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DNA Hydrogel as a Template for Synthesis of Ultrasmall Gold Nanoparticles for Catalytic Applications

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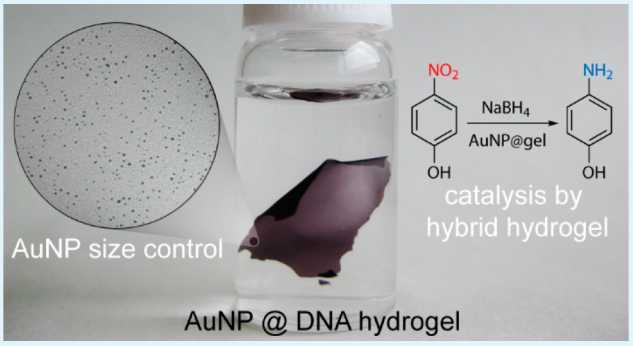
Supporting Information

ABSTRACT: DNA cross-linked hydrogel was used as a matrix for synthesis of gold nanoparticles. DNA possesses a strong affinity to transition metals such as gold, which allows for the concentration of Au precursor inside a hydrogel. Further reduction of $HAuCl_4$ inside DNA hydrogel yields well dispersed, non-aggregated spherical Au nanoparticles of 2−3 nm size. The average size of these Au nanoparticles synthesized in DNA hydrogel is the smallest reported so far for in-gel metal nanoparticles synthesis. DNA hybrid hydrogel containing gold nanoparticles showed high catalytic activity in the hydrogenation reaction of nitrophenol to aminophenol. The proposed soft hybrid material is promising as environmentally friendly and sustainable material for catalytic applications.



KEYWORDS: *DNA hydrogel, gold nanoparticles, catalysis, nitrophenol reduction*

INTRODUCTION

The affinity of nucleic acids to transition metals, in particular to gold, is well known from earlier biochemical studies originated in the 1970s.[1,2] Au(III) coordinates with DNA bases and forms stable complexes of the compositions [Au]/[nucleotide] = 0.5 and higher.[3,4] The strong DNA affinity to transition metals favored its choice as a template for synthesis of inorganic nanowires,[5−9] metallization of surface-absorbed[10,11] and folded DNA condensates,[12−14] metallization of self-assembled "DNA origami",[15,16] and other DNA molecular architectures.[17,18] However, currently available DNA metallization protocols are limited by those based on one-dimensional (DNA macromolecule) or two-dimensional (DNA adsorbed on surfaces) templates. It is promising to further extend the dimensionality of the DNA templates to three-dimensional molecular architectures in order to construct a bulk material containing nanosized metal structures distributed within its volume that can find potential applications in catalysts, sensors, etc.

One suitable example of the three-dimensional matrix composed of the DNA is a hydrogel, which can be employed as a platform for templating of a material formed in various chemical reactions. DNA hydrogel was first prepared by DNA crosslinking with epoxide by Tanaka et al.,[19] who studied DNA hydrogels in relation to phase transition in low-polar solvents. The understanding of physico-chemical properties of DNA hydrogel was significantly deepened in recent works of Costa et al.[20−22] and Okay et al.[23−25] Another robust biological method based on the ligase-mediated construction of a DNA hydrogel from branched DNA was also reported.[26−28]

DNA is a particularly suitable natural polymer for concentrating transition metal ions because purine and pyrimidine bases and, to some extent, phosphate groups of DNA act as efficient chelation sites. Very recently, we reported the utilization of DNA hydrogel as an absorbent for extraction of transition and rare-earth metals from aqueous solutions.[29] Therefore, DNA hydrogel containing transition metal ions is promising as a "reactor" for controllable synthesis of metal nanoparticles, where strong interaction of DNA with transition metals must play an important role to control the growth of inorganic nanoparticles. It is worth noting that the industrial scale of low-cost DNA extracted from fish milt, the waste product of the marine industry, is considered for use in various material applications.[30−33]

In the present study, we focused on gold nanoparticles synthesis inside DNA hydrogel by performing a reduction of hydrogel-absorbed Au(III) directly inside the hydrogel matrix. We report the formation of ultrasmall, non-aggregated, and kinetically stable gold nanoparticles of 2−3 nm size inside DNA hydrogel and demonstrate the application of the resulted soft hybrid material in a catalytic hydrogenation of nitrophenol.

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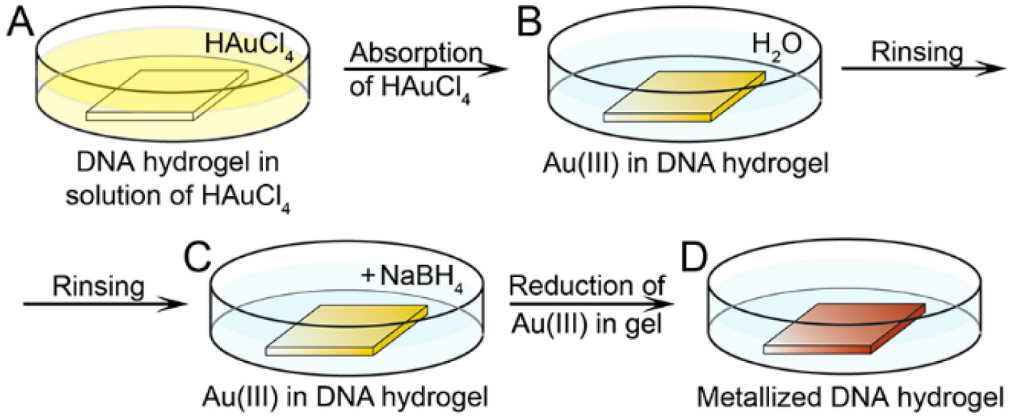
Scheme 1. Protocol for Preparation of Hybrid Hydrogel[a]



[a](A) Absorption of $HAuCl_4$ by DNA hydrogel; (B) rinsing of DNA hydrogel by distilled water; (C) addition of the reduction agent ($NaBH_4$) into solution with DNA hydrogel; (D) reduction of Au(III) inside hydrogel.

EXPERIMENTAL SECTION

Materials. DNA sodium salt (ca. 10–20 kbp, *ca.* 90% purity) extracted from salmon milt was a gift from Maruha Nichiro Holdings, Inc. (Japan). Hydrogen tetrachloroaurate $HAuCl_4$ (30 wt % solution in dilute hydrochloric acid, 99.99%) and *N,N,N,N*-tetramethyl-ethylenediamine (TEMED) were from Sigma (USA); ethylene glycol diglycidyl ether (EGDE) was from TCI (Japan). Sodium borohydride ($NaBH_4$) was from Aldrich (USA); *p*-nitrophenol, sodium hydroxide (NaOH), and sodium chloride (NaCl) from Wako (Japan) were used as received. Milli-Q water purified by Simplicity UV apparatus (Millipore, Japan) was used in all experiments.

Preparation of DNA cross-linked hydrogel film. 1% solution of DNA was prepared in Milli-Q water by stirring at room temperature over 2 days. To 5 mL of a 1% solution of DNA were added 50 μL of 0.5 M NaOH, 15 μL of cross-linking agent, EGDE, and 5 μL of initiator TEMED. The components were thoroughly mixed by vortex, and the resulted viscous liquid was transferred onto a 42 mm diameter Petri dish, which was heated at 90 °C for 20 min, covered with the lid to minimize evaporation of water, and then at 50 °C for 2 h in the open air. DNA hydrogel film was repeatedly washed by 100 mL of 1 mM NaCl solution to remove non-cross-linked DNA and other unreacted chemicals.

Synthesis of Gold Nanoparticles Inside Hydrogel. Synthesis of gold nanoparticles inside DNA hydrogel is schematically illustrated on Scheme 1. DNA hydrogel film (0.1 g) was placed into a 5 mL solution of 4 mM $HAuCl_4$ and incubated overnight. The decrease of $HAuCl_4$ contents in the solution above DNA hydrogel was monitored by UV-vis spectroscopy at λ = 300 nm. The resulted hydrogel film was quickly rinsed by Milli-Q water within several seconds and placed into the Petri dish, and 5 mL of freshly prepared solution of 10 mM $NaBH_4$ was added to the hydrogel to induce Au(III) reduction.

Catalytic Reduction of *p*-Nitrophenol. To 1 mL of a 0.2 mM solution of *p*-nitrophenol in distilled water containing $NaBH_4$ (1 mM) 0.1 g of hybrid hydrogel was added directly into the spectroscopic cell, and time-resolved spectra of the solution above the hydrogel were recorded.

UV-Vis Spectroscopy. UV-vis spectra of hydrogels homogenized by sonication (VP-5S, TAIREC (Japan), 20 kHz, <50 W) were recorded on a Jasco V-630 (Japan) spectrophotometer in 1 mL (1.0 × 0.2 × 0.5 cm) quartz cells at room temperature. Spectra of Au(III) were recorded between 200 and 400 nm; spectra of Au nanoparticles were recorded between 300 and 900 nm. Direct UV-vis spectroscopy measurements of hydrogel film were performed by placing the hydrogel between two glass plates (0.3 × 40 × 15 mm, Matsunami, (Japan)) set up perpendicularly to the direction of light beam direction in the spectrometer.

Fluorescence Absorption Spectroscopy. Fluorescence spectra of PicoGreen in solutions of homogenized DNA hydrogel were recorded on a FP-6600 spectrofluorimeter (Jasco, (Japan)) in 1.0 × 1.0 × 5.0 cm quartz cells at room temperature according to the protocol (http://probes.invitrogen.com/media/pis/mp07581.pdf) provided by Invitrogen (Japan).

Transmission Electron Microscopy (TEM). TEM observations were performed at room temperature on a HITACHI H-800 microscope (Japan) at 200 kV acceleration voltage. Hybrid hydrogel was homogenized by sonication; 20 μL of the resulted solution was placed onto a 3 mm copper grid covered with a collodion film. After 3 minutes, the solution was removed with a filter paper, and the sample was dried under ambient conditions overnight prior to observations.

RESULTS AND DISCUSSION

DNA hydrogel was prepared on the basis of the original procedure of Tanaka et al.[19] but modified to obtain a hydrogel *film* with enhanced mechanical characteristics. DNA in 1% aqueous solution was cross-linked by a reaction with ethylene glycol diglycidyl ether (EGDE). Epoxy groups of EGDE interact with amino groups of DNA bases under alkaline conditions and elevated temperatures favoring DNA denaturation and thereby exposure of reacting amino groups into solution. The hydrogel film was allowed to swell and washed by 1 mM NaCl solution to completely remove non-crosslinked DNA and unreacted chemicals. By comparison between the DNA amount in hydrogel and the DNA amount in collected solutions after DNA washing using UV-vis spectroscopy, the ratio of non-crosslinked DNA was found to be less than 1%. The concentration of DNA in swollen hydrogel (1 mM aqueous NaCl) was calculated from spectroscopic data of homogenized (20 kHz, 10 min) hydrogel and was found to be *ca.* 30 mM (in DNA phosphates per hydrogel volume), which roughly corresponds to about 1% (w/w). DNA double-helix content in the hydrogel was analyzed using PicoGreen fluorescence assay (Supporting information, Figure S1), and the ratio of double-helical DNA in hydrogel was found to be less than 5%; i.e., the matrix of DNA hydrogel is predominately composed of crosslinked single-stranded DNA chains. The overwhelming single-stranded DNA composition of the hydrogel results from the crosslinking scenario, where after the crosslinking of denaturated DNA chains by EGDE and the formation of hydrogel's 3-dimensional matrix, the reverse process (renaturation of single- to double-stranded DNA) is forbidden due to a dense crosslinking.

DNA is well known as a good biomolecular template in preparation of various metal nanostructures,[18] and utilization of

DNA hydrogel represents an almost unexplored yet attractive strategy for the construction of three-dimensional architectures of inorganic nanomaterials. DNA hydrogel metallization was done following the two-step process illustrated by Scheme 1, i.e., (i) absorption of $HAuCl_4$ by DNA hydrogel (Scheme 1 A→B) and (ii) successive reduction of Au(III) inside the hydrogel matrix by adding $NaBH_4$ solution (Scheme 1 C→D).

The first step on Scheme 1 A→B, Au(III) absorption by DNA hydrogel, was carried out in a similar way as we reported previously for concentration of noble and rare-earth metals inside the DNA hydrogel.[29] When DNA hydrogel film was placed into a yellow solution of 4 mM $HAuCl_4$, the color of the film changed gradually from transparent to yellow−brown (Figure 1A) and the hydrogel contracted by *ca.* 30−40%.

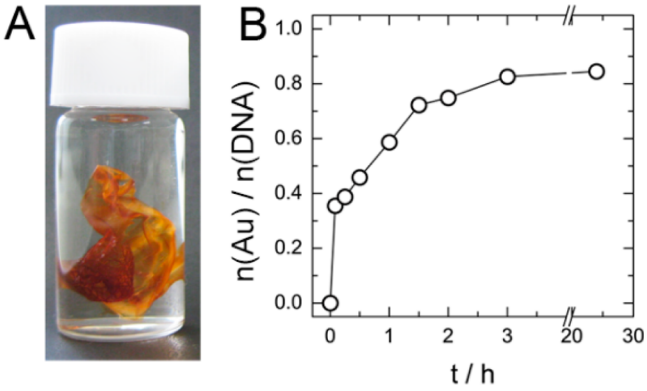


Figure 1. Absorption of Au(III) by DNA hydrogel. (A) Photographic image of DNA hydrogel film (1 g) after extraction of Au(III) from 5 mL of 4 mM $HAuCl_4$ solution. (B) Time-dependent $HAuCl_4$ uptake by DNA hydrogel film from a 5 mL solution containing 4 mM $HAuCl_4$ shown as a molar ratio of absorbed Au(III) to DNA monomers (nucleotides). Au(III) uptake was measured by UV-vis spectroscopy as a decrease of $HAuCl_4$ solution absorbance at λ = 300 nm at room temperature.

Different colors of Au(III) in the hydrogel than in solution and the contraction of the hydrogel caused by the diminishing of electrostatic repulsion between DNA chins in the polyelectrolyte network indicated the formation of Au(III)−DNA complex inside the hydrogel. Time-dependent Au(III) uptake from the solution above the hydrogel is shown in Figure 1B as a change in a molar ratio between Au(III) and DNA monomers in the hydrogel. Au(III) absorption is characterized by a rapid uptake of Au(III) during the first several minutes and relatively slow absorption during the next several hours. The existence of these two regions of Au(III) uptake might point to the formation of different DNA−Au(III) complexes suggested earlier where Au(III) binding site and properties of the resulted complexes differed depending on DNA to Au(III) ratios.[3] The saturation of the hydrogel by Au(III) was reached after *ca.* 3 h, and the final average amount of absorbed Au(III) by hydrogel was calculated to be 0.86 ± 0.03 Au(III) ions per DNA phosphate group. Therefore, taking into account the contraction of DNA in the hydrogel, the concentration of Au(III) inside the hydrogel is approximately 10 times higher than the Au(III) concentration in the outer solution as a result of strong chemical bonding of Au(III) to DNA.

Next, DNA hydrogel containing Au(III) was quickly rinsed by distilled water (Scheme 1 B→C) and placed into a Petri dish, and 5 mL of 10 mM $NaBH_4$ solution was added. Figure 2 shows photographic snapshots of the hydrogel film after addition of reduction agent taken at an interval of 1.5 s (movie clip file showing hydrogel metallization is available as Supporting Information). Within several seconds after addition of $NaBH_4$ solution, the color of the hydrogel film changed to brown and then to dark-purple indicating the formation of gold nanoparticles inside the hydrogel. The color change was accompanied by the hydrogel swelling apparently due to the dissociation of DNA−Au(III) complex caused by Au(III) reduction to Au(0) and recovery of electrostatic repulsion between DNA phosphates in the hybrid hydrogel. Neither outer solution color change nor the other visible evidences of hydrogel contents release into the outer solution was observed during reduction; thus, it was concluded that the reaction took place exclusively inside the DNA hydrogel. The hybrid hydrogel films are stable in water solutions for at least 6 months from the moment of metallization showing no breakage of hydrogel film or release of DNA or the colored contents.

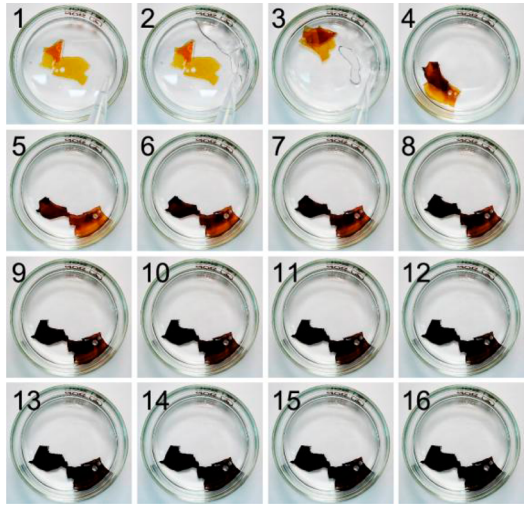


Figure 2. Reduction of Au(III) in the DNA hydrogel. Photographic images of the DNA hydrogel film containing Au(III) after addition of 5 mL of a solution of 10 mM $NaBH_4$. The time interval between snapshots is 1.5 s (movie clip file of hydrogel metallization is available as Supporting Information).

Absorbance spectroscopy is a useful tool for studying metal nanoparticles because the position and shape of surface plasmon absorbance are sensitive to the particle size. The hybrid hydrogel film was homogenized by means of sonication, and the resulted stable violet colloidal dispersion was measured by UV-vis spectroscopy. The spectrum of the homogenized hydrogel in Figure 3A has a weak absorbance band at λ = 550 nm, which is a typical plasmon absorbance signal for gold nanostructures larger than 2 nm. A similar spectrum was obtained measuring intact (as-prepared) hydrogel film (Supporting information, Figure S3), which means that the sonication of the DNA hydrogel had no influence on the properties of Au nanoparticles. It was reported earlier that Au nanoparticles larger than 2 nm typically have a plasmon band in the range of 500−550 nm,[34] and when the particle size is less than 2 nm, the distinctive plasmon band is replaced by a featureless absorbance, which increases monotonically toward higher energies.[35−37] Because the absorbance band of hybrid hydrogel is weak despite a high absorbance between 400 and 600 nm (Figure 3A), it can be concluded that the size of the nanoparticles is only a few nanometers.[38,39] Indeed, the

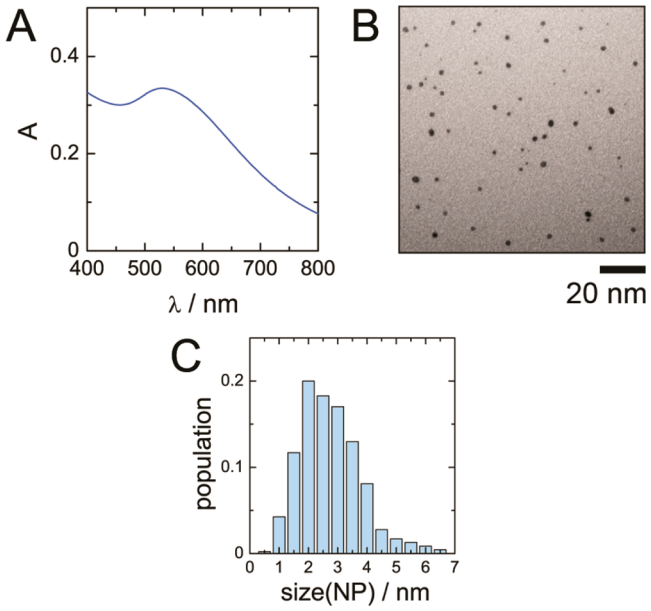


Figure 3. Gold nanoparticles formation inside the hydrogel matrix. (A) UV-vis spectra of hybrid DNA hydrogel film shown in Figure 2 obtained by a reduction of Au(III) inside the DNA hydrogel matrix using $NaBH_4$ and after sonication at 20 kHz for 1 min. (B) Typical TEM images of sonicated hybrid hydrogel sample prepared as described for A. (C) Statistical distributions of gold nanoparticles' size based on the TEM micrograph. The distribution was obtained by measuring around 500 nanoparticles in two independently prepared hybrid hydrogel.

spectrum in Figure 3A is very similar to the spectrum of 3 nm particles reported earlier.[40]

For direct visualization of gold nanostructures formed in DNA hydrogel, transmission electron microscopy (TEM) was used. Because the direct observation of DNA hydrogel film by TEM is not possible, samples for TEM were prepared by 10 min sonication of the hybrid DNA hydrogel before observation. Figure 3 shows a TEM image (B) and the size-distribution histograms of Au nanoparticles synthesized inside the hydrogel (C). The images show well separated Au nanoparticles with the average size of 2.8 ± 1.0 nm.

The possibility to obtain and stabilize such small Au clusters can be party ascribed to the high affinity of the DNA bases to gold demonstrated earlier,[3,4] yet the role of hydrogel matrix environment in stabilization of Au nanoparticles required further clarification. In order to compare the formation of gold nanoparticles in the hydrogel and in a similar non-crosslinked environment, we performed the reduction of $HAuCl_4$ in solution of the same DNA and at the same concentration (30 mM) as DNA in hydrogel. Addition of $HAuCl_4$ at 4 mM concentration into a solution of 30 mM DNA, incubation for 6 h, and final reduction by $NaBH_4$ at 10 mM concentration caused immediate color change of the solution from yellow–brown to gray–violet, similar to the changes observed in the hydrogel film. The sample taken immediately after reaction was subjected to TEM analysis. It was found that the predominant structures were gold nanoparticles, their average size was only slightly larger than those in the hydrogel, and the size distribution was comparable (3.2 ± 1.3 nm), but many aggregates were also observed (Supporting information, Figure S4). Furthermore, when the same experiment was performed at a 100 times lower DNA concentration (0.3 mM), addition of $NaBH_4$ first caused a similar color change of the solution from yellow–brown to dark-violet, but then, the fast precipitation of the entire amount of Au nanoparticles occurred and a colorless transparent liquid remained. Therefore, it becomes clear that for stabilization of small gold nanoparticles a high concentration of DNA is crucial, while the size of the nanoparticles is rather a function of DNA concentration and not significantly influenced by the crosslinking of DNA to the hydrogel structure.

The schematic formation of small Au nanoparticles in DNA hydrogel is illustrated by Figure 4. First, Au(III) ions bind to DNA macromolecules (A). The following reduction of Au(III) results in the formation of Au(0) atoms, in which lateral mobility along DNA chains facilitates formation of metal clusters growing into small Au nanoparticles on the DNA chain (Figure 5C). Time-resolved spectra of the sonicated hydrogel at different times of reduction (Supporting information, Figure S2) indicate that the band corresponding to larger than 2 nm

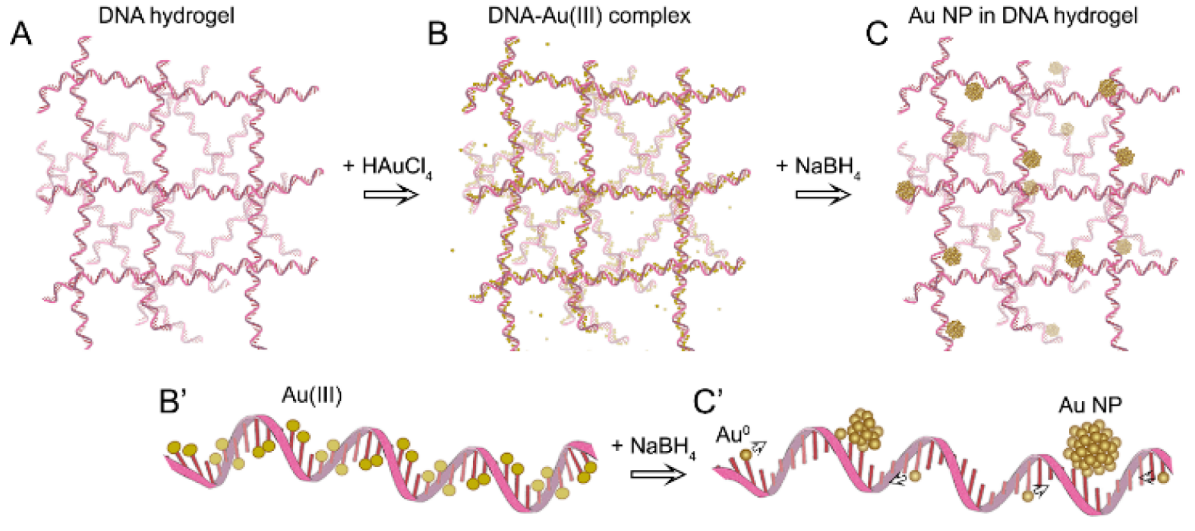


Figure 4. Schematic illustration of Au(III) reduction in DNA hydrogel matrix and formation of nanoparticles locally bound to DNA. (A) DNA hydrogel; (B and B′) DNA complex with Au(III) complex; (C and C′) gold nanoparticles bound to the DNA scaffold of hydrogel.

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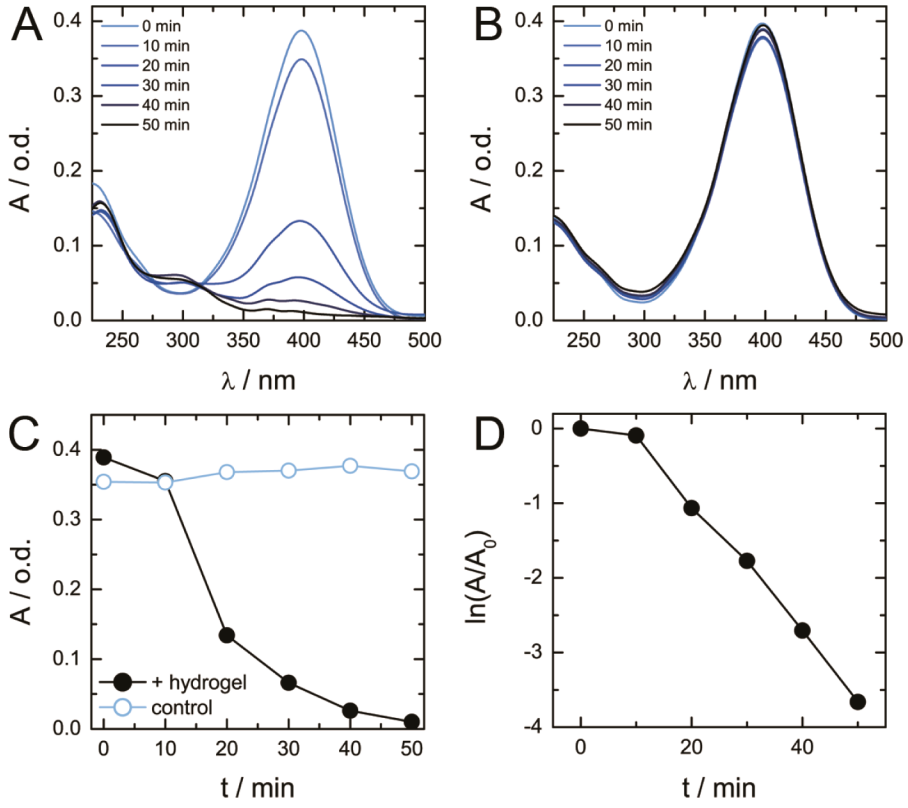

Figure 5. (A and B) Time dependent changes in UV-vis absorbance spectra of *p*-nitrophenol solution (0.2 mM) with (A) and without (B) added hybrid hydrogel (0.1 g) after addition of $NaBH_4$ (1 mM) in 1 mL of water solution. (C) Time dependence of nitrophenol absorbance at λ = 400 nm in solution with (filled circles) and without (open circles) hybrid hydrogel. (D) Time dependence of the normalized nitrophenol absorbance at λ = 400 nm built in logarithmic coordinates.

Table 1. Earlier Reported Examples of Au Nanoparticles Synthesis in Macromolecular Hydrogels, the Diameter of Such Nanoparticles, and Their Applications for the Catalysis of Certain Reactions (If Performed)

polymer matrix/precursors of NP	diameter of NP, nm	catalytic reaction (if performed)	ref
poly-*N*-isopropylacrylamide (microgel)/ $HAuCl_4$ + tetrakis(hydroxymethyl) phosphonium chloride	60−120		41
poly(vinyl alcohol)/$HAuCl_4$ + ascorbic acid	20−80		42
polyethylene glycol-polyurethane/$HAuCl_4$ + $NaBH_4$	6−10	*o*-nitroaniline → 1,2-benzenediamine	43
poly-*N*-isopropylacrylamide/$HAuCl_4$ + γ-irradiation	4−7	*o*-nitroaniline → 1,2-benzenediamine	44
chitosan/$HAuCl_4$ + heating (40−80 °C)	∼5	nitrophenol → aminophenol	45
poly(vinyl alcohol)/$HAuCl_4$ + $NaBH_4$	∼4		42
(this work) DNA/$HAuCl_4$/$NaBH_4$	∼2.8	nitrophenol → aminophenol	

nanoparticles appears only at the later stages of Au(III) reduction and corresponds to brown−violet or violet−blue color hydrogels.

It should be noted that synthesis of gold nanoparticles inside polymeric hydrogels attracted increasing attention (Table 1) due to potential application of such systems in catalysis. Importantly, the diameter of nanoparticles obtained in these studies largely varied but, to the best of our knowledge, using DNA hydrogel, we succeeded to obtain the soft hybrid material containing the smallest gold nanoparticles (2−3 nm) reported so far.

Having discussed the synthesis and the structure of the hybrid DNA hydrogel, we now turn to its catalytic properties. The catalysis on gold nanoparticles has been intensively studied during the past decade and applied to many organic reactions.[46,47]

It was also demonstrated that certain organic reactions can be catalyzed by gold nanoparticles dispersed inside the matrix of a synthetic hydrogel. Table 1 shows several studies of a successful catalysis by gold nanoparticles in hydrogel. Taking into account the small size of gold nanoparticles prepared in DNA hydrogel in this study, the high catalytic activity due to their large surface area was expected. As a model reaction, we used catalytic reduction of *p*-nitrophenol by $NaBH_4$. Nitrophenols, known for their toxicity and possible accumulation in the environment, represent a pollutant of industrial wastewaters, and this reaction was rigorously investigated in the field of environmental chemistry.[48,49] Conversion of *p*-nitrophenol to aminophenol was monitored spectroscopically. Figure 5A,B shows time-dependent changes of the 0.2 mM nitrophenol solution spectrum after addition of 1 mM $NaBH_4$ into a solution containing hybrid hydrogel (0.1 g) (A) and into solution without hydrogel (B). In the solution with added

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hybrid hydrogel, the intensity of the peak at 400 nm, the signal of nitrophenol, gradually decreased, and after less than 1 h of reduction, no peak of nitrophenol was detected. Simultaneously, an increase in the lower intensity absorbance peak at *ca.* 300 nm, corresponding to the formation of aminophenol, was observed. In contrast, the control experiment without hydrogel in Figure 5B shows essentially no spectral changes during 50 min from the moment of adding reduction agent. Time-dependent absorbance changes are compared in Figure 5C. In the presence of the hybrid hydrogel, half-conversion time was shorter than 20 min, and about 97% conversion of nitrophenol to aminophenol after 50 min of reduction was achieved.

When the data in Figure 5C were rebuilt in the coordinates of the logarithm of the normalized nitrophenol absorbance versus time (Figure 5D), the resulted dependence was linear after *ca.* a 5 min induction period. The linear region is the first-order reduction kinetics reported earlier for gold nanoparticles' catalysis (see relevant references in Table 1). The rate constant was calculated using the rate law for the first-order kinetics: $\ln(c/c_0) = \ln(A/A_0) = -kt$, where c, A, and k are concentration of *p*-nitrophenol, absorbance of *p*-nitrophenol, and apparent rate constant, respectively. From the slope of linear part in Figure 5D, k was found to be 1.5×10^{-3} s^{-1}. Thus, DNA-based hydrogel with ultrasmall gold nanoparticles showed faster reduction kinetics in comparison to the analogous system with larger 4−7 nm Au nanoparticles, for which k was found to be 2.8×10^{-4} s^{-1}.[44]

CONCLUSIONS

By utilizing a strong DNA affinity to the transition metal ions, we succeeded to synthesize ultrasmall 2−3 nm Au nanoparticles inside DNA crosslinked hydrogel and showed that DNA hydrogel containing Au nanoparticles is a promising catalytic material. This hybrid material has several important advantages compared to solutions of nanosized catalysts. First, the problem of small nanoparticles stabilization can be overcome by incorporating them into the hydrogel matrix. This is especially important in the case of the small nanoparticles having a very high surface energy and easily aggregating. The fixation of nanoparticles inside the hydrogel matrix should also diminish a possible effect of reactants on the nanoparticles stability such as, for example, dissolution of nanoparticles' stabilizing chemicals (capping agents) by an organic reactant. Second, nanoparticles recovery after synthesis, i.e., separation from reaction mixture, and re-dispersion into a new reaction solution, can be avoided. Finally, the use of the DNA from marine waste represents a novel, environmentally friendly approach towards sustainable materials.

ASSOCIATED CONTENT

Supporting Information

PicoGreen protocol for determination of double-helix DNA contents in DNA hydrogel; time-resolved UV-vis spectra of DNA hydrogel metallization, UV-vis spectra of hybrid DNA hydrogel film as-prepared; size distributions of gold nanoparticles obtained in concentrated DNA solutions; movie clip showing reduction of Au(III) in DNA hydrogel. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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