Photoacoustic Gold Nanorods: Synthesis and Characterization

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Introduction

- **Photoacoustic effect**: (1) nanosecond laser pulse absorbed by material (2) rapid heating and thermal expansion (3) generation of pressure that propagates as ultrasound wave (4) contraction back to original state.

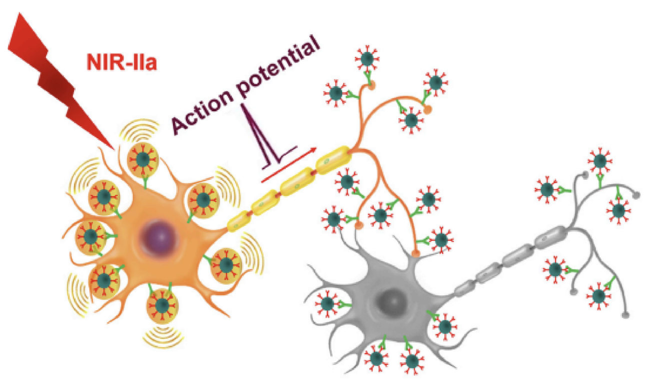


***Figure 1:** Ultrasound can stimulate neurons by activating ion channels in the cell membrane.*

- **Key Application**: PA effect can treat blindness by stimulating remaining healthy retinal cells.
- **Gold nanorods (GNRs)** are particularly effective photoacoustic materials:
  - Biocompatibility, which can be enhanced through functionalization
  - **Non-invasive delivery through eyedrops**
  - **Tunable peak light absorption (LSPR)**

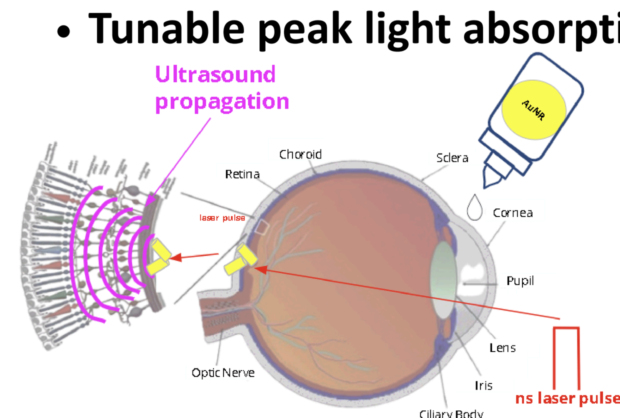


***Figure 2:** Eyedrop GNRs for PA stimulation. GNR length bet. 50-100 nm allows for eye penetration.*

- **Aspect ratio** (length / diameter) of roughly 6 corresponds to a wavelength of 1030 nm. This wavelength provides limited interference with residual vision and low H_2O light absorption.

Methods

Volumes and concentrations of **HCl, $AgNO_3$, CTAB, and seed solution** were varied to tune GNR absorption peak, aspect ratio, and size.

Seed solution: contains cubic octahedral Au^0 particles that later serve as Au deposition sites

- At 30°C: CTAB (forms micelles with chloroaurate)→ $HAuCl_4$ (introduces gold as Au^{3+})→ $NaBH_4$ (rapidly reduces gold to Au^0)

Growth solution: the environment for nanorods to grow by depositing gold on seeds

- At 50°C: Dissolve CTAB (forms bilayers over nanorods later) and NaOL (surfactant and reduces Au^{3+} to Au^+)
- At 30°C: add **$AgNO_3$ (selectively binds to {250} facets)** → $HAuCl_4$ → **HCl (dec. ascorbic acid reducing power)** → AA (reduces Au^+ to Au^0) → Seed solution → Grow for 12 hrs

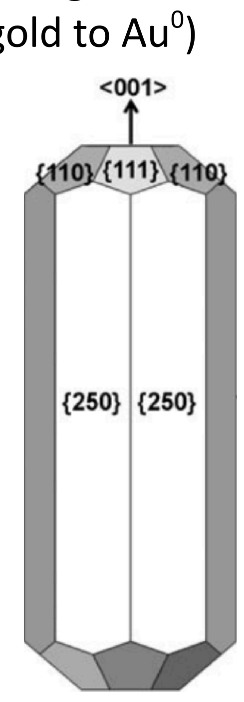


***Figure 3:** Facets of GNRs*

PA Characterization

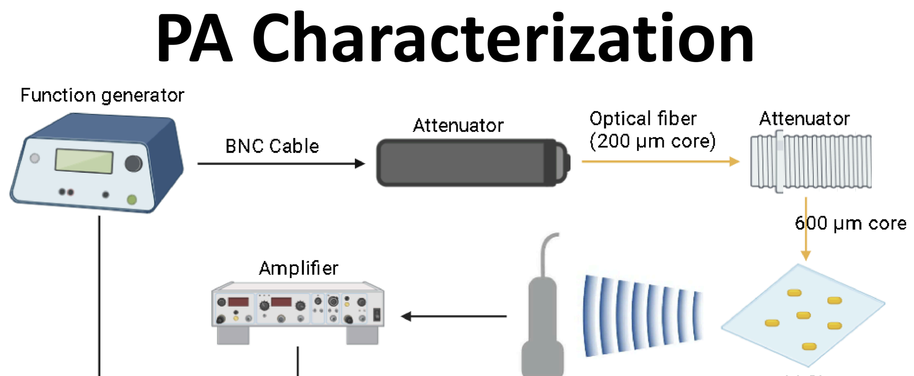


***Figure 4:** Schematic of photoacoustic setup; parameters include 10 kHz frequency, 40% duty cycle, 5 V amplitude, 3 ns square wave, 40 dB amplifier; attenuator lengths were varied to control power*

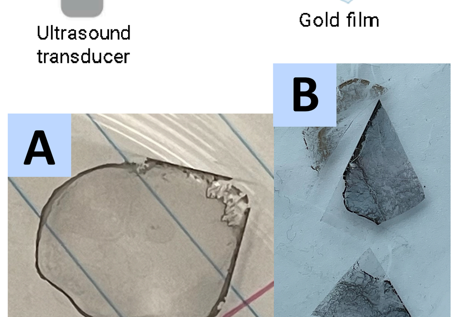


***Figure 5:** Films created by drop-casting after centrifuging growth solution; (A) T10 film 1 (B) T6 ultra-concentrated*

Results

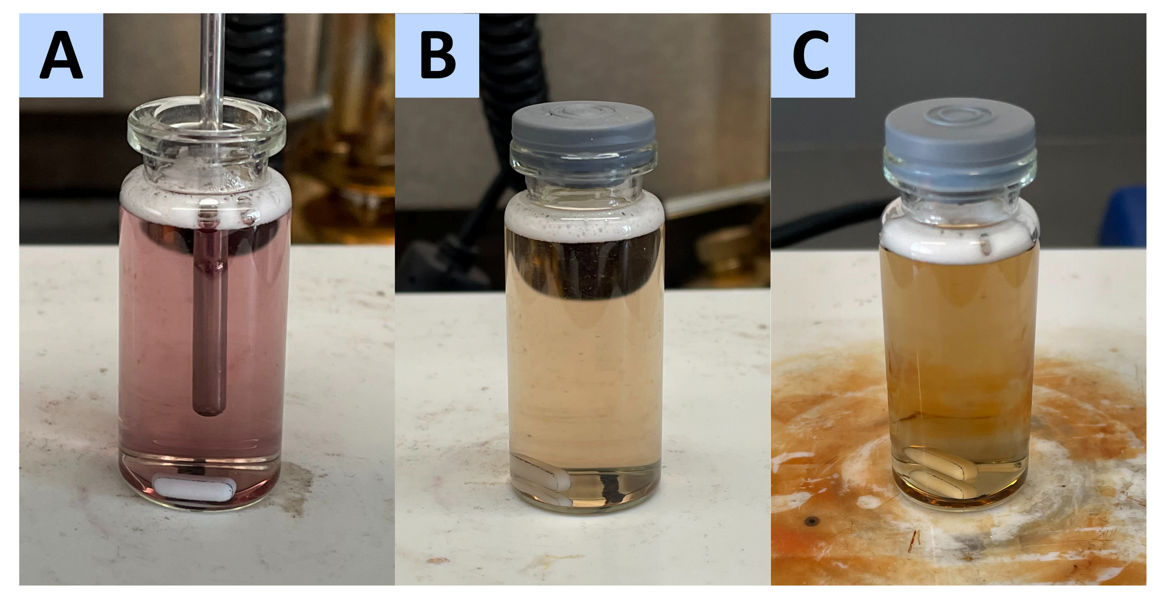


***Figure 6:** (A) Light pink seed solution indicates NP aggregation (B) Light gold color indicates incomplete Au^{3+} reduction (C) Light brown / deeper gold indicates high-quality seed*

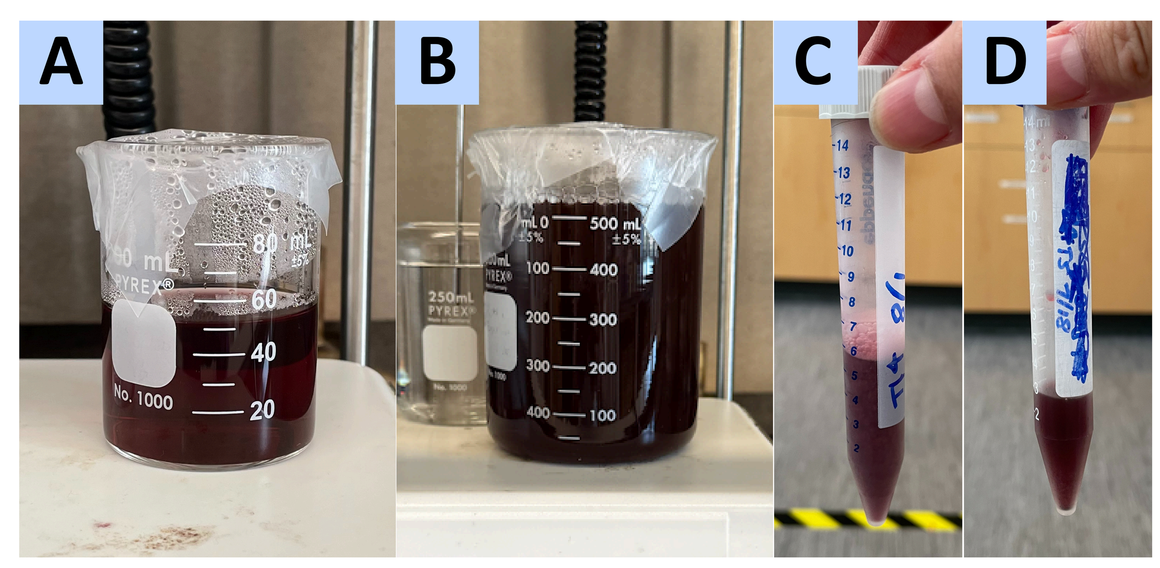


***Figure 7:** (A) Trial 14 ~18 hrs after injection of seed; red solution color generally indicates spherical impurities (B) T7 – high quality growth, dark purple hue (C) 1x centrifuged growth solution (D) 3x centrifuged growth*

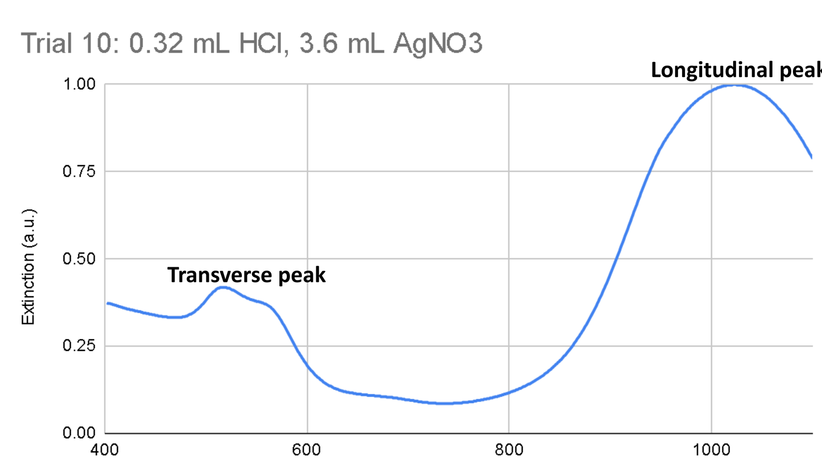


***Figure 8:** High-quality synthesis with absorption peak at ~1020 nm; FW at HM of ~250 nm and transverse absorption of ~0.4*

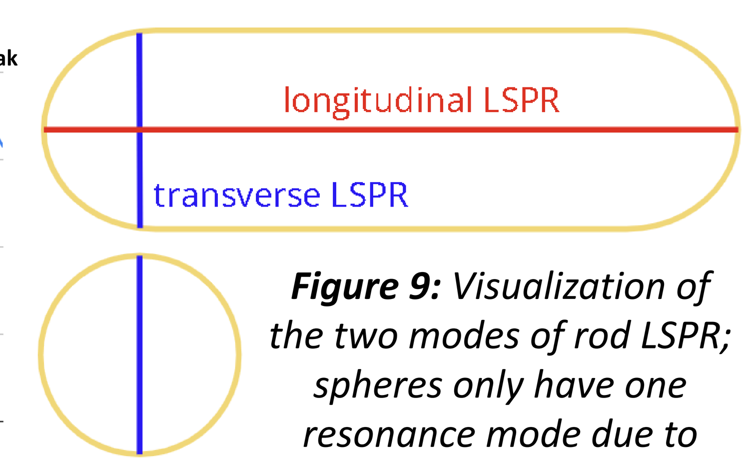


***Figure 9:** Visualization of the two modes of rod LSPR; spheres only have one resonance mode due to their symmetry*

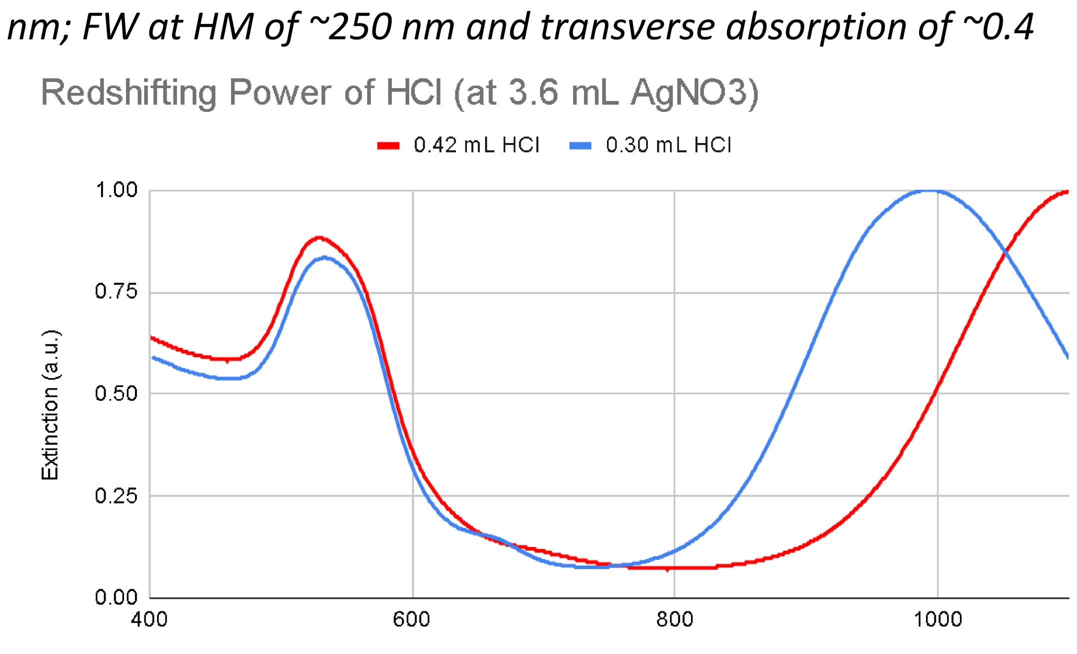
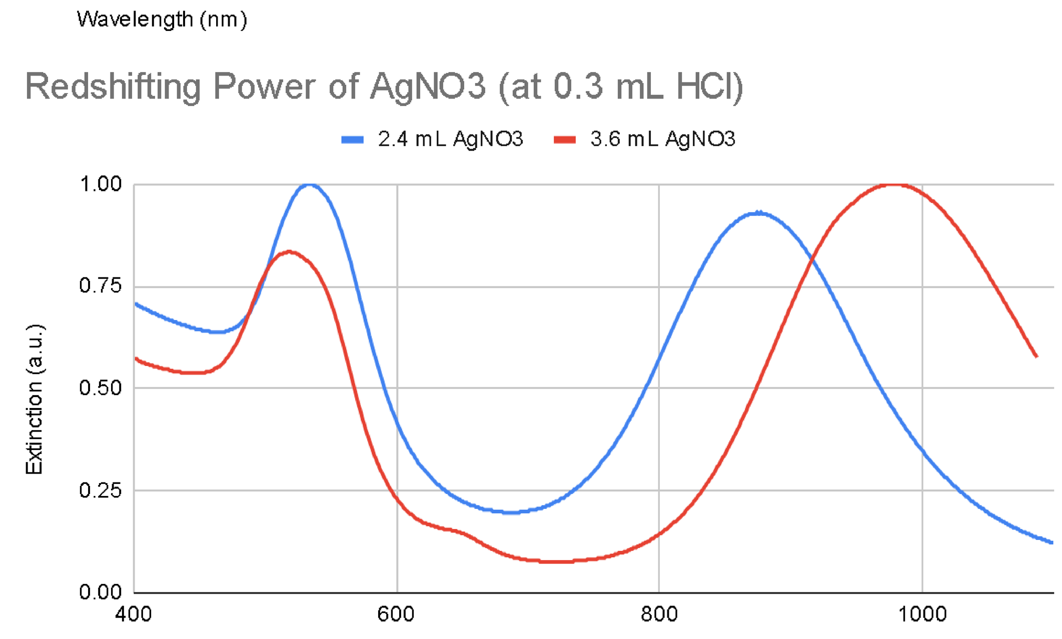


***Figure 10:** Increasing HCl redshifts the peak absorption by providing kinetic control; similar relationships were found between T12 vs. T13 and T3 vs. T14*

***Figure 11:** AgNO3 redshifts the peak by providing kinetic and thermodynamic control; a similar pattern was exhibited between T8 vs. T12; the difference between 0.3 vs. 0.32 mL HCl was insignificant*



Photoacoustic Data

Figure 12

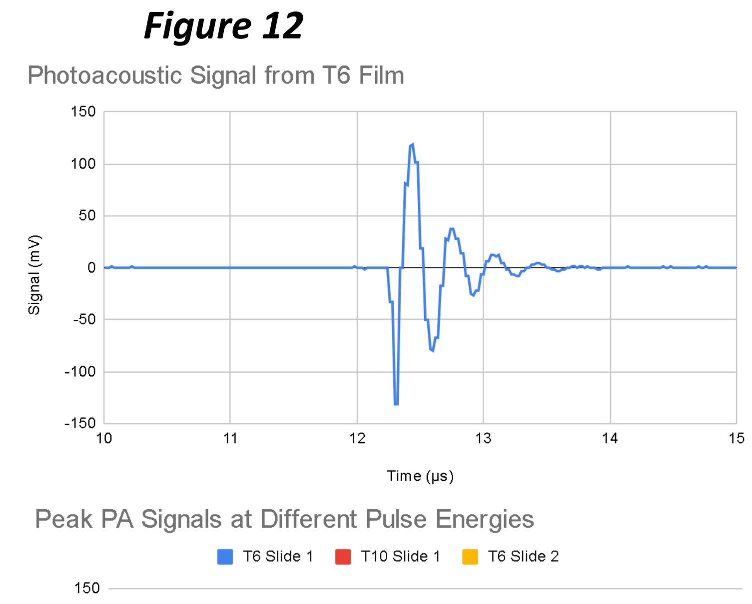
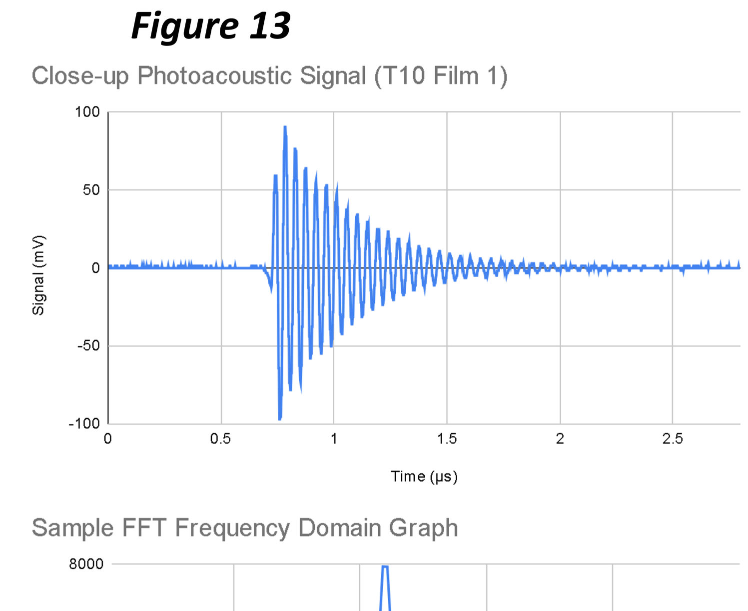


Figure 13



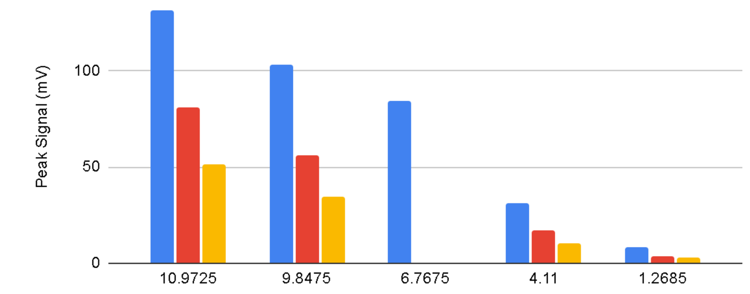


***Figure 14:** 1.4 mm attenuator unavailable for 2 trials*

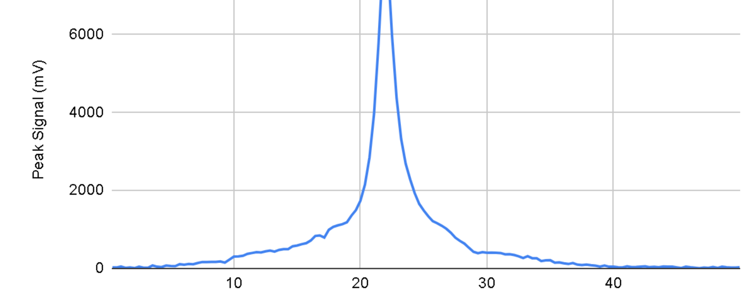


***Figure 15:** Taken from T10 film; all signals had similar frequency graphs*

Discussion

Synthesis

- Gold nanorods with peak absorptions very close to 1030 nm were synthesized under multiple conditions (0.3 mL and 0.32 mL HCl w/ 3.6 mL AgNO3, 0.39 mL HCl w/ 2.4 mL AgNO3)
- Peak transverse absorbance was ~1/3-1/2 of longitudinal absorbance: low concentration of spherical impurities
- Full width at half maximum was ~150-250 nm: nanorods were monodisperse
- Seed quality was not perfectly indicative of final GNR product quality
- $AgNO_3$ mechanism of action was supported: blocked gold deposition by forming Ag complex to passivate the sides of the rods, causing longer A.R.
- HCl candidate mechanism: lower pH → lower AA reducing power → slower Au^0 formation → more time for Au to diffuse to rod tips → longer A.R.

PA Characterization

- Photoacoustic performance was highly dependent on film quality
  - Coffee ring film shape: indicates rapid drying or low concentration of nanorods in purified solution
- Gold may have began dispersing in water bath, decreasing signal strength over time
- All gold trials displayed dominant frequency of ~22 MHz, close to the attenuator's natural freq. of ~25 MHz
- Attenuator length is inversely correlated to power, and lower power is directly correlated to a smaller signal

Future Research

- Functionalization to reduce CTAB cytotoxicity (citrate stabilization, PEGylation)
- Use of more consistent methods for thin-film creation (spin coating)
- PA testing on colloidal suspensions of gold nanorods
- In vitro PA testing on retinal cells

References

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