Supporting Information

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A General Strategy Toward pH-Controlled Aggregation-Dispersion of Gold Nanoparticles as Well as Single-Walled Carbon Nanotubes
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Experimental

*Synthesis of negatively charged AuNPs: 6 nm (from TEM analysis) AuNPs were synthesized by the citrate-tannic acid method following the published standard procedures. To increase the stability of the as-synthesized gold nanoparticles, bis (p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (Strem chemicals, Newburyport, MA) was added to the gold nanoparticle solution (2 mg / 10 mL), and the mixture was shaken overnight, and the resulting gold nanoparticles would be negatively charged. Solid sodium chloride was then added to the above solution until the solution became blue colored. The solution was then centrifuged and the precipitated gold nanoparticles were collected and dispersed in doubly distilled water (ddH2O).

Preparation of DNA-wrapped SWNTs: To 100 μL of aqueous solution containing about 0.1 mg single walled carbon nanotubes (Sigma Chemicals) and 0.1 M NaCl was added 0.025 mg d(GT)20 DNA (Custom-synthesized by Shanghai Sangon Biological Engineering Technology and Services Co., Ltd., China). This solution was then sonicated for 1.5 hours using a UH-100A probe-type sonicator (Tianjin AutoScience Instrument Co., Ltd, China) operated at 4 W in an ice-water bath. The DNA-wrapped SWNTs were also negatively charged (see Figure S6 for an electrophoretogram of this DNA-SWNT sample).

pH switching solution: The solution used for pH adjustment contains 0.4 mM Tris, 0.02 mM EDTA and 0.5~2.0 mM ethylenediamine. Acetic acid was added to the above solution until a pH of 8.6 was reached. Periodical pH switchings between 5.0 and 8.6 could then be done by careful additions of HCl and NaOH (in equal-mole amount) alternatively.

Dynamic light scattering (DLS) measurement: gold nanoparticles were added to ethylenediamine solutions pre-adjusted with hydrochloric acid to get different pHs varying from 5.0 to 9.0. After a waiting time of 5 minutes, 12 μL of each sample solution was added to a DLS microcell and light scattering data were collected with a DynaPro-MS800 instrument (Protein Solutions, Lakewood, NJ, USA). The waiting time of 5 minutes was used to ensure the aggregations to reach a relatively stable phase, which could facilitate the relatively time-consuming (several minutes, typically) DLS measurements. In order to make comparisons with the DLS data, corresponding absorbance spectra of a similar set of samples were collected after 5-minute waiting times. Note that in other optical absorbance measurements no such waiting time were purposely employed since the measurements were fast.

TEM sample preparation and imaging: Typically, 5~10 μl gold nanoparticle solution was spotted onto a carbon-coated copper grid (200 mesh). The liquid drop was then allowed to stay on the carbon film for 5~10 minutes (a humidity chamber might be needed if the air is too dry) before it was removed with a small piece of thick folded paper towel. Samples were further air-dried and placed in a TEM storage box. TEM imaging was performed with a JEOL-2010 transmission electron microscope equipped with a 1024x1024 CCD camera.

Figure S1. Calculated concentration profiles for different protonated forms of ethylenediamine molecules as a function of solution pH. EN denotes ethylenediamine, and EN.H+ and EN.H22+ are singly and doubly protonated forms of ethylenediamine, respectively.

Equations used to calculate the pH-dependent concentrations of different ionization states of ethylenediamine in solution:

(1) $\text{EN} + \text{H}^+ \rightarrow \text{EN.H}^+$ \hspace{1cm} ($\lg K_1 = 9.92$)$^S4$
(2) $\text{EN.H}^+ + \text{H}^+ \rightarrow \text{EN.H}_2^{2+}$ \hspace{1cm} ($\lg K_2 = 6.85$)$^S4$
(3) $[\text{EN}] + [\text{EN.H}^+] + [\text{EN.H}_2^{2+}] = C$

Combine (1) – (3), it is easy to obtain:

(4) $[\text{EN}] = \frac{C}{1 + K_1[H^+](1 + K_2[H^+])}$
(5) $[\text{EN.H}^+] = K_1[H^+][\text{EN}]$
(6) $[\text{EN.H}_2^{2+}] = K_2[H^+][\text{EN.H}^+]$

where “$C$” can be simply assigned a value “1” since we only need to get the percentages. These three equations (4)-(6) can be used to calculate the concentration profiles for different ionization species of ethylenediamine in solution.

Figure S2. SPR absorbance peak positions (a) and hydrodynamic radii ($R_H$) obtained from DLS measurements (b) are plotted against solution pH. The $R_H$ at pH 7.0 has two major distributions (open squares), one is centered at 16.0 nm (mass ratio: 74.4%) and the other one is centered at 97.3 nm (mass ratio: 25.6%). An average value (36.8 nm based on the mass ratios) for $R_H$ at pH 7.0 based on the mass distribution ratios was used for the plotting. All the measurements were made after a waiting time of 5 min to ensure the system had reached a relatively stable phase. To be consistent with the DLS measurements, absorbance data were also collected in 5 minutes after the solutions were prepared. It can be seen that the peak wavelength at pH 5.0 has a red shift of about 10 nm compared to other measurements without the 5-minute waiting time.
Figure S3. Control experiments conducted in the absence of ethylenediamine. As shown are absorbance curves for a 6 nm gold nanoparticle solution before and after the cycling experiment as in Figure 2 at pH 5.0 and 8.6 respectively. It can be seen that adjusting pH between 5.0 and 8.6 has very minor influence on the absorbance of 6 nm gold nanoparticle solution. Based on many experiments we have performed, the observable slight differences for the absorbance curves in the same cycle are mostly due to measurement instabilities as well as the dilution effect, not the pH.
Figure S4. Two TEM images showing the coexistence of some smaller gold nanoparticle aggregates in the same sample as that in Figure 4c. Scale bars in (a) and (b) are 220nm and 40 nm, respectively.
Figure S5. Absorbance curves for 6 nm gold nanoparticle solution before and after the cycling experiment as in Figure 2 at pH 5.0 and 8.6 respectively. Inset shows the gold nanoparticles in a pH 8.6 buffer in the absence of ethylenediamine (left tube), pH 5.0 buffer in the presence of 1.5 mM ethylenediamine (middle tube), and the same solution as in the middle tube with the pH adjusted from 5.0 to 8.6 (right tube, in contrast to the middle tube).
Figure S6. Optical absorbance shows that gold nanoparticles gradually get aggregated due to the addition of more NaCl to the solution (as compared to Figure 5 in the main text of this paper). Ethylenediamine has a fixed concentration of 1.5 mM for all curves shown in this figure.
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**Figure S7.** The upper picture shows that the gold nanoparticle solution changes color from red (left tube) to blue (middle tube) after adding 1.5 mM ethylenediamine and adjusting its pH to 5.0, further addition of 0.1 M NaCl makes it change back to red again (right tube). Note that the color of the right tube solution in the upper picture looks slightly different from the left tube, but reducing ethylenediamine concentration to 0.5 mM can assure a complete color recovery, which is shown the lower picture.
Figure S8. 1% agarose gel electrophoresis of DNA wrapped carbon nanotubes showing that the nanotubes are negatively charged since they move in the gel toward the positive electrode.