Electronic Supplementary Information for:

In Situ Monitoring, Separation, and Characterization of Gold Nanorod Transformation during Seed-Mediated Synthesis

Thao M. Nguyen,[a,§] John M. Pettibone,[a] Julien Gigault,[b] and Vincent A. Hackley[a,*]

[a]Materials Measurement Science Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8520; [b]Université de Bordeaux; 351 Cours de la Libération, 33405 Talence Cedex, France

[*] corresponding author: vince.hackley@nist.gov, (301) 975-5790, FAX (301) 975-6589

[§] current address: ANSER, 5727 Leesburg Pike N-5000, Falls Church, VA 22041

Table S1: A4F fractionation parameters used for GNR transformation experiments.

Channel parameters	Membrane	polyethersulfone (PES)
	Membrane cut-off	10 kDa
	Spacer	250 µm
Fractionation time	Elution	2 min
	Focusing time	2 min
	Focus + Injection time	3 min
	Focusing time	2 min
	Elution time	45-65 min
Fractionation step, flow and volume	Injection volume	100 µL
	Injection flow	0.2 mL min^{-1}
	Elution flow (V_p)	0.5 mL min^{-1}
	Cross flow (V_c)	2.0 mL min^{-1}

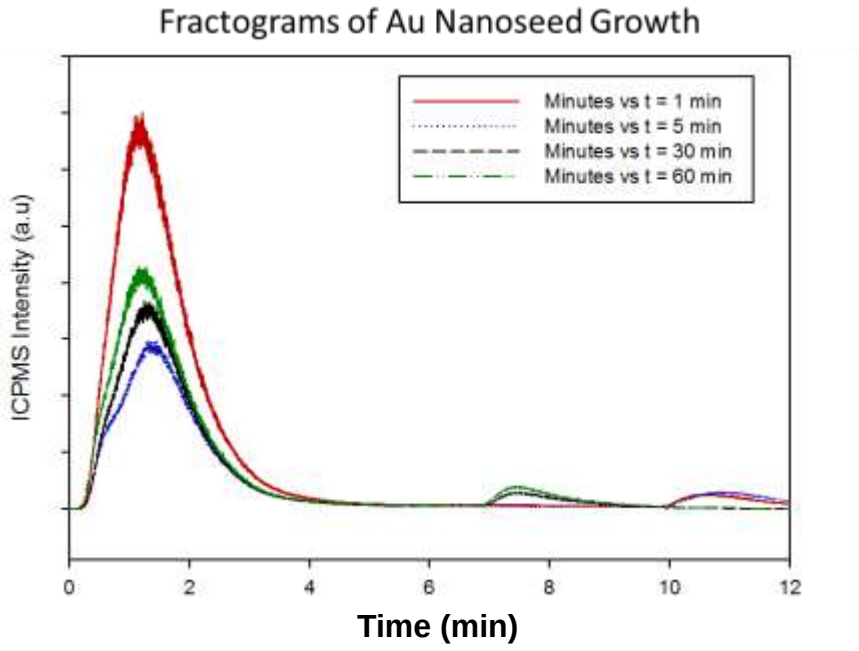

Figure S1: Representative fractograms traced using A4F coupled ICP-MS (7700x, Agilent Technologies, Santa Clara, CA) measurement of Au^{197} for early phase gold nano-seed growth at specified times under the following fractionation conditions: 10 kDa PES membrane, 490 µm spacer thickness, V_c = 2.0 mL min^{-1}, V_p = 0.5 mL min^{-1}, and a mobile phase containing 0.15 mmol L^{-1} CTAB and 0.35 mmol $^{-1}$ NH_4NO_3. Previous experiments indicated that an ionic strength of 0.5 mmol L-1 provided an optimal condition for analysis of gold nanoparticles. CTAB is added to the mobile phase to ensure that the membrane and particles are compatible. During method development, optimal peak resolution was investigated at a V_c from 1.0 mL min^{-1} to 2.5 mL mil^{-1}. The fractograms exhibit a shift in the t_R of nano-seeds as reaction time increases, but the fluctuations in intensity are not linear with time using similar preparation methods outlined for larger species. The source of this behavior is currently being investigated (although it should be noted that the presence of CTAB appears to impact these measurements). In addition, after t = 1 min, the presence of additional peaks becomes evident. The ^{197}Au trace was utilized to definitively confirm that fractionated peaks arise from gold nano-seeds and not from surfactant or micelles alone.

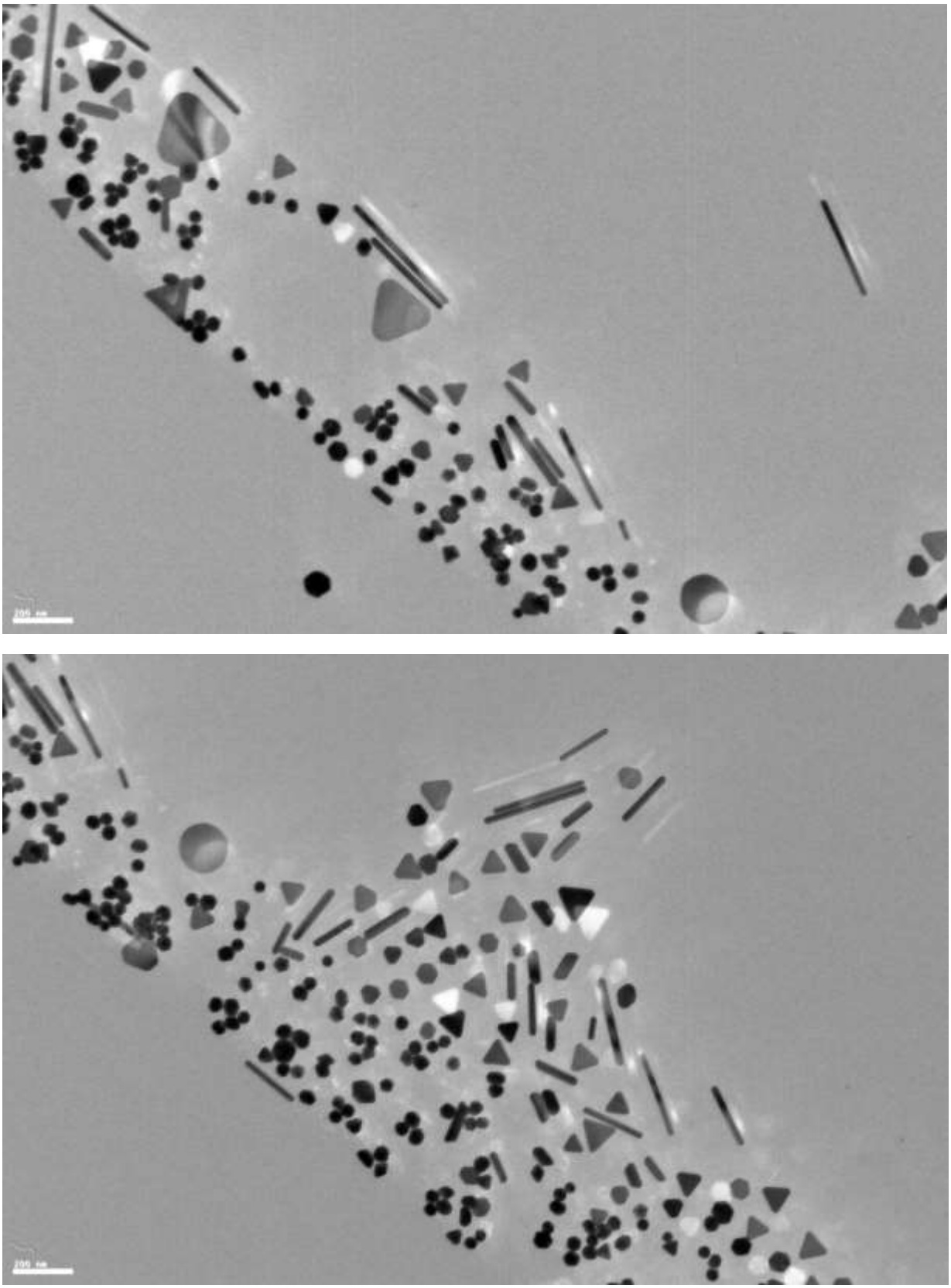

Figure S2: TEM images of GNR solution at t = 72 h. Scale bars are 200 nm.

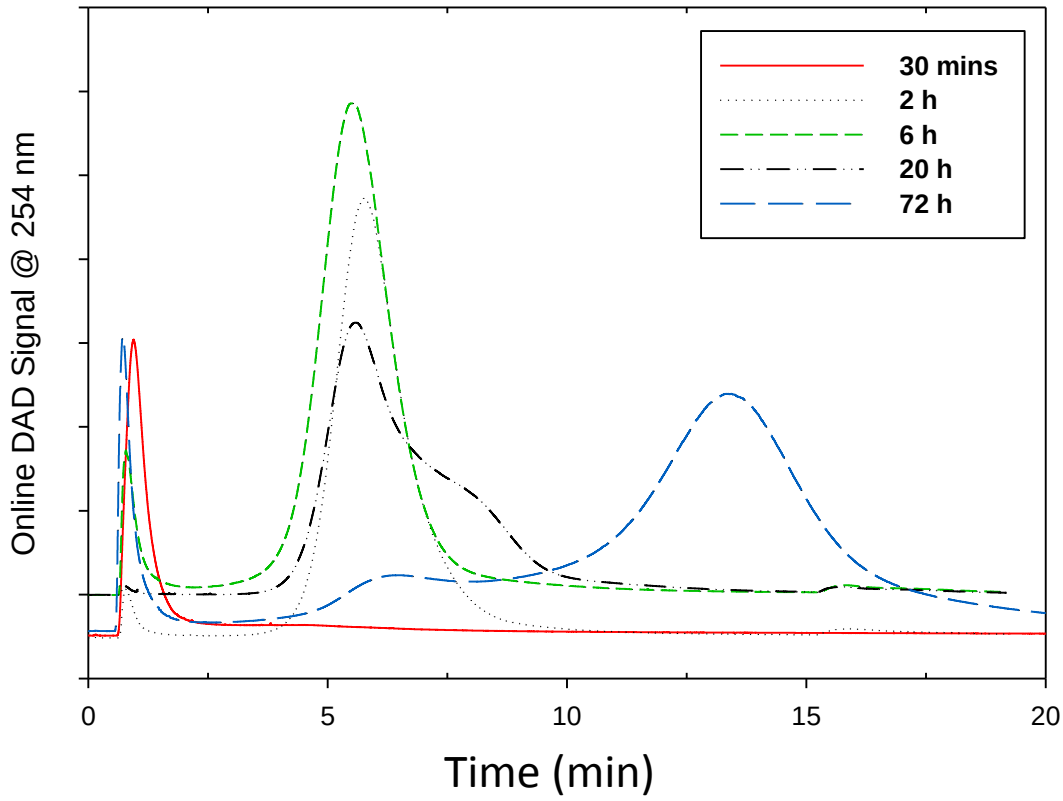

Figure S3: Representative online UV-Vis DAD traces at 254 nm during elution for GNRs measured at designated sampling times after Hq addition. The fractograms clearly demonstrate transformation changes of the sample over 72 h. At $t \leq 6$ h, there is a single resolved peak observed; however, as time increases different nano-species begin to form, indicated by the shoulder exhibited in the fractogram collected at 20 h and the appearance of two resolved peaks at 72 h. At $t = 30$ min, resolving distinct populations of products resulting from initial seed growth was not tractable using the reported conditions with the 250 μm spacer, but results do demonstrate the time period necessary to begin observing products with diffusion coefficients similar to 10 nm spheres. Investigation of the earliest time points must be conducted under similar conditions outlined in Figure S1.

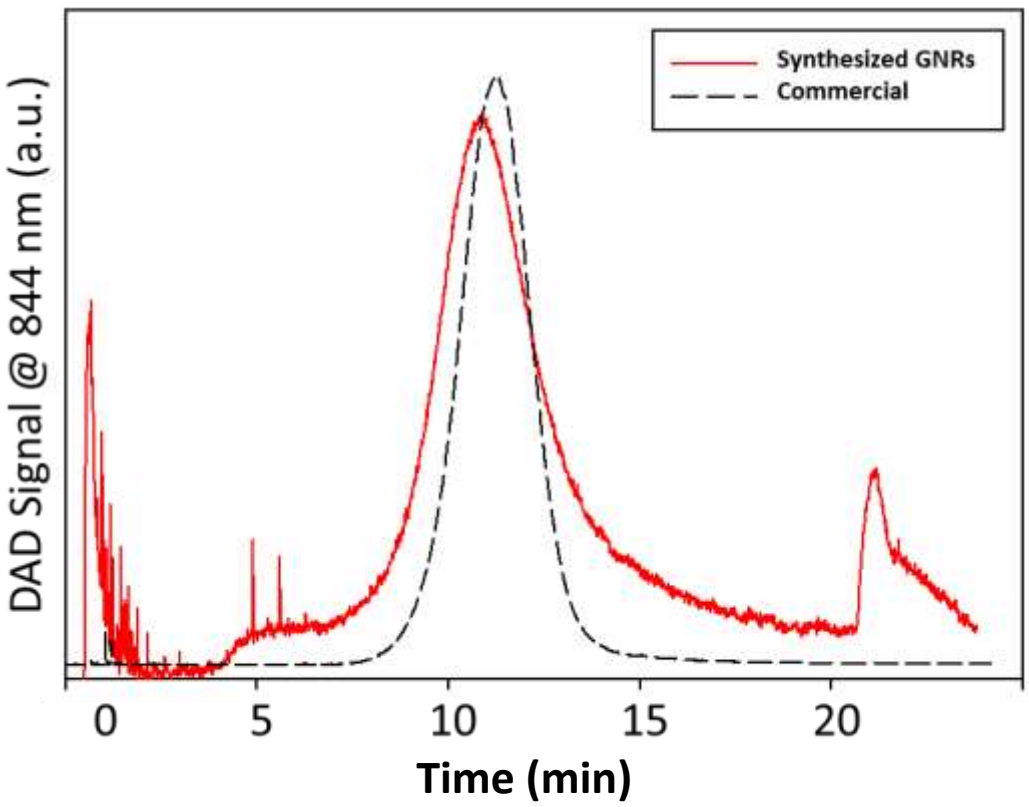

Figure S4: Overlaid fractograms of the GNR reaction suspension at 72 h after Hq addition and commercially purchased material with known AR exhibiting an absorbance maximum at 844 nm, which has a diameter and length of 25 nm and 113 nm, respectively. The diameters of the synthesized and commercial GNRs were of similar size.