Supporting Information

Gold Nanorods Encapsulated Bubbles

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Experimental Section

Materials. All chemicals (≥ 99%) were used as received, unless otherwise specified. Hexadecyltrimethylammonium bromide (CTAB) was purchased from Sigma Aldrich. Tetrachloroauric (III) acid ($HAuCl_4.xH_2O$) and silver nitrate ($AgNO_3$) were purchased from Alfa Aesar. Sodium borohyride granular ($NaBH_4$) and L-ascorbic acid were obtained from Aldrich and Fluka, respectively. Silicon (p-type; 100, Silicon Inc.) was used as received. DI water (18.2 $M\Omega cm^{-1}$) treated through reverse osmosis (Thermo Scientific) was used for preparing all solutions.

Synthesis of Nanobubbles. A well-defined method described by Smith et al. for synthesis of gold nanorods (GNRs) via seed mediated growth was adapted.[1] All reactions were carried out at room temperature (≈25ºC). The seed solution was first prepared under nitrogen (N_2) or argon (Ar) gas flow with varying rates by adding fresh ice-cold sodium borohydride solution (0.01 M, 0.6 ml) to 10 ml of aqueous solution containing CTAB (0.1 M, 9.75 ml) and HAuCl4 (0.01 M, 0.25 ml). After addition, the solution was stirred for two minutes under gas flow. Separately, CTAB (0.1 M, 9.5 ml) was mixed with $AgNO_3$ (0.01 M, 60-150 µl), HAuCl4 (0.01 M, 0.5 ml) and ascorbic acid (0.1 M, 55 µl), respectively. 12-30 µl of the seed solution was then added to this mixture. The growth solution was then stored overnight.

In separate control experiments, the same procedure was followed by applying N_2 flow to both seed and growth solutions and also without any gas flow. Additionally, the synthesis procedure was repeated by applying gas flow to growth solution only. The final mixtures were centrifuged at 9074g for 20 min and the supernatant was replaced with fresh DI water. The centrifugation was repeated once again and the supernatant was removed. In each centrifugation cycle, UV-Vis measurements were performed after precipitates redispersed in DI water.

Synthesis of Nanoparticles. A method described by Jana et al. for seedless (single step) synthesis of GNRs was adapted. Briefly, HAuCl4 (2 mM, 5 ml), CTAB (0.2 M, 5 ml), AgNO3 (0.0084 M, 250 µl), ascorbic acid (0.084 M, 250 µl) and $NaBH_4$ (0.001 M, 100 µl) were mixed under the flow of N_2 or Ar with varying velocities for 20 minutes. In a separate control experiment, the same procedure was repeated without gas flow.

UV-Vis / Near IR Spectroscopy. UV-Vis measurements were carried out using an Ocean Optics USB2000+VIS/NIR spectrometer (350-1100 nm) built by Nanodev Ltd. (Bilkent, Cyberpark). All absorbance spectra were collected using quartz cuvettes.

Atomic Force Microscopy (AFM). A Nanosurf FlexAFM system operating in tapping mode at room temperature in air was used to obtain topographic data. All imaging operations were conducted with 512 x 512 data acquisitions at a various scan speed. Oxide-sharpened silicon nitride tips with integrated cantilever with a nominal spring constant of 48 N/m were used. For AFM micrographs, a drop of the solution was fixed on Si (111) previously cleaned using Piranha (CAUTION) solution.

Scanning Electron Microscopy (SEM). SEM micrographs were obtained using a Zeiss Ultra Plus High Resolution FE-SEM equipped with an in-lens secondary-electron detector at operating range 2-20 keV depending on sample charging. For SEM micrographs, a drop of the solution was fixed on Si (111) previously cleaned using Piranha (CAUTION) solution.

Raman Spectroscopy. Raman Measurements: Raman spectrometer XploRA (Horiba) equipped with a confocal microscope was used. The Raman signals were recorded in a spectral range of 450–3000 cm^{-1} using a 532nm laser excitation, at 50mW power, in combination with a 10x objective magnification (NA= 0.25) of an Olympus BX41 transmission and reflection illumination microscope (Olympus, France) for focus and collection of Raman-scattered light. For each sample, the Raman experiment was repeated 5 times to check the reproducibility of the measurement. Each spectrum was normalized using the Labspec software. To investigate the existence of N_2 gas in bubbles, pure water with and without bubbles was placed in a polypropylene tube and purged with Argon gas (Ar) and the final solutions were analyzed by Raman spectroscopy.

Laser Photothermal Heating of GNB Solution. GNB solution at 15.2 mg/L mg/ml was irradiated by a 808 nm laser with the power density of 150 mW for predetermined time points. The temperature of the solution was monitored using a thermocouple and heat camera.

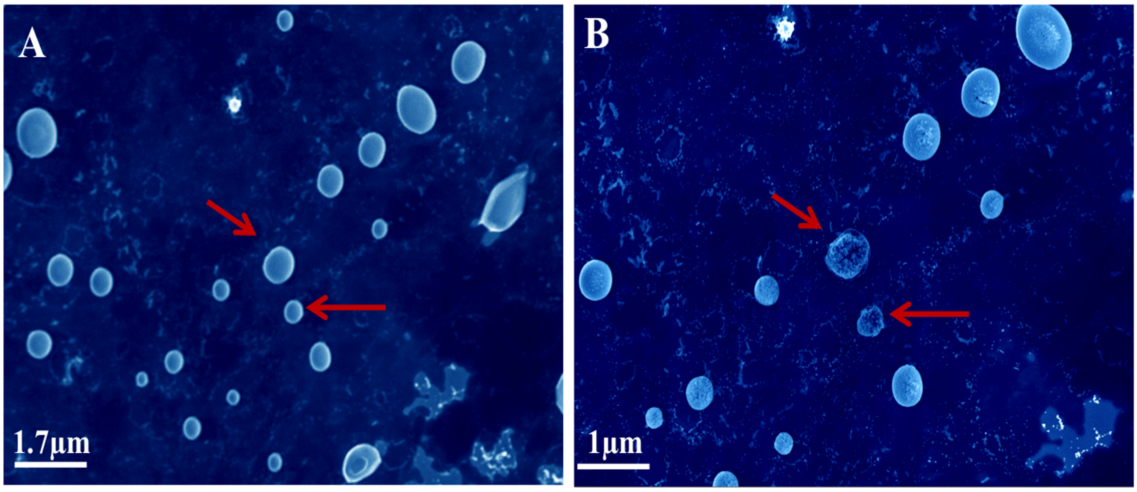

Figure S1. SEM image of nanobubbles (A) under low keV, (B) under high keV.

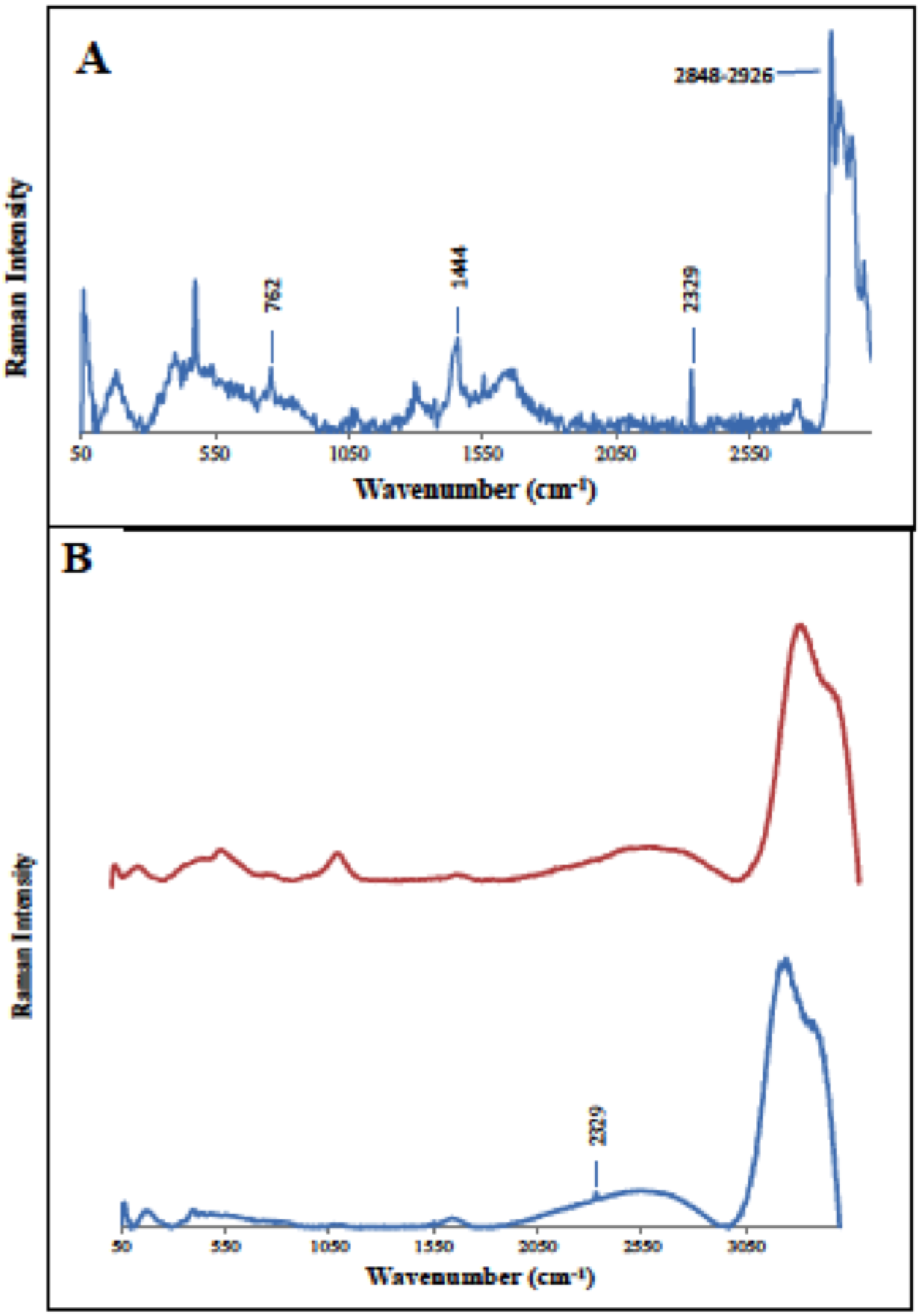

Figure S2. Raman spectra of (A) bubble solution in water after purging with Ar gas (B) water before (BLUE) and after (RED) purging with Ar gas, and.

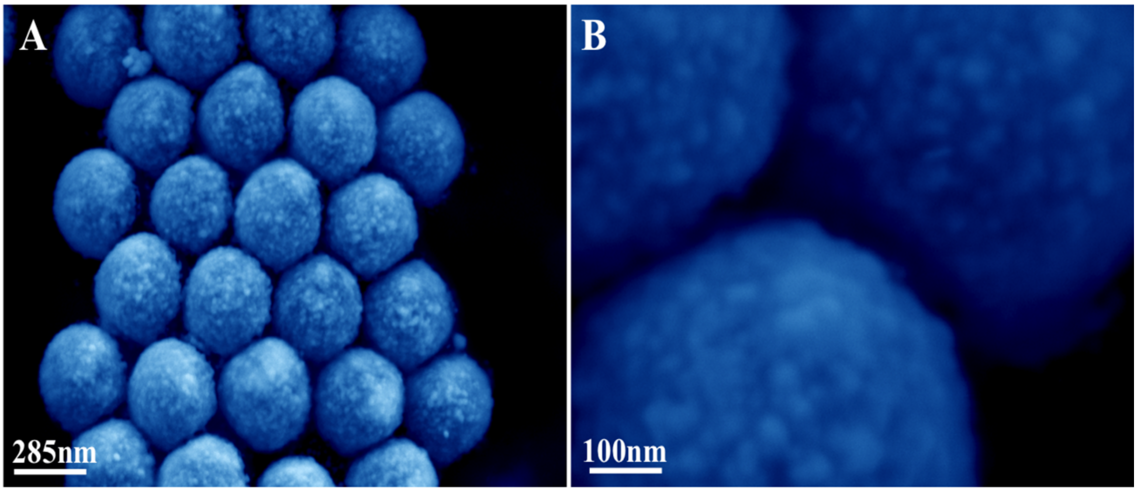

Figure S3. SEM images of nanorods and particles embedded in the walls of bubbles.

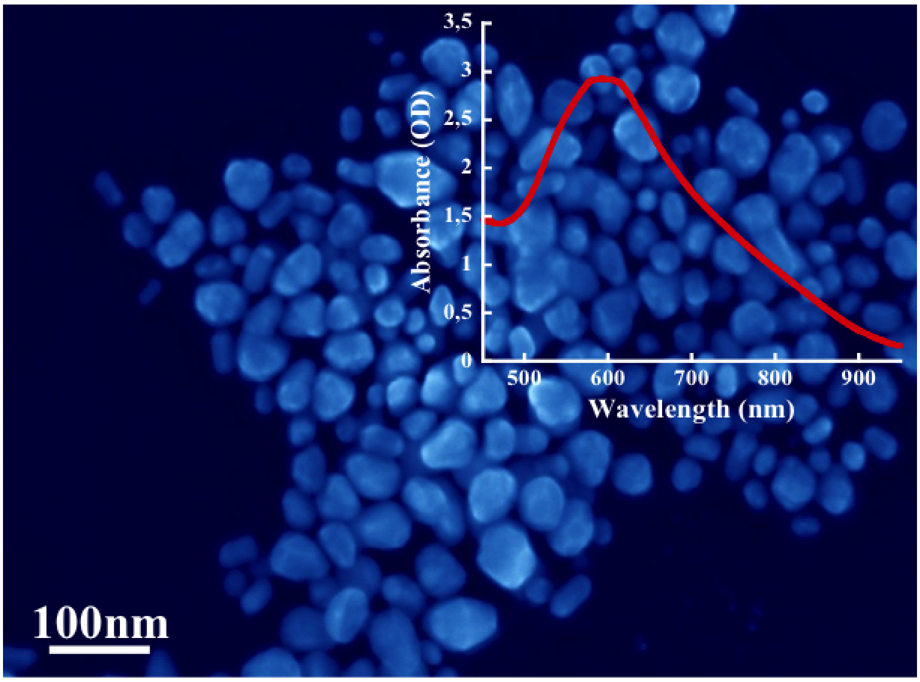

Figure S4. SEM micrograph and UV-Vis of the structures obtained via seed-mediated method under Ar gas.

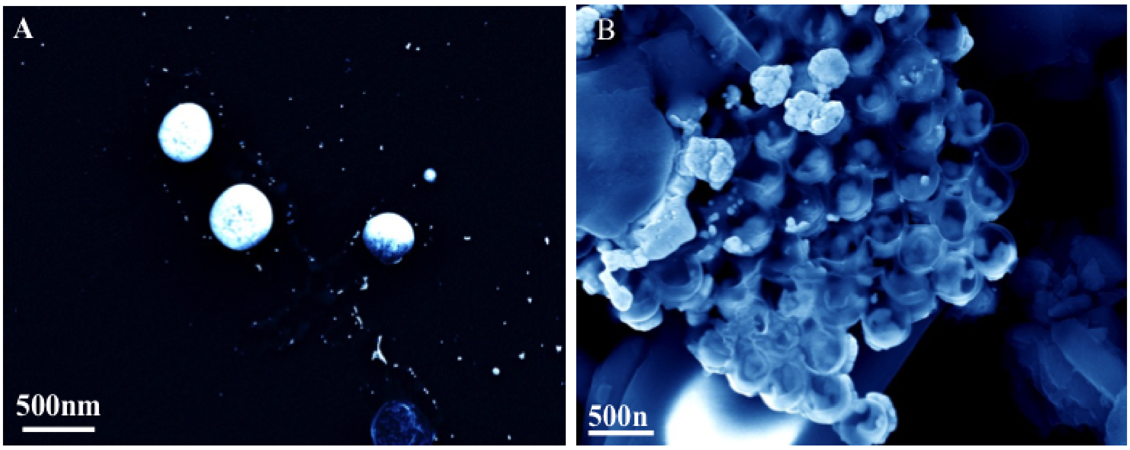

Figure S5. SEM images of bubbles in solution after (A) 5 months and (B) 6 months.

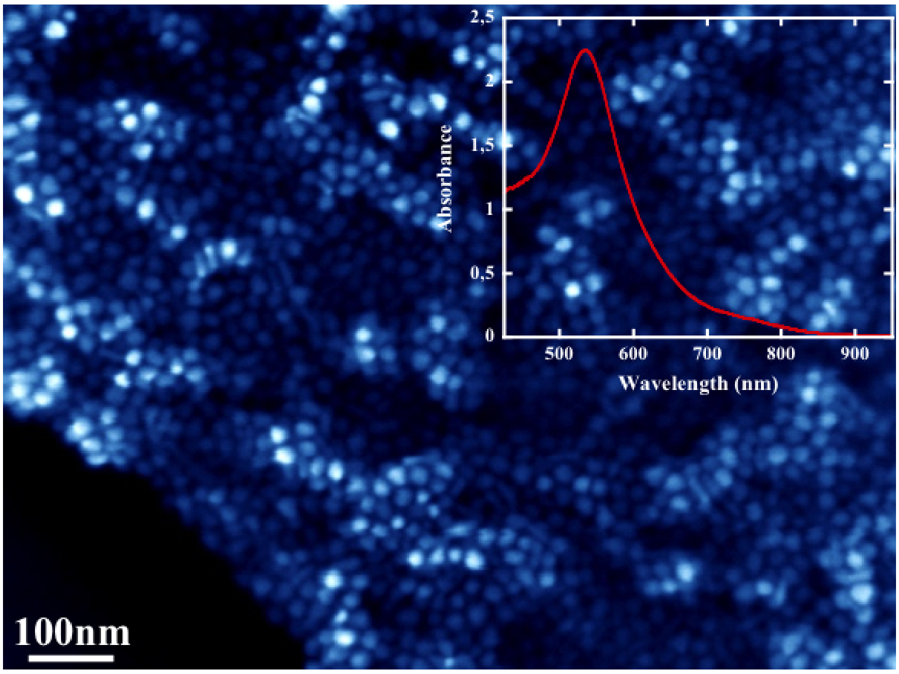

Figure S6. SEM micrograph and UV-Vis of the structures obtained via seedless method under Ar gas.

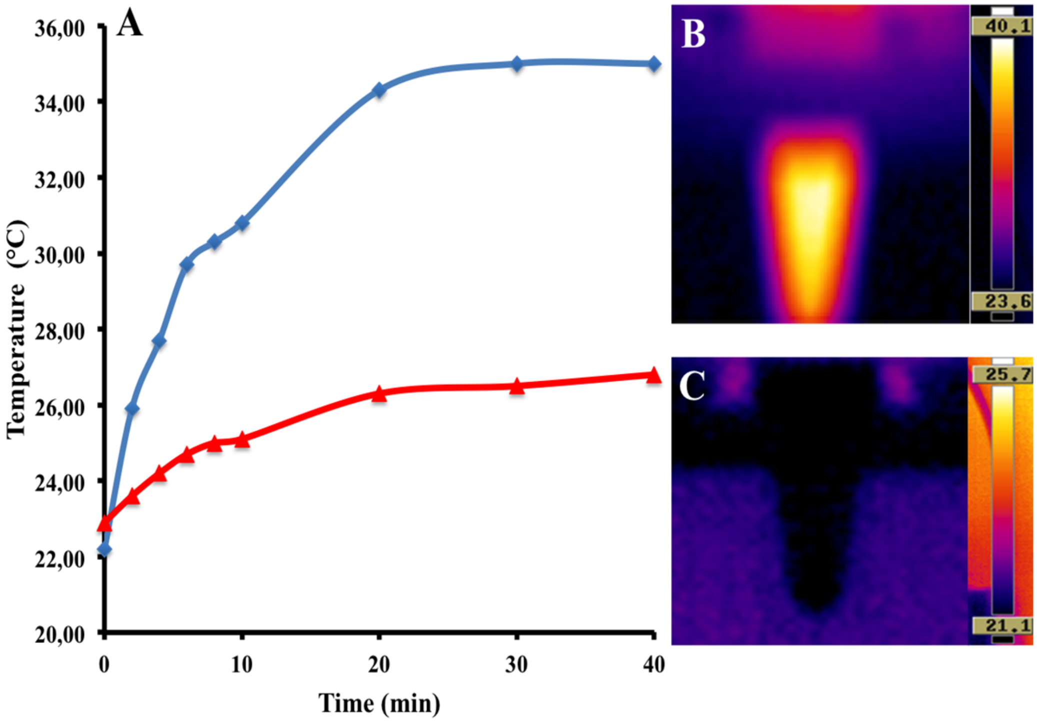

Figure S7. (A) Temperature changes of gold nanobubble suspension(blue line) and water(red line) under laser irradiation. (B-C) Thermal camera images of gold nanobubble suspension and water after laser exposure.