Pd atoms.^[17a] The observation of large NPs (> 15 nm) in Figure 5b could be due to recrystallization. The HRTEM image in Figure S10 in the Supporting Information reveals that these NPs are single crystals, which grow along the {111} planes having the lowest surface energy among low-index crystallographic facets to minimize the surface energy.^[17a] These large NPs should be generated by homogeneous nucleation because {111} facets were not dominant in the seed nanocubes. It should be noted that when the surface of Pd nanocubes is firmly protected by the Pd-1 peptide at pH 7.5, no notable size or shape changes of Pd nanocubes are observed (Figure S9b in the Supporting Information) under these conditions.

The desorbed Pd species (Pd atoms or Pd ions) are reactive in a polar solution and, under these conditions, there is no capping on NPs, which also leads to nucleation and crystal growth along the low energy facets, that is, {111}, thermodynamically.^[17a,22] To better understand the shape developing mechanism, a series of TEM images were recorded of 12 nm Pd nanocubes capped with Pd-1 peptide incubated at pH 2.2 (glycine/HCl, 0.2 M) with time. As shown in Figure S11a in the Supporting Information, the size distribution of Pd NPs becomes more poly-disperse after 2 h of incubation than that in Figure 3a. Some particles have a quasi-spherical shape (highlighted with arrows in Figure S11a in the Supporting Information) with sizes of about 2 nm, and HRTEM analysis reveals the single-crystalline characteristics growing along {111} facets (Figure S11b in the Supporting Information). After 4 h of incubation, 2 nm crystals disappear and larger NPs with sizes of about 20 nm appear (Figure S11c in the Supporting Information). While these newly formed NPs have a quasi-spherical shape, the cubic outline of about 12 nm NPs is still observable until 6 h of incubation. Then, nanocubes start to decrease in size and their {100} facets become concave (highlighted with an arrow in Figure S11d in the Supporting Information). These observations indicate that large NPs shown in Figure S11c and d in the Supporting Information and in Figure 5b could be mainly generated through homogeneous nucleation and subsequent growth along {111} that have the thermodynamically lowest surface energy in solution as Pd-1 peptide is released from Pd surfaces at pH 2.2, which also accounts for less definition in the NP shapes in Figure 5b.

4 Conclusions

After phage clones that are specifically bound to Pd nanocubes were selected from phage-display peptide library, the selectivity and adsorption behavior onto the facets of Pd NPs were investigated. By comparing the binding affinity of these phages to Pd NPs with random shapes, Pd-1 and Pd-3 phage clones were shown to be more selective to {100} facets. Quantitative analysis suggested that the Pd-1 clone possessed the best pH response to the {100} face of Pd because lowering the pH led to the release of Pd-1 phages from Pd surfaces. In this study, the particle size of Pd nanocubes had no influence on their adsorption. In addition, Pd-1, which was the peptide free from the phage virus body, still showed a high affinity to Pd nanocubes. The Pd-1 peptide was a smart capping agent on and off of the {100} facets of Pd, depending on pH, and the shape evolution of Pd NPs was observed in solution because Pd nanocubes became unprotected when Pd-1 peptides were released by lowering the pH.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Schematic illustration of the biopanning procedure for the selection of Pd nanocube recognition peptides.

Figure 2. Schematic illustration of the phage ELISA to analyze the affinity of phage clones on Pd NPs. (a) Mixing Pd-1 nanocubes with a random phage library. (b) Completion of binding between peptides on phages and Pd nanocubes. (c) Separation of Pd nano-cubes bound with phages by centrifugation. (d) Phage ELISA: phages on Pd nanocubes were labeled with HRP/Anti-M13 antibody and the relative amounts of bound phages were quantified by measuring the absorbance of the product peak at 410 nm.

Figure 3.

(a) TEM image of 12 nm Pd nanocubes, (b) TEM image of 40 nm Pd nanocubes. Inset: higher magnification image, (c) TEM image of Pd NPs with various shapes. (d) The relative binding amount of phage clones on 12 nm Pd nanocubes. (e) The relative binding amount of phage clones on 40 nm Pd nanocubes. (f) The relative binding amount of phage clones on Pd NPs with random shapes. In (d)-(f), white bars represent the incubation at neutral pH, whereas red bars show the amount of phages bound on NPs at pH 2.2. Error bars represent the standard deviation (s.d.; $n = 3$).

Figure 4.

QCM tests on the binding affinity of Pd-1 peptide and control 7-mer synthetic peptide (DYFSSPC) on to the Pd nanocubes. According to Sauerbrey's equation, the saturated amount of bound Pd-1 peptides is 920 ng/cm², while that for the control peptide is 130 ng/cm².

Figure 5.

TEM images of Pd NPs after overnight incubation at pH 2.2. (a) Pd nanocubes capped with CTAB. (b) Pd nanocubes capped with Pd-1 peptide. (c) HRTEM of a Pd concave nanocage in (b). The inset shows its corresponding FFT pattern.