Small DNA Additives to Polyelectrolyte Multilayers Promote Formation of Ultrafine Gold Nanoparticles with Enhanced Catalytic Activity

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Abstract

Polymer matrices are important host materials for nesting nanoparticles to be used in photonic, catalytic, environmental, and other applications. Several past studies suggested a unique role of DNA macromolecular template in the process of noble metal nanoparticles (NP) formation and growth yet no comparative studies with other polymeric matrices were performed. In order to address the effect of DNA on metal NP formation and catalytic performance, we synthesized Au NP in PSSNa/PAH/DNA multilayered films containing varied amounts of DNA and systematically studied morphology of multilayers, structure of gold NP formed in the multilayers, and catalytic properties of the NP. We found that decrease of Au NP size due to

increase of DNA contents in the multilayers caused significant enhancement in the hybrid material catalytic properties.

Introduction

During several past decades, applications of DNA-based materials as functional biomatrices,[1-3] adsorbent for environmental pollutants[4] as well as valuable metals[5-7], scaffolds for catalytic NP,[8] etc.[9-11] have been actively explored. In particular, DNA was utilized as a macromolecular template for preparation of various inorganic nanostructures ranging from individual nanoparticles to nanowires[12] and more complex 2- and 3-dimensional nano-architectures[13-16] to be further used in catalytic applications[16] and nanoelectronics.[17] We and others reported applications of DNA for templating of noble metal nanoparticles in DNA-based hydrogels,[8, 18] multilayers,[19] fibers,[20] etc.

Construction of multilayered films from oppositely charged polymers and colloids by layer-by-layer deposition (LbL) is a well-known technique which was broadly used for preparation of functional two and three-dimensional materials[21-23] that find broad application in biomedical, environmental, and other fields. Recently, we showed that multilayers containing DNA can be also used as matrices for *in situ* growth Au nanoparticles to prepare organic-inorganic hybrid films with catalytic properties.[19] However, while the role of DNA in stabilization of noble metal NP growth has been recognized, there have been no studies comparing DNA with other synthetic polyelectrolyte templates in the process of NP formation on polymeric scaffolds. To make it clear, in the present study, we compared the formation of gold nanoparticles in mixed multilayers composed of DNA and other synthetic anionic polyelectrolyte to clarify the unique role of DNA in metal NP templating process.

In our recent report we showed that utilization of DNA for construction of multilayers is promising in preparation of small Au NP.[2] In the present report we focused on a unique role of DNA and its difference from other polyelectrolytes in the construction of polyelectrolyte multilayers for nesting catalytic nanoparticles. Herein, we show that by adding only small amounts (several % w/w) of DNA to polyelectrolyte multilayers, allows to control the NP size at the level of several nm, thus DNA plays an important role stabilizing NP growth in polyelectrolyte (PE) matrix. NP size stabilization also results in a substantial increase (over 5-fold) of gold NP catalytic performance of the hybrid material in reduction of nitroaromatic compounds in aqueous solutions.

Experimental Section

Materials

DNA sodium salt (300 bp in average) extracted from salmon milt was a gift from Maruha Nichiro Holdings, Inc. (Japan). Poly(diallyldimethylammonium) chloride solution (PDADMAC, M_w = 100,000 – 200,000, 20% w/v), poly(sodium-4-styrene sulfonate) (PSSNa), hydrogen tetrachloroaurate $HAuCl_4$ (30 wt % solution in dilute hydrochloric acid, 99.99%), and sodium borohydride ($NaBH_4$) were from Sigma-Aldrich (USA). Sodium carbonate (Na_2CO_3, 99.8%) was from Kanto Chemical (Japan). Calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$, 99.0%), sodium acetate (CH_3COONa, 98.5%), sodium chloride (NaCl), sodium hydroxide (NaOH), and *p*-nitrophenol were from Wako Pure Chemical Industry Co., Ltd (Japan). Acetic acid (CH_3COOH, 99.5%) was from Tokyo Chemical Industries Ltd. (Japan). Disodium dihydrogen ethylendiaminetetraacetate dihydrate (EDTA) and ethanol were from Nacalai Tesque, Inc.

(Japan). Milli-Q water was purified by Simplicity UV apparatus (Millipore, Japan) to reach resistivity of 18.2 MΩ·cm at 25 °C and was used in all experiments.

Methods

UV-vis spectroscopy. UV-vis spectra of metallized multilayered capsules were recorded in a range 400-800 nm at scanning speed of 1000 nm/min on a Jasco V-630 (Japan) spectrophotometer in 1 mL, 1 cm light pass quartz cells at 25±1 °C.

Transmission Electron Microscopy (TEM). TEM observations and element composition analysis of metallized multilayers were performed at room temperature on a HITACHI H-800 microscope (Japan) equipped with an energy dispersive spectroscopy (EDS) detector at 150-200 kV acceleration voltage. Before observations, $CaCO_3$ cores were dissolved by adding 0.1 M EDTA solution (pH = 7.2) and further TEM analyses were performed using the hollow capsules. Twenty μL of 0.5% w/w microcapsules solution was placed onto a 3 mm copper grid covered with a collodion film. After 5 min, the solution was blotted with a filter paper and the samples were dried in a dry box under 10-20% relative humidity overnight prior to observations.

Sample preparation

Preparation of $CaCO_3$ microparticles. Fifty mL of 0.33 M Na_2CO_3 solution were rapidly poured into an equal volume of 0.33 M $CaCl_2$ solution at a room temperature. After intense agitation on a magnetic stirrer for 1 min, the precipitate was allowed to settle down, filtered off, and washed once with Milli-Q water and twice with ethanol, and dried at 85 °C in a dry oven for 3 hours. Freshly prepared $CaCO_3$ beads were used for multilayer deposition.

Deposition of PSS/PDADMAC/(DNA-PSS) multilayers on $CaCO_3$ template. DNA solution was prepared in 0.01 M acetate buffer (pH = 4.0) by stirring at room temperature over 1 day. $(PSS)_1(PDADMAC)_1(DNA\text{-}PSS)_1$ multilayers containing three layers of polyelectrolytes were prepared by consecutive incubation of $CaCO_3$ microparticles (0.5% w/w) in 0.1 M NaCl solution of PSSNa (1 g/L), 0.1 M NaCl solution of PDADMAC 1 g/L, and 0.1 M NaCl solution of a mixture of PSSNa and DNA (1 g/L each) at varied ratios ($\frac{c(\mathrm{DNA})}{c(\mathrm{DNA})+c(\mathrm{PSSNa})} \times 100\%$), 0%, 1%, 5%, 10%, 25%, 50%, and 100%. In should be noted that the above percentage indicate the DNA contents in the third upper layer, therefore, the percentage values of DNA in the entire multilayered film was approximately 3-fold lower. After each PE adsorption cycle performed by 3 min vigorous agitation using vortex, precipitates were washed twice (each for 2 min) with 0.05 M NaCl solution to remove non-bound polyelectrolytes, separated by centrifugation at 1000 rpm for 3 min, and finally stored at 4 °C in 0.05 M NaCl solution.

Synthesis of gold nanoparticles inside multilayered microcapsules. To the beads containing $(PSS)_1(PDADMAC)_1(DNA\text{-}PSS)_1$ multilayers (0.5% w/v, 1 mL), 30 μL solution of 0.1 M $HAuCl_4$ was added and incubated for 3 h. The resulted microbeads were rinsed by 0.05 M NaCl solution, separated by centrifugation (300 g, 5 min), redispersed in 1 mL of Milli-Q water, and 200 μL of freshly prepared 10 mM $NaBH_4$ solution was added to induce Au ion reduction. The resulted beads with metallized multilayers were stored in Milli-Q water. For spectroscopy and microscopy characterizations of gold nanostructures formed inside the polyelectrolyte multilayer, $CaCO_3$ cores were dissolved by adding 0.1 M EDTA solution (pH = 7.2) followed by centrifuge separation at 1000 rpm for 3 min and repeated washing with 0.05 M NaCl solution.

Catalytic reduction of *p*-nitrophenol in the presence of metallized multilayers. 2 mL of 0.02 mM solution of *p*-nitrophenol in Milli-Q water containing freshly prepared $NaBH_4$ (10 mM) and

10 μL of 2.5% w/w metallized microbeads solution were mixed directly in the spectroscopic cell, and time resolved spectra of the supernatant were recorded. Note that in catalytic experiments the $CaCO_3$ core of metalized beads was not dissolved.

Results and Discussion

Assembly and metallization of mixed polyelectrolyte multilayers. Polyelectrolyte multilayers from cationic PDADAMC (poly(diallyldimethylammonium) and anionic DNA and poly(sodium-4-styrene sulfonate) (PSSNa) polyelectrolytes were assembled as schematically illustrated in **Figure 1A-E**. First, $CaCO_3$ beads that are typically 5-10 μm in diameter were synthesized by a reaction between $CaCl_2$ and Na_2CO_3 as described earlier.[19] The obtained $CaCO_3$ beads were further used as sacrificial templates for multilayer deposition. Next, oppositely charged polyelectrolytes were electrostatically assembled on a surface of bead template. Multilayers containing three polyelectrolyte layers were constructed by depositing a layer of anionic PSS (first layer), a layer of cationic PDADAMC (second layer), and a layer composed of a mixture of DNA and PSS (third layer) with varying contents of DNA between 0% and 100% (**Figure 1F**). Next, polyelectrolyte films deposited on $CaCO_3$ beads (0.5% w/v) were saturated with Au^{3+} by dispersing and incubating of the beads in a solution of $HAuCl_4$ (2.9 mM) for 3 hours. It should be noted that under such acidic conditions glycosidic N bond can be broken that may result in a partial loss of purine bases.[24] Followed by separation of beads from the solution containing remained $HAuCl_4$ precursor, the adsorbed Au^{3+} in the multilayers was reduced by adding $NaBH_4$ (10 mM) to obtain Au nanoparticles inside the polyelectrolyte films. After reduction, the color of beads dispersion with varied DNA contents turned purple with no significant change in dispersity of beads in solution. UV-vis spectra of metallized beads

containing different amount of DNA (**Figure 2**) show characteristic peak of gold nanoparticles surface plasmon at *ca.* 500 nm indicating the formation of Au nanoparticles in the polymer matrix.

To investigate the morphology of the multilayers and Au NP formed in the multilayered film, $CaCO_3$ cores were dissolved by adding EDTA and the remained hybrid capsules were observed by transmission electron microscopy (TEM). **Figure 3** shows TEM images of metallized capsules containing varying amount of DNA. First, upon change of DNA contents (α) in mixed multilayers from 0% to 100%, morphology of films gradually changed from rough and porous (α(DNA) < 5%) to smooth and homogeneous (α(DNA) > 5%). This change is attributed to a significantly higher rigidity of DNA (persistence length *ca.* 50 nm in 0.1 M salt[25]) in comparison to PSS (persistence length *ca.* 10 nm at 0.1 M salt[26]). It was also recently shown that decoration of DNA by gold nanoparticles further increases the stiffness of the double-stranded DNA.[27] Therefore, conformational mobility of DNA inside multilayered films is significantly suppressed compared to PSS and multilayers containing larger fractions of DNA appear more mechanically stable after removal of $CaCO_3$ core. On the other hand, flexible PSS is able to diffuse inside the multilayers to adjacent regions with non-compensated charges and this results in the appearance of voids in capsules after film reorganization.

More importantly, DNA contents in the multilayers significantly affected the size and spatial distribution of gold nanoparticles formed in multilayers during reduction of metal precursor Au^{3+} (**Figure 3, 4**). Size distributions of Au NP obtained in mixed multilayers of various compositions are shown in **Figure 4** together with NP average sizes. Higher DNA contents in multilayers apparently favored formation of well-dispersed NP of a smaller size (~2 nm) were evenly distributed inside the multilayer films. Depletion of DNA in the multilayers resulted in

an increase of average NPs size above 10 nm and appearance of high polydispersity in the size distribution. Furthermore, decrease of DNA contents in the polyelectrolyte multilayers was accompanied by a severe Au NP aggregation that caused inhomogeneous distribution of Au NP in the multilayers. Noteworthy, the most dramatic changes were observed when DNA percentage increased from 0% to 5%, while at higher DNA ratios there were only moderate changes in NP size and film morphology.

The observed changes in multilayer morphology and structure of gold nanoparticles (**Figure 3**) clearly demonstrates the important role of DNA in formation of small size well dispersed Au NP inside the hybrid films. The mechanism of this change is interpreted by considering fast nucleation rates of Au NP on a DNA molecule suggested in past studies[8] as well as their local stabilization on DNA due to strong coordination of NP surface atoms with DNA bases.[28] Fast nucleation rates result in the formation of a large number of NP nuclei that grow to NP of small diameter.[29] Similar tendency can be found comparing size of Au NP formed in hydrogels of DNA and in hydrogels of other synthetic polymers, where the size of formed NP was remarkably smaller.[8]

Catalysis in hybrid films. Catalysis is one of promising applications of gold NP,[30] and polyelectrolyte matrices such as multilayered films or hydrogels were broadly utilized as support materials for nesting of nanocatalysts.[18, 31] In order to make clear the consequent effect of DNA on the catalytic properties of Au NP generated in multilayers, we studied catalytic performance of $(PSS)_1(PDADMAC)_1(DNA\text{-}PSS)_1$ multilayers with embedded gold NP in the reduction of nitroaromatic compound to aromatic amine by sodium borohydride ($NaBH_4$), (**Figure 5A**).

The same quantity of capsules with varied DNA/PSS ratios were added to an aqueous solution of *p*-nitrophenol (0.02 mM) and $NaBH_4$ (10 mM), and the conversion of *p*-nitrophenol to *p*-aminophenol was measured spectroscopically as a decrease of *p*-nitrophenol UV absorbance at λ = 400 nm and increase of *p*-aminophenol absorbance at λ = 310 nm. Spectroscopic data of *p*-nitrophenol reduction catalyzed by gold NP in hybrid multilayers are shown in **Figure 5B** in the coordinates of pseudo-first-order reaction kinetics, i.e. as the dependences of $\ln\left(\frac{A}{A_0}\right)$ on the time of the reaction (t), where A and A_0 are *p*-nitrophenol absorbances (λ = 400) at time t and at $t_0 = 0$, respectively. The obtained logarithmic dependences obeyed the first-order reactions kinetics in a good agreement with past studies.[32] As expected, metallized capsules with a higher initial DNA contents showed higher catalytic rates of *p*-nitrophenol reduction. The apparent rate constants (k_{app}) were calculated from the slopes of the corresponding curves and build as a function of DNA ratio in mixed multilayers (**Figure 5C**). Apparent rate constants elevated with an increase of DNA contents in multilayers and the degree of the catalytic activity increase remarkably correlated with the size change of Au NP formed in the multilayers shown in **Figure 4**. Significant decrease of Au NP size and size distribution upon increase of DNA contents in multilayers from 0% to ca 10% resulted in a strong increase in the catalytic activity of the hybrid material, yet at DNA contents above 10% there was a progressive but less pronounced further increase of catalytic performance.

Conclusions

In present study, we demonstrated a unique role of DNA in the formation of multilayered films to use as a scaffold for growing metal nanoparticles in polymeric matrices. Superior mechanical

characteristic of double stranded DNA molecule provides multilayered capsules with high mechanical stability by introducing only several percent DNA to the multilayers. Similarly, the presence of small DNA additives in the multilayers promote the formation of very small metal nanoparticles that are homogeneously distributed inside the polymer matrix. It is suggested that formation of small Au NP on DNA scaffold is a result of substantial decrease of Au NP nucleation energy in the presence of DNA coordinating with a large number of transition metal ions and surface atoms of NP. The described effect may be used for enhancement of catalytic properties of hybrid thin films with noble metal NP by adding small amounts of DNA at the stage of NP synthesis.

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Conflict of interest. The authors declare that they have no conflict of interest.

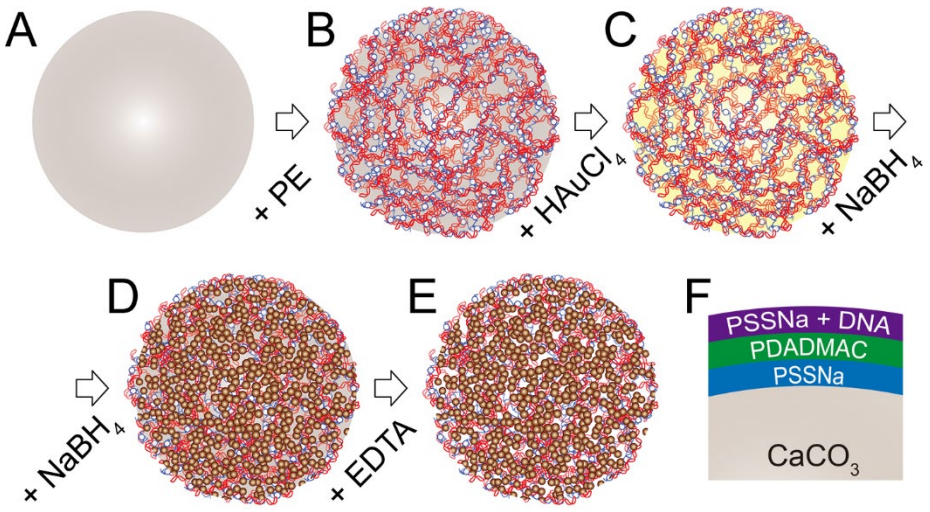

Figure 1. General schematics illustrating the construction of mixed multilayers and their metallization with gold NP. (**A → B**) Deposition of polyelectrolyte multilayer on a surface of $CaCO_3$ template, **(B → C)** absorption of gold precursor ($HAuCl_4$) by multilayered film, **(C → D)** metallization of the multilayer by reduction of adsorbed gold precursor, **(D → E)** removal of the sacrificial $CaCO_3$ template by EDTA. (**F**) Schematic representation of the composition of hybrid multilayer assembled on $CaCO_3$ bead template.

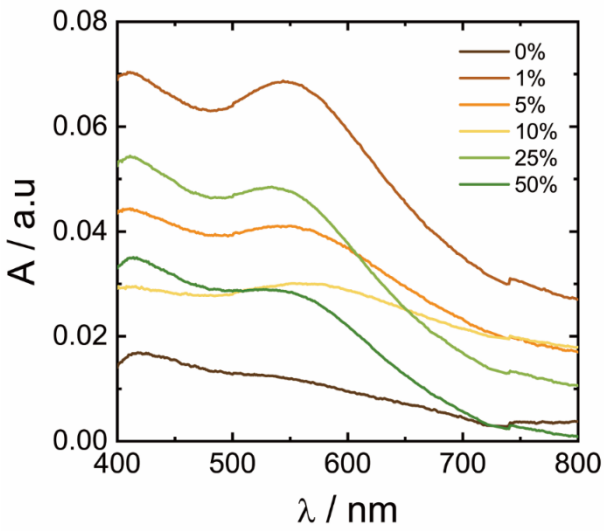

Figure 2. Optical properties of metallized hybrid multilayers. UV-vis spectra of multilayered capsules $(PSS)_1(PDADMAC)_1(DNA\text{-}PSS)_1$ containing different amount of DNA after adsorption of $HAuCl_4$, its reduction by $NaBH_4$, and removal of $CaCO_3$ core by treatment with EDTA. Percentage values indicate the amount of DNA in the third upper layer.

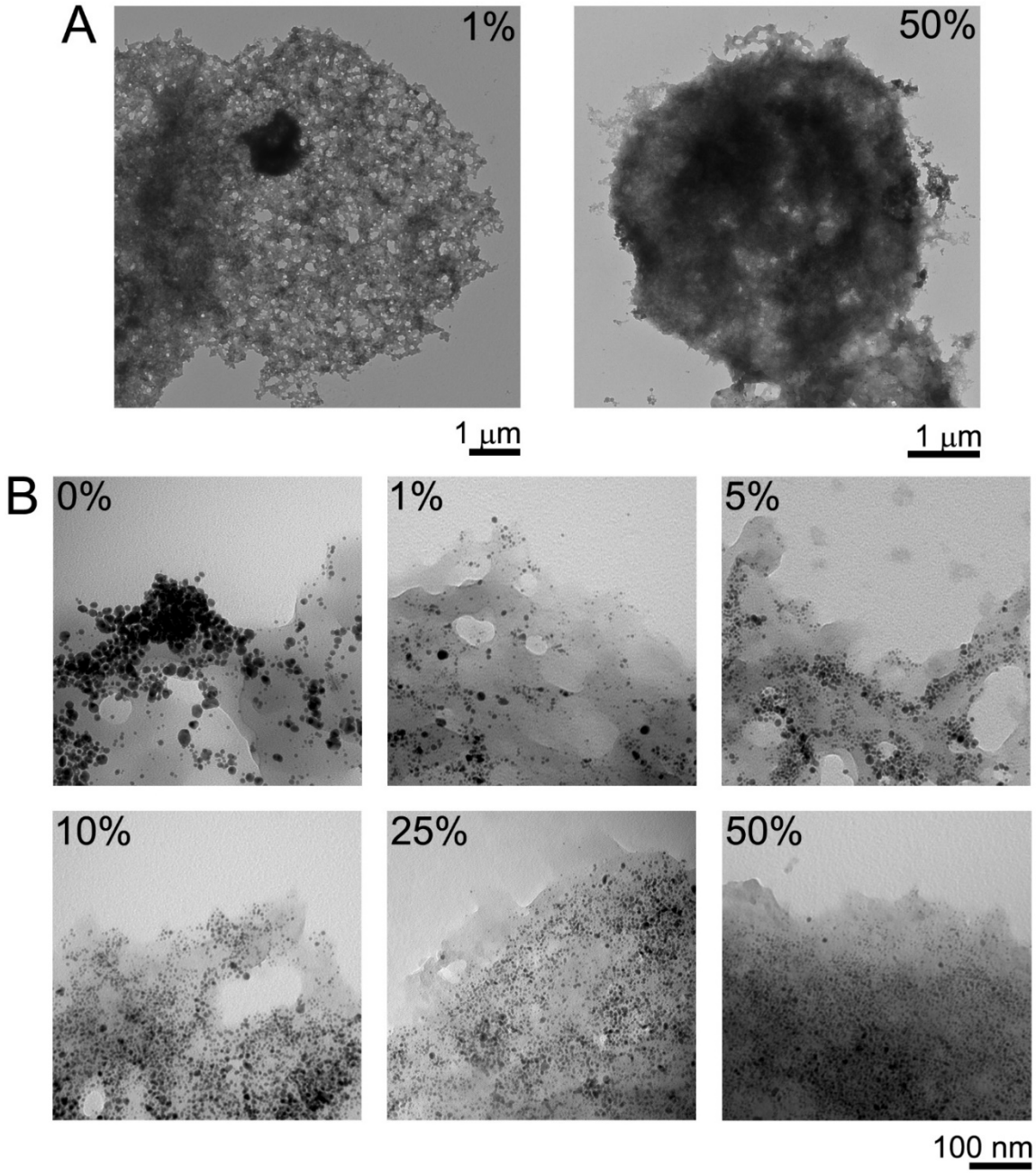

Figure 3. TEM images of gold NP in hybrid multilayers. (**A**) Transmission electron microscopy images of single hybrid capsules $(PSS)_1(PDADMAC)_1(DNA\text{-}PSS)_1$ containing different initial amount of DNA after adsorption of $HAuCl_4$, its reduction by $NaBH_4$, and removal of $CaCO_3$ core by treatment with EDTA. (**B**) TEM images of fragments of multilayered capsules containing various fractions of DNA after adsorption of $HAuCl_4$, its reduction by $NaBH_4$, and removal of $CaCO_3$ core by treatment with EDTA.

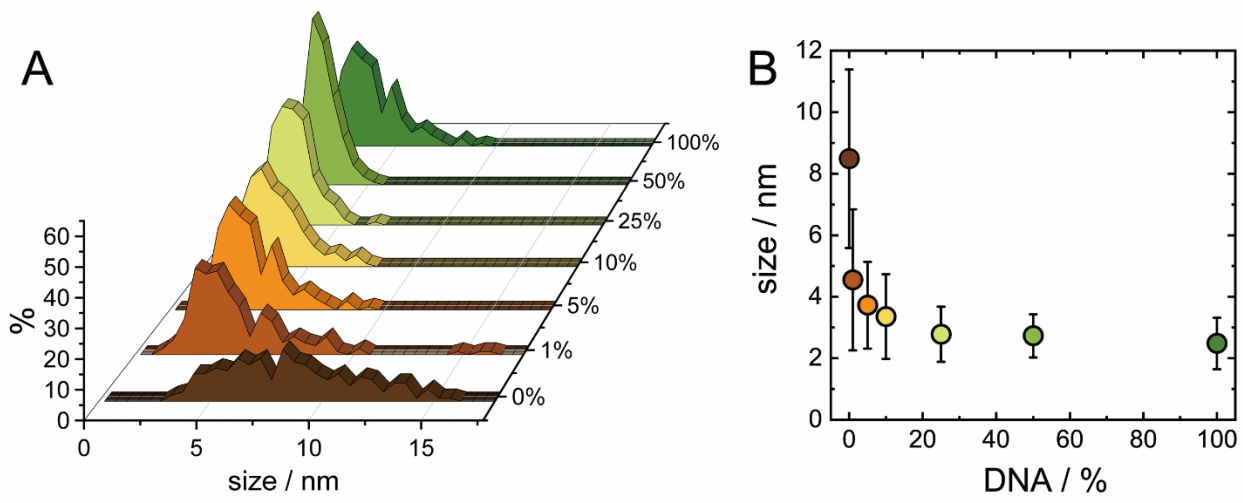

Figure 4. Size distributions of gold nanoparticles. (**A**) Size distributions of gold nanoparticles synthesized in $(PSS)_1(PDADMAC)_1(DNA\text{-}PSS)_1$ multilayers containing different DNA to PSS ratios in the third upper layer. (**B**) Dependence of the average size of gold nanoparticles synthesized in multilayers on the ratio of DNA in multilayers. At least 100 Au NP were measured to build the distributions. The error bars are statistical deviations from the average values.

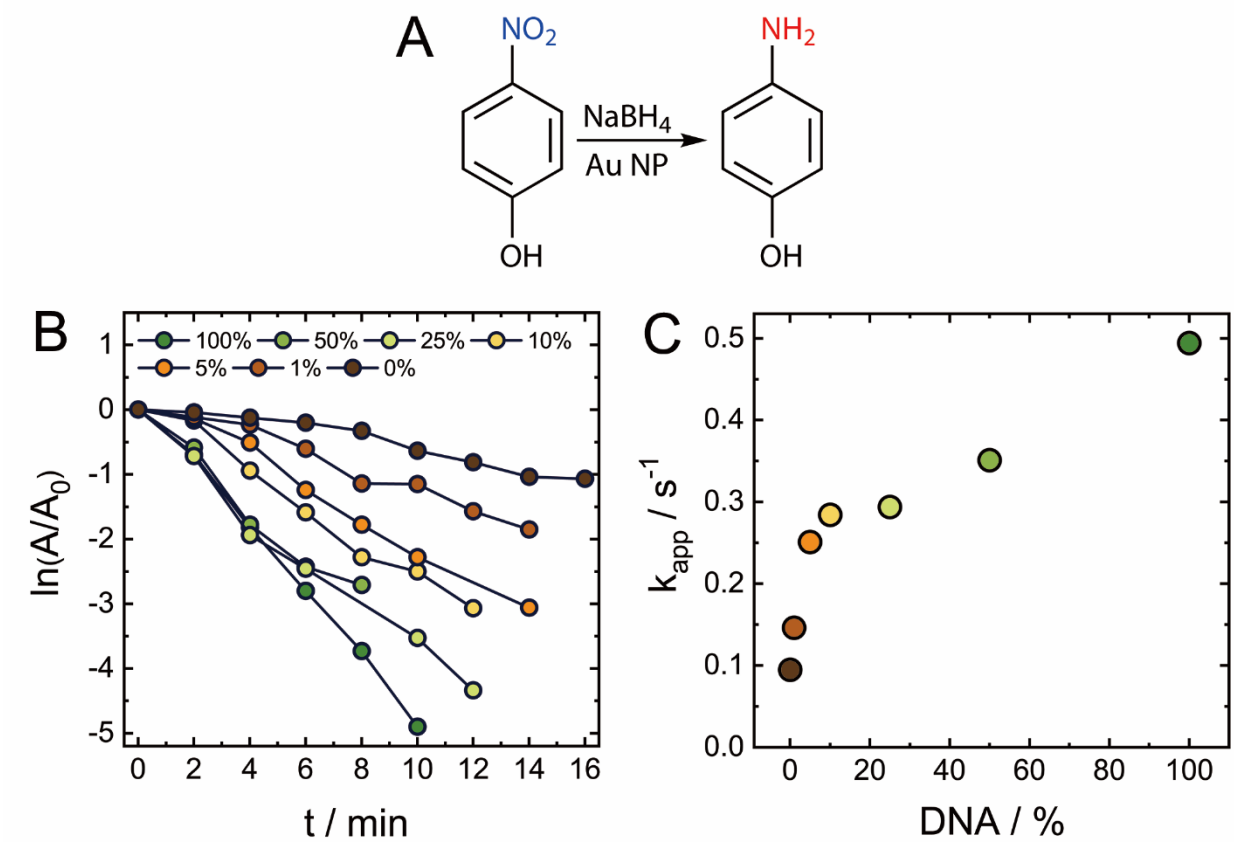

Figure 5. Catalysis by gold nanoparticles embedded into DNA-containing multilayers. (**A**) Chemical reaction of *p*-nitrophenol reduction by sodium borohydride in presence of gold nanoparticles as a catalyst. (**B**) Time dependence of the logarithm of normalized *p*-nitrophenol absorbance at λ= 400 nm in solutions containing the same concentration of capsules with a different percentage of DNA. (**C**) Dependence of apparent kinetic constants of *p*-nitrophenol reduction (k_{app}) on the initial amount of DNA in the multilayered capsules.

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