Factors that Affect the Synthesis of Gold Nanorods

Alice MacQueen

Biology and Biochemistry, University of Virginia

NNIN REU Site: Microelectronics Research Center, The University of Texas at Austin
NNIN REU Principal Investigator: Brian A. Korgel, Chemical Engineering, The University of Texas at Austin
NNIN REU Mentor: Danielle K. Smith, Chemical Engineering, The University of Texas at Austin
Contact: alicem@virginia.edu, korgel@che.utexas.edu, dsmith@che.utexas.edu

Introduction

Gold nanorods have two plasmon resonance peaks in their absorbance spectra: a higher-energy peak related to their diameter and a lower-energy peak associated with their length. Typically, the low energy peak occurs at ~ 750 nm. Nanorods with an optical signal within the 700-1000 nm range are interesting for medical imaging of tissue at cellular resolutions. This range corresponds to an "optical window" where light absorption is minimal, thus allowing deeper tissue penetration. For example, we have previously explored the use of near-infrared two-photon luminescence (TPL) for epithelial pre-cancer cell detection [1]. Lengthening the nanorods shifts the lower-energy plasmon to longer wavelengths, improving the optical penetration depth.

In this project, we focused on synthesizing gold (Au) nanorods with longitudinal plasmon peaks around 900 nm. We prepared colloidal Au nanorods using a seed-mediated approach and studied the effect of the additives hydrochloric acid (HCl) and sodium sulfide (Na_2S) [2]. Then, we measured absorbance spectra of the Au nanorods, and quantified the nanorod aspect ratios using transmission electron microscopy. Longitudinal plasmon resonances were red-shifted to wavelengths as long as 994 nm by adding both Na_2S and HCl.

Experimental Procedure

Gold nanorods were synthesized in aqueous solutions using a seed-mediated approach. Au seeds were first prepared by adding sodium borohydride (0.01 M, 600 μL) to a preparation of cetyltrimethylammonium bromide (CTAB, 0.1 M, 9.75 mL) and hydrogen tetrachloroaurate (0.01 M, 250 μL), and stirring for two minutes. Next, 12 μL of this gold seed solution was injected into a growth solution containing CTAB (0.1 M, 9.5 mL), silver nitrate (0.01 M, 75 μL), Au tetrachloroaurate (0.01 M, 500 μL), and ascorbic acid (0.1 M, 55 μL). Additional compounds were combined with this "typical" growth solution to adjust the wavelength of the longitudinal plasmon peak.

In the first experiment, hydrochloric acid (0.1 M, varying amounts between 50 and 2000 μL) was added just before injecting the seed solution. The second experiment involved adding sodium sulfide (Na_2S, 0.1 M), which quenches the growth solution [2]. Na_2S was added in two molar ratios of sulfur (S) to metal (M, both Au and Ag) at different times following seed injection (both 15 and 30 minutes afterwards, in a 2:1 and 4:1 S:M ratio). In the third experiment, both hydrochloric acid (0.1 M, amounts between 50 and 1000 μL) and Na_2S (0.1 M, 4:1 S:M ratio at 30 minutes) were added to the growth solution.

The Au nanorods were purified by two cycles of centrifugation at 8500 rpm for 10 minutes, followed by suspension in deionized water. Nanorods were characterized using UV-Vis spectroscopy and transmission electron microscopy.

Results

Experiment 1. Adding up to 500 μL of HCl shifted the lower-energy plasmon resonance peak out to a maximum of ~ 800 nm.

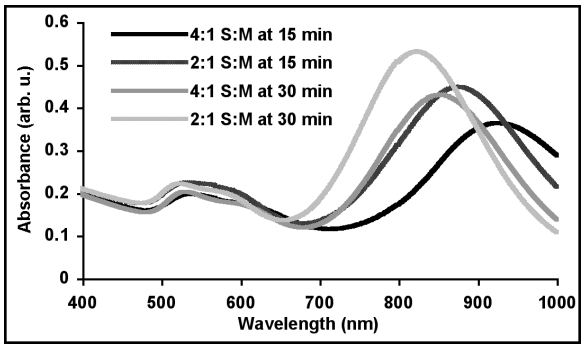

Figure 1: Addition of sodium sulfide to the growth solution.

Larger HCl additions seemed to poison the growth solution, blue-shifting the low-energy peak back toward the wavelength of the control (Figures 1 and 4B). Adding more HCl also lowered the yield of rods, as evidenced by the decreased absorbance ratio between the low- and high-energy peaks. A higher transverse peak, relative to the longitudinal plasmon peak, precluded formation of a higher population of spheres (gold particles without a longitudinal dimension).

Experiment 2. Injecting Na_2S at a larger S:M ratio and shorter time into growth shifted the longitudinal plasmon farther to the red (Figure 2). Changing the time of addition had a greater effect on nanorod length than varying S:M. Also, nanorod yield decreased while red-shifting the longitudinal plasmon.

Experiment 3. Adding Na_2S and up to 100 μL of HCl red-shifted the maximum wavelength of the second plasmon peak to 994 nm. Additional HCl lowered the rod yield and blue-shifted the longitudinal peak away from the 994 nm maximum. As shown in

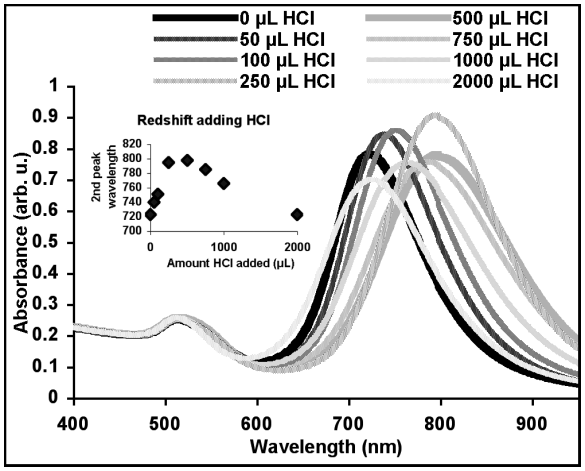

Figure 2: Addition of hydrochloric acid to the growth solution.

Figure 3, adding both Na_2S and HCl during rod growth lowered the longitudinal peak height; thus, rod yield was compromised by including these additives. However, Figure 4C exhibits nanorod samples with an absorbance peak positioned near the lower energy boundary of the "optical window" for cellular imaging, making them interesting agents for TPL imaging.

Conclusions

Longitudinal plasmon resonances were red-shifted as far as 994 nm with the addition of 100 μL 0.1M HCl followed by Na_2S in a 4:1 S:M ratio 30 minutes after the growth reaction was seeded. Adding Na_2S alone could not mimic this result; rods obtained with only Na_2S had a longitudinal peak red-shifted to 925 nm, and were obtained in much poorer yield. Adding HCl alone resulted in nanorods with a longitudinal peak having a maximum red-shift of 800 nm. Larger HCl additions blue-shifted this peak wavelength away from this maximum. Rods with the most potential for TPL imaging were obtained by adding 50 μL 0.1M HCl and. Na_2S at a 4:1 S:M ratio at 30 min, and had a longitudinal peak at 915 nm.

Future Work

Future work could involve increasing the monodispersity of the gold nanorod lengths in these altered procedures, as indicated by the breadth of the longitudinal plasmon peak. The yield of rods could also be increased by more delicately tuning the ratio of sodium sulfide or the time at which it is added.

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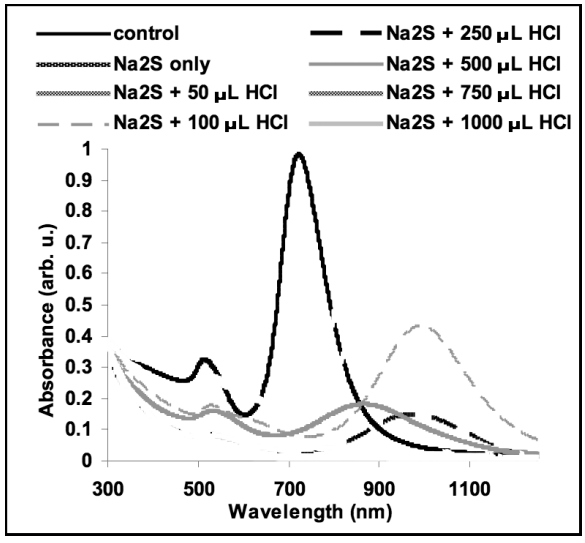

Figure 3: Addition of both HCl and Na_2S to the growth solution.

Figure 4, right: TEMs of gold nanorods synthesized in the presence of various additives with the most red-shifted second plasmon peak.