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DNA templated fluorescent gold nanoclusters reduced by Good's buffer: from blue emitting seeds to red and near infrared emitters

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Abstract

DNA templated fluorescent gold nanoclusters (AuNCs) have been recently prepared, showing higher photostability than the silver counterpart. In this work, we examined the effect of pH, DNA length, sequence and reducing agent. Citrate, HEPES and MES produce blue emitters, glucose and $NaBH_4$ cannot produce fluorescent AuNCs, while ascorbate shows blue emission even in the absence of DNA. This is the first report of using Good's buffer for making fluorescent AuNCs. Dimethylamine borane (DMAB) produces red emitter. Poly-C DNA produces AuNCs only at low pH and each DNA chain can only bind to a few gold atoms, regardless of the DNA length. Otherwise, large nonfluorescent gold nanoparticles (AuNPs) are formed. Each poly-A DNA might template a few independent AuNCs. The blue emitters can be further reduced to form red emitters

by adding DMAB. The emission color is mainly determined by the type of reducing agent instead of DNA sequence.

Key words: nanoclusters, DNA, Good's buffer, fluorescence, gold

Introduction

Few-atom fluorescent gold and silver nanoclusters (Au and AgNCs) have shown promising applications in biosensor development, imaging, and catalysis.[1-8] At the same time, they are important for fundamental nanoscience. Nanoclusters are typically synthesized by reducing noble metal salts in the presence of a stabilizing agent, such as synthetic polymers,[9,10] proteins,[11] nucleic acids,[12-17] or small molecule ligands.[18-25] Amongst these stabilizers, DNA is very attractive due to its excellent programmability, stability and cost-effectiveness.[26-30] Taking advantage of the strong binding interaction between cytosine and Ag^+, a wide range of emission colors are obtained by using various cytosine-rich DNA sequences,[12-17,31,32] where $NaBH_4$ has been the exclusively used reducing agent.

One problem of AgNCs is low stability and photobleaching, where fluorescence is gradually lost and sometimes shifts to other wavelengths after exposing samples to light. Many research groups including our own showed that photobleaching of AgNCs is related to oxidation.[33-35] In this regard, AuNC might be a useful alternative since gold is more resistant to oxidation than silver. While adsorption of DNA by gold nanoparticles (AuNPs) have been extensively studied since the 1990s,[36-40] using DNA for making AuNCs has been reported only very recently. For example, we identified that low pH is needed for C_{30} (i.e. DNA with 30 cytosine bases) to produce blue fluorescence.[16] On the other hand, A_{30} produces fluorescence at neutral pH, where a 1:1 ratio between the number of adenine bases and gold is optimal. In both cases,

citrate was used as the reducing agent and as buffer to control pH. We also reported blue fluorescent AuNCs and complexes templated by (deoxy)adenosine, AMP and ATP using citrate as a reducing agent.[22] In all the citrate-reduced AuNCs, only blue emission was observed. Recently, red emitting AuNCs templated by a few DNA sequences were reported using dimethylamine borane (DMAB) as the reducing agent.[17,41] DMAB has stronger reducing power than citrate. If an even stronger reducing agent $NaBH_4$ is used, only large non-fluorescent AuNPs are obtained. It appears that the emission color of DNA stabilized AuNCs is strongly related to the type of reducing agent, while the DNA sequence plays a minor role. So far, only a few types of reducing agents have been tested; it is interesting to expand the range to achieve full understanding.

Emission color is related to the size of a NC, its oxidation state, as well as the ligand chemistry around it. Therefore, changing such conditions might induce a shift in the emission color. For example, DNA hairpin stabilized Ag_{11} (green emitter) and Ag_{13} (or Ag_{12}, red emitter) were coupled by a redox reaction.[33,34,42,43] A pH jump can also convert pepsin-stabilized AuNCs from green (Au_{13}) to blue emitters (Au_5 and Au_8).[44] An interesting question is whether such a conversion could be achieved with DNA stabilized AuNCs, given that two emission colors have already been reported. The control of emission color is also useful for biosensor development. Herein, we report that DNA-templated blue emitting AuNCs can be further reduced to red emitters. We have also identified Good's buffers to be useful reducing agents for promoting this conversion. The effect of DNA sequence, length, and pH has been systematically investigated.

Materials and Methods

Chemicals. All the DNA samples were purchased from Integrated DNA Technologies (Coralville, IA) and purified by standard desalting. $HAuCl_4$, dimethylamine borane (DMAB), glucose, ascorbate, $NaBH_4$, and NaH_2PO_4 were from Sigma-Aldrich. Hydrochloric acid was from VWR (Mississauga, ON). Trisodium citrate, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid and its sodium salt (HEPES), and 2-(*N*-morpholino)ethanesulfonic acid (MES) were from Mandel Scientific (Guelph, ON). Milli-Q water was used for all experiments.

AuNC preparation and characterization. In a typical synthesis, 8 µL of 500 mM pH 4 phosphate buffer (final concentration: 20 mM) and 10 µL of 100 mM HEPES buffer (final concentration: 5 mM) was added to 157 µL of water. To this mixture, 13 µL of 1 mM C_5 DNA (final concentration: 65 µM) was added quickly followed by 10 µL of 5 mM $HAuCl_4$ (final concentration: 250 µM). This mixture was allowed to incubate for 5 hrs resulting in the formation of the blue emitters. To make the red emitter, to 97.5 µL of blue emitter, 2.5 µL of freshly prepared 50 mM DMAB was added. The solution was allowed 4 h of incubation in the dark, resulting in the formation of red emitters. Reaction conditions and synthesis parameters were varied before these optimized values were obtained. For other reducing agents, most were used at 5 mM concentration, except for $NaBH_4$ (0.25 mM).

Fluorescence and UV-vis spectroscopy. To measure fluorescence spectrum, 100 µL of this sample was diluted with 500 µL water to obtain a total volume of 600 µL. The fluorescence was measured with an Eclipse fluorometer (Varian). The samples were also observed in ambient light, as well as a 245 nm UV lamp and pictures were taken using a digital camera (Canon PowerShot SD 1200 IS). UV-vis absorption spectra were obtained using an Agilent 8453A spectrometer.

Results and discussion

1. Switching of blue-to-red emission. In this study, we first used the C_5 DNA (i.e. DNA with 5 cytosine bases) as a stabilizer and DMAB as a reducing agent. $HAuCl_4$ was mixed with C_5 and various concentrations of DMAB in 20 mM phosphate buffer (pH 4). The samples were then imaged under UV light excitation and also under ambient day light (Figure 1A). To our surprise, with increasing DMAB concentration, the emission color gradually transitioned from bluish to red. Note that the first tube on the left did not contain any DMAB, where weak blue fluorescence was still observed. After careful control experiments, we found that a trace amount of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer was acting as the reducing agent. We dissolved our DNA stock solution in 5 mM HEPES (pH 7.6). Although the reaction buffer was phosphate, this small amount of HEPES was sufficient to reduce gold. The Good's buffers such as HEPES and MES were previously reported to reduce $HAuCl_4$ to form AuNPs.[45] It appears that they could also promote the growth of AuNCs in the presence of DNA.

Figure 1A shows that the optimal concentration of DMAB is ~1.2 mM; further increase of DMAB results in fluorescence quenching. All the samples appear red under ambient light, suggesting that a fraction of gold is reduced to AuNPs. The fluorescence spectra of these samples show two peaks at 470 nm and 660 nm (Figure 1C). There is an anti-correlation between these two peaks when the DMAB concentration is below 1.2 mM (Figure 1D). After that, both peaks decrease in the presence of higher DMAB concentrations. Therefore, the growth of the red peak is at the cost of the blue one. In other words, there might be a conversion of blue emitter to the red one (Figure 1B). By using 1.2 mM DMAB, the conversion of blue to red emitter takes ~8 h (Figure S1).

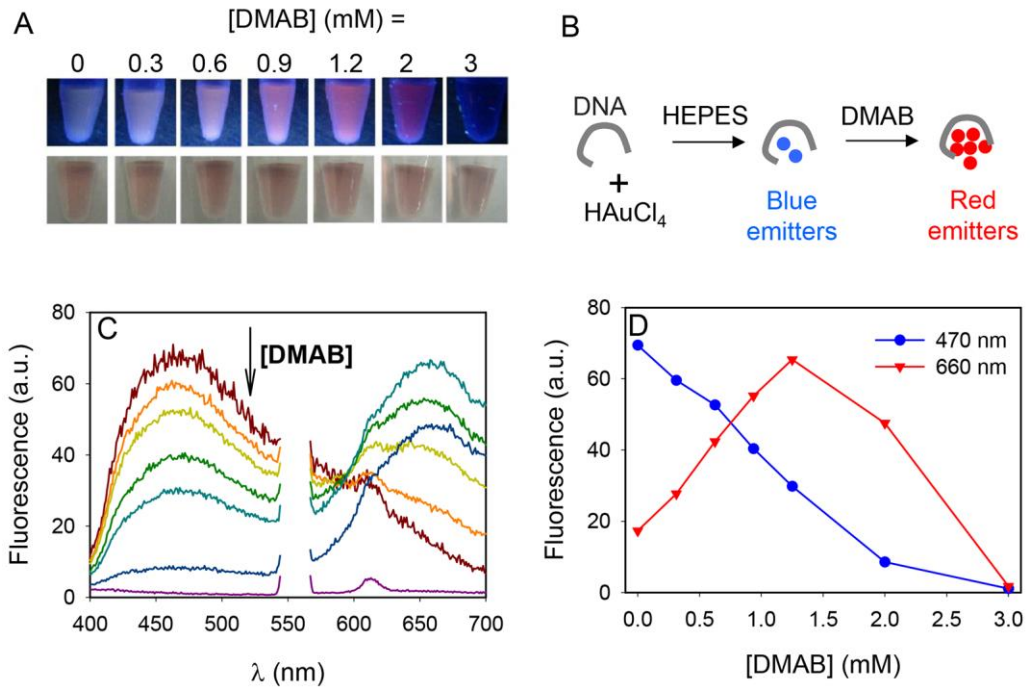

Figure 1. (A) Photograph in a dark room under UV excitation (upper row) and under ambient light (bottom row) for AuNCs prepared with increasing of DMAB concentrations. (B) Schematics of generating blue emitters followed by red emitters in the presence of different reducing agents. (C) Fluorescence spectra of the samples in (A) excited at 275 nm. The arrow head points to the direction of DMAB concentration increase. (D) Fluorescence peak intensity as a function of DMAB concentration.

2. Effect of reducing agent. The above experiment indicates that in addition to citrate and DMAB, HEPES is another reducing agent for preparing DNA-stabilized AuNCs. To have a more complete understanding, a few more common reducing agents were tested, where pH was maintained at 6 for all the experiments (Figure 2A). MES is another common Good's buffer to maintain pH at ~6.

We found that it can also act as an effective reducing agent for $HAuCl_4$, producing strong blue emission with A_5 DNA. C_5 produced only weak fluorescence due to the higher pH in this assay (*vide infra*). Ascorbate is a commonly used reducing agent and it produces fluorescence for all the DNA samples, including T_5 and G_5. We also performed a test with ascorbate alone without DNA, where weak fluorescence was still observed. Therefore, ascorbate itself can act as a stabilizer for AuNCs. Glucose appears to be a poor reducing agent for this purpose and barely any fluorescence was produced for all the tested DNA sequences. DMBA produced relatively strong red fluorescence only with C_5 DNA (note this sample did not contain any HEPES). $NaBH_4$ produced no fluorescence at all. Taken together, we only observed two types of emission colour: blue and red. The emission colour appears to be more related to the type of reducing agent than to the DNA sequence. Some DNA sequences (e.g. A, C rich) are more effective in stabilizing AuNCs than others (G, T rich).

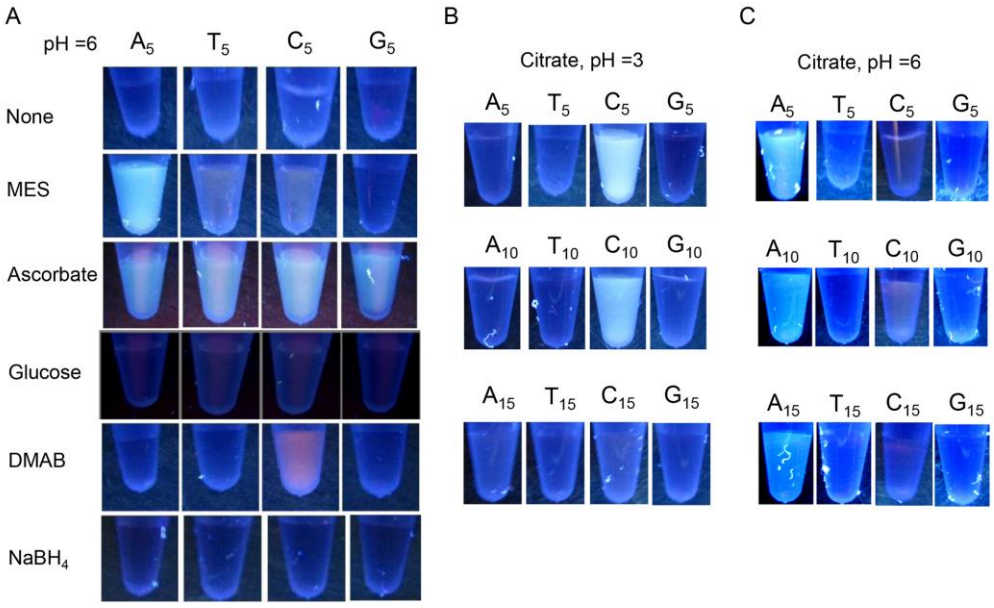

Figure 2. (A) Fluorescence photographs showing the effect of different reducing agents in preparing DNA stabilized AuNCs. Fluorescence photograph of samples prepared by mixing $HAuCl_4$ mixed with various DNA at pH 3 (B) or pH 6 (C) overnight using citrate as buffer and reducing agent. The ratio between $HAuCl_4$ and the bases is maintained at 1:1.

3. Effect of DNA length, sequence and pH. To further control the synthesis, we varied pH, DNA length and DNA sequence. For this study, we chose to use citrate as reducing agent since it is also a buffer in the pH range of the test. An interesting observation is that at pH 3, only the short poly-C DNAs produced fluorescence. In this experiment, we maintained the ratio between the cytosine base and $HAuCl_4$ to be 1:1. We previously showed that for C_{30} to produce fluorescent AuNCs, a large excess of the cytosine bases was required.[16] These experiments suggest that each poly-C DNA can only accommodate a few gold atoms to produce AuNCs. With a long chain and high gold concentration, it is more likely to form larger clusters and non-fluorescent AuNPs. Interestingly, it was recently reported that cytidine nucleoside can also template fluorescent AuNCs using citrate as a reducing agent.[24,25]

At pH 6, poly-C DNA produced relatively weak fluorescence. The pK_a of cytosine is 4.2 and therefore protonation of C is favorable for making fluorescent AuNCs. Metal binding to cytosine requires deprotonation of this site.[46] Therefore, protonation is a way to reduce the binding affinity; when the affinity between cytosine and metal is too strong, the fluorescent AuNC formation might be impeded. Interestingly, C-rich DNA is quite effective to produce fluorescent AgNCs at neutral pH,[13,33] suggesting the binding affinity between cytosine and silver is weaker than that with gold. Fluorescence was observed with poly-A for all the A lengths tested at pH 6. This may suggest that for a long chain of poly-A DNA, a few independent AuNCs may have formed. The formation of

adenosine stabilized AuNC network has been previously reported.[22] Therefore, it is not surprising that poly-A can achieve a similar AuNC environment.

So far we only obtained blue emission and the emission peak is around 470 nm. We determined the quantum yield of the AuNCs templated by the C_5 DNA to be ~1%. Other DNA should produce AuNCs with even lower quantum yield. Guanine-rich sequences are also effective in preparing fluorescent AgNCs.[31] However, we did not observed any fluorescent AuNCs with all the tested poly-G DNA.

4. Seeded reduction. By now, we have studied a number of factors that may affect the fluorescence property of AuNCs, and only two emission colors were observed. The conversion of these two color can also take place for the sample prepared with the C_5 DNA and HEPES (Figure 1). In the rest of the paper, we aim to further understand this change of emission color. The experiment in Figure 1 was performed by mixing all the reagents quickly. To control this blue-to-red transition, we carried out the reaction in two steps. We first varied the DNA concentration and used 5 mM HEPES as reducing agent (Figure 3A). The blue fluorescence increased with increasing DNA concentration until ~100 μM DNA was reached. It is interesting to note that the amount of AuNPs (e.g. red color in the bottom row) decreased with increasing DNA concentration, suggesting more gold species were converted into fluorescent AuNCs. DMAB was then added to each tube and red fluorescence was observed for most of the samples with DNA concentration higher than 25 μM, where ~65 μM DNA produced the strongest red fluorescence (see Figure S2 for fluorescence spectra). This experiment directly confirms that the red emitters can be converted from the blue emitters. The same DNA can stabilize both emitters, and the reducing agent is the determining factor for the emission color.

Next we varied the HEPES concentration from 0 to 50 mM by fixing DNA at 65 μM (Figure 3B). Bright blue fluorescence was produced with 2-5 mM HEPES. Even higher concentration of HEPES produced weaker greenish emission. The fluorescence spectra of these samples are shown in Figure 3E, where the initial blue peak at 470 nm shifts to ~520 nm with 50 mM HEPES (see Figure S2 for spectra). After forming blue-emitters, we then added DMAB. Red emitters were produced for most of the samples and their fluorescence spectra are shown in Figure 3F. The strongest red emission was produced with 5 mM HEPES.

Since using HEPES as the reducing agent for making AuNCs was discovered accidently, we next tested other reducing agents. Interestingly, similar blue-to-red transition was also observed with MES (Figure 3C). On the other hand, while citrate generated bright blue fluorescence (Figure 3D), little red emitters were produced. It seems that Good's buffers are more effective to produce emitters that can be further converted. To further understand this difference, we compared their rate for reducing $HAuCl_4$ in the absence of DNA to generate AuNPs at room temperature, where both HEPES and MES showed faster reduction than citrate (Figure S3). Therefore, Good's buffers are able to reduce $HAuCl_4$ to a state that is readily further reduced by DMAB to produce the red emitters. While the red emitters can form directly or from the seeded reduction, the latter method has higher fluorescence yield.

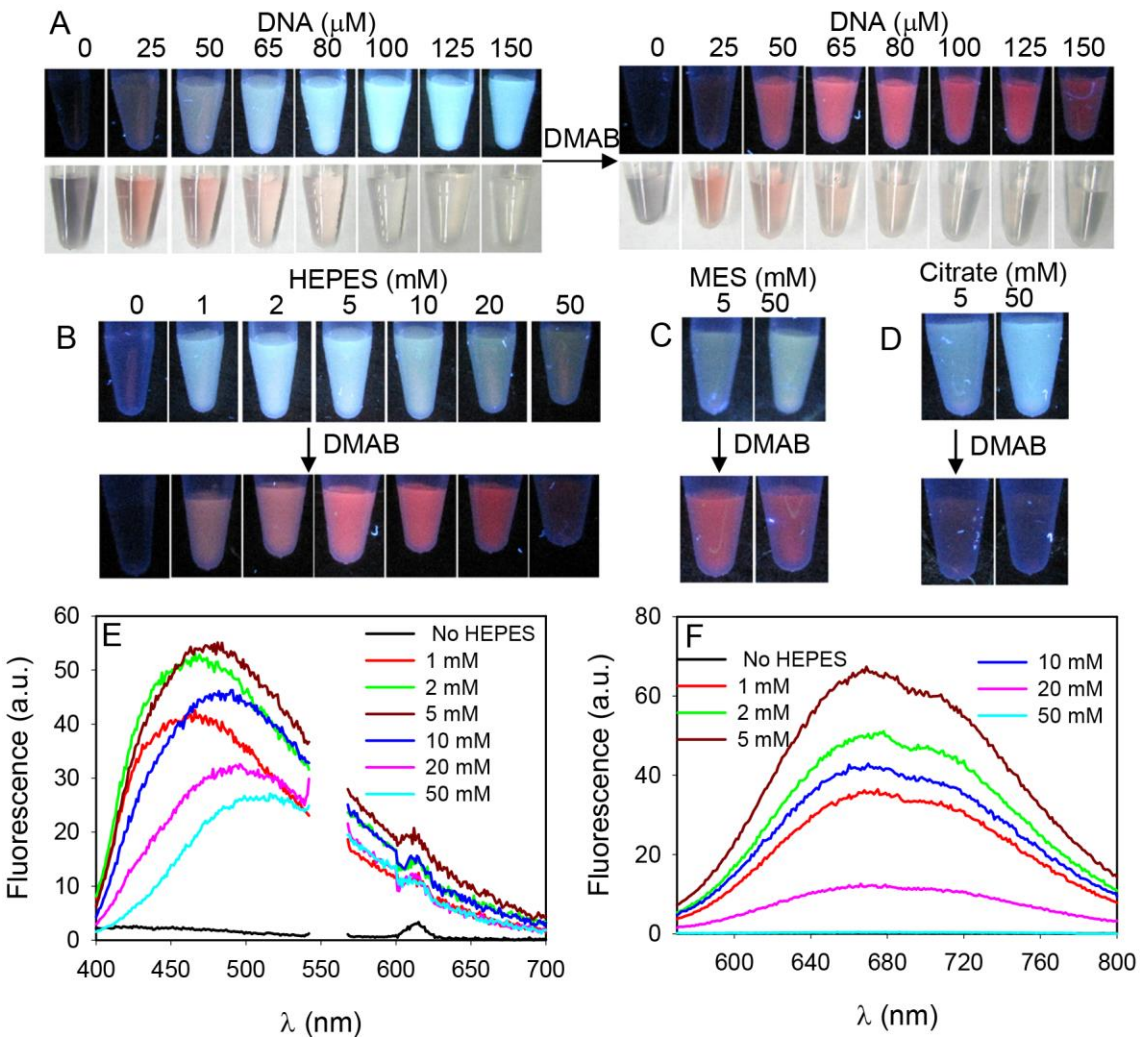

Figure 3. (A) Photograph of fluorescence under UV excitation and under ambient light of samples prepared with various concentrations of the C_5 DNA. The HEPES was fixed at 5 mM. The initial $HAuCl_4$ concentration was 250 μM. Photographs of samples prepared with various concentrations of (B) HEPES, (C) MES and (D) citrate before and after adding DMAB. Fluorescence emission spectra of the samples in (B) before DMAB addition (E) and after DMAB addition (F).

Since the red emitters showed red color, we measured its UV-vis absorption spectrum (black trace, Figure 4A) and the characteristic plasmon peak at ~520 nm was indeed observed. After

centrifugation, the supernatant became clear while maintained the strong red fluorescence (Figure 4C), suggesting that the fluorescent species is not associated with large AuNPs in the pellet. The supernatant UV-vis spectrum (red trace) is quite complex, showing peaks at 330, 447, 548, 697 and 780 nm. Such complex absorption spectrum might be an indication of a mixture of various AuNC species. In general, larger AuNCs should have longer absorption wavelengths.[47,48] Kumar and Jin studied the electronic transition of Au_{25} NCs in various environment and the same spectrum was observed under all the tested conditions,[49] suggesting that the electronic transition within AuNCs is quite insensitive to the environmental changes. Therefore, it is likely that our sample contains a mixture of different AuNCs. By exciting the AuNCs at various wavelengths, we observed three different emission peaks at 644, 764 and 820 nm (Figure 4B). The excitation spectra at each of these wavelengths were also collected (Figure 4C), where the two near IR emission peaks (764 and 820 nm) can only be effectively excited at the longest excitation wavelengths (Stokes shift = 43 nm and 51 nm, respectively, similar to typical molecular fluorophores). The 560 nm excitation can excite both the 644 and the 764 peak while all the shorter excitation wavelengths only excite the 644 nm peak, showing much longer Stokes shifts. The positions of the excitation peaks agree very well with the UV-vis spectra. The quantum yield of the red emitter is calculated to be ~3% using rhodamine-B as the standard.

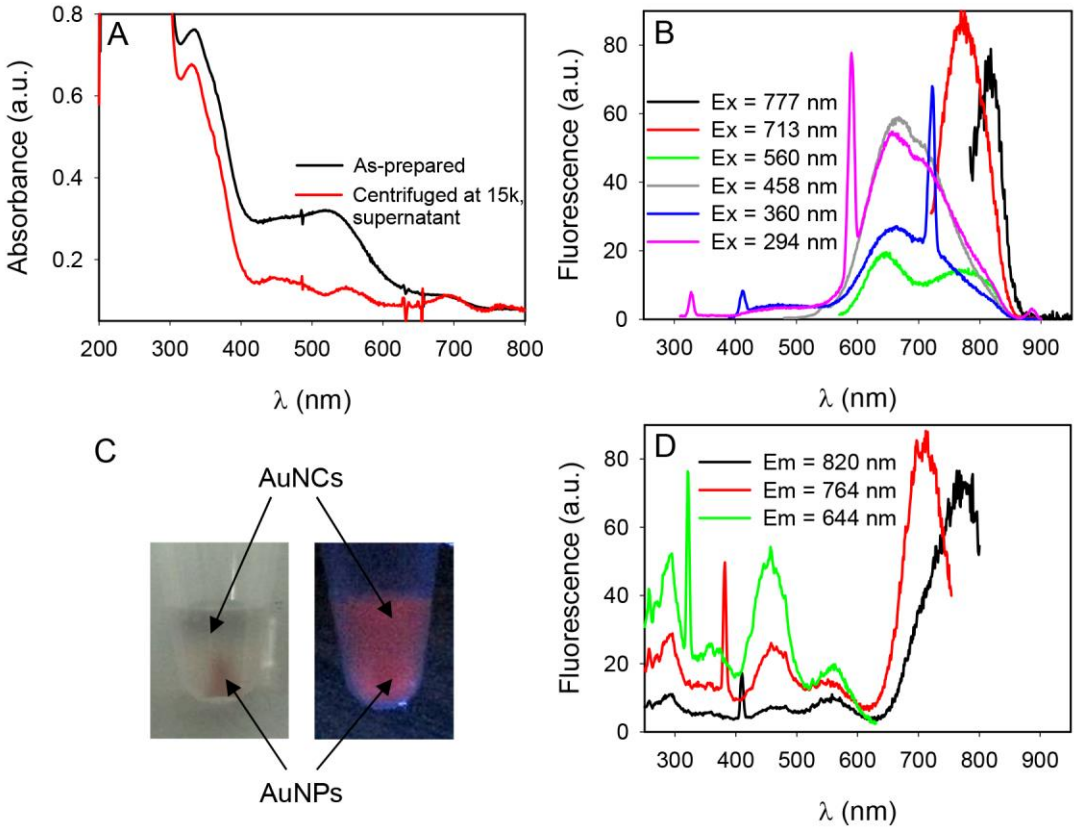

Figure 4. (A) UV-vis spectrum of as-prepared red emitters and after centrifugation to remove large AuNPs. (B) Fluorescence emission spectra of the red emitters by exciting at different wavelengths. (D) Fluorescence excitation spectra of the red emitters by monitoring several emission wavelengths. (C) Photograph of samples after centrifugation showing precipitation of AuNPs. The red emitters are still in the supernatant as judged from the fluorescence photograph (the right panel).

Conclusions

In summary, we have systematically investigated the effect of various reducing agents on the production of fluorescent AuNCs templated by DNA. The emission color is mainly controlled by

the degree of metal reduction while the DNA sequence plays only a minor role. We also reported that DNA templated red emitting AuNCs can be obtained from the blue emitting seeds stabilized by the same DNA. While many mild reducing agents can produce blue emitters, the production of red emitters requires a strong DMAB reducing agent. On the other hand, if very strong $NaBH_4$ is used, no fluorescent emitters are produced (data not shown). The Good's buffers turned out to be an excellent reducing agent for preparing blue emitters and such emitters can be converted to red ones. This study provides a basis for understanding and controlling DNA stabilized AuNCs that might be used for biosensor development and imaging.

Supplementary material

Supplementary material is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/. Supporting information: additional fluorescence spectroscopic characterization, rate of $HAuCl_4$ reduction to form nanoparticles, and quantum yield determination.

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