Ultrapure water is used in all syntheses. Glassware and stir bars are cleaned using nitric acid or aqua regia - only use these in a fume hood! Follow your lab's chemical hygiene plan and SOPs. Wear the appropriate personal protective equipment.

Materials

Sigma: polyvinylpyrrolidone, hydrogen tetrachloroaurate trihydrate, copper (II) chloride dihydrate, thioctic acid (also called lipoic acid), 6-amino-1-hexanethiol hydrochloride (also called 6-mercaptohexylamine hydrochloride), cetyltrimethylammonium bromide (also called hexadecyltrimethylammonium bromide), sodium selenite, polyallylamine hydrochloride, sodium borohydride, ascorbic acid, thioacetamide, glutathione, fluorescein isothiocyanate, sodium phosphate dibasic
Gelest: 3-aminopropyltriethoxysilane
VWR: ethanol, sodium citrate dihydrate, sodium hydroxide, tannic acid, silver nitrate (my favorite manufacturer of silver nitrate is Strem Chemicals, you can get it from VWR)
Fisher: gum arabic, ethylene glycol, nitric acid, hydrochloric acid, acetic acid

*hydrogen tetrachloroaurate and copper chloride are corrosive – they will corrode a metal spatula. To avoid contamination, use a plastic spatula or wrap Teflon tape around the metal spatula. They are both also hygroscopic, especially the hydrogen tetrachloroaurate. For the hydrogen tetrachloroaurate, I typically use all of the material and make a stock solution directly in the original bottle so that I don't have to weigh it and chance corrosion or absorption of water. For copper chloride, I use a plastic spatula to weigh out the amount I need.

Gold nanoparticles, 12-nm, citrate-stabilized (Au-CIT)

In a round-bottom flask equipped with a condenser, bring 1 L of 1 mM hydrogen tetrachloroaurate in water to reflux while stirring. Add 4 mL of 1 M sodium citrate all at once, and continue reflux and stirring for 20 min. Remove the red suspension from heat, and continue stirring until cool [1,2]. Store at 4-8°C.
This synthesis can be scaled down without a significant change in size. You can use either a heating mantle or an oil bath.
DO NOT FREEZE, DO NOT DRY
Purification is not recommended because removal of citrate can result in irreversible aggregation of the particles.

[1] Turkevich, J; Stevenson, PC; and Hillier, J. "A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold," *Discussions of the Faraday Society* **1951**,

11, 55-75.
[2] Frens, G. "Particle Size and Sol Stability in Metal Colloids," *Colloid and Polymer Science, Kolloid-Zeitschrift & Zeitschrift fur Polymere* **1972,** *250(7),* 736-741.

Modification of 12-nm citrate-stabilized gold nanoparticles

*for all of the modifications listed here, you can centrifuge once to purify – if you centrifuge more than once, they usually don't stay stable

Gold nanoparticles, 12-nm, PVP(55K)-coated
50 ml of 12-nm Au-CIT, stir
+ 50 mg of PVP(55K)
-stir for 4 days (could probably stir for less time, but 4 days is definitely enough
-centrifuge one time at 46,000 x g for 1 h, resuspend in water
-store at 4-8°C

Gold nanoparticles, 12-nm, gum arabic-coated
50 ml of 12-nm Au-CIT, stir
+ 50 mg of gum arabic
-stir for 4 days (could probably stir for less time, but 4 days is definitely enough
-centrifuge one time at 46,000 x g for 1 h, resuspend in water
-store at 4-8°C
*this procedure can be used to modify 12-nm Au-CIT with other steric stabilizers, you will have to try it

Gold nanoparticles, 12-nm, glutathione-functionalized
100 ml of 12-nm Au-CIT, stir
+10 ml of 10 mM glutathione in water
+0.7 ml of 0.5 M NaOH to adjust pH to 7 (you can start with less and measure pH, add until you reach pH 7)
-cap and stir overnight
-centrifuge one time at 46,000 x g for 1 h, resuspend in water
-store at 4-8°C

Gold nanoparticles, 12-nm, amine-functionalized
-when trying to modify gold NPs with a thiol, in many cases, the NPs aggregate irreversibly. In this procedure, the gold NPs are first modified with thioctic acid (also called lipoic acid), which is an organosulfur molecule that binds to the NPs to better stabilize them, but can then be displaced by a thiol. [3,4]
87 ml of 12-nm Au-CIT, stir
+ 8.7 ml of 4mM thioctic acid in ethanol
-stir for 2 days
-centrifuge one time at 46,000 x g for 1 h, resuspend in water to 87 ml
-place container in an ice bath on a stirrer and stir
+ 8.7 ml of 4mM aminohexanethiol in ethanol

-stir for 1 h
-during this time, the NPs will look purple or aggregated – don't worry, this is reversible
+ 8.7 ml of 1M HCl → at this point, if they were completely aggregated before the addition of HCl, they should look purple. If they were already purple, then they should look less purple and more red
-continue stirring for 4 days
-at the end of the 4 days, they should be red
-centrifuge one time at 46,000 x g for 1 h, then resuspend in water
-store at 4-8°C
*remember that these NPs will now need to be positively charged in order to repel each other and remain unaggregated. Nanopure water should have a low enough pH to accomplish this, but if not, try adjusting the pH with HCl.

[3] Ivanov, MR; Bednar, HR; and Haes, AJ. "Investigations of the Mechanism of Gold Nanoparticle Stability and Surface Functionalization in Capillary Electrophoresis," *ACS Nano* **2009**, *3(2)*, 386-394.
[4] Lin, S-Y; Tsai, Y-T; Chen, C-C; Lin, C-M; and Chen, C-h. "Two-Step Functionalization of Neutral and Positively Charged Thiols onto Citrate-Stabilized Au Nanoparticles," *J. Phys. Chem. B* **2004**, *108*, 2134-2139.

Gold nanoparticles, 40-nm, citrate-stabilized (Au-CIT)

-this is a seeded preparation with a step-wise growth [5]
-in a 250-ml round-bottom flask equipped with a stir bar and a reflux condenser, 98 ml of water
+ 1 ml of 12-nm citrate-stabilized gold nanoparticles
+ 0.5 ml of 40 mM sodium citrate dihydrate
-stir and bring to reflux using an oil bath placed on top of a hot plate
+ a total of 0.5 ml of 0.1 M hydrogen tetrachloroaurate trihydrate **added in 50 µl aliquots every 15 min**
-after you add the final aliquot, continue heating for 15 more min, then remove from heat and stir until cool
-store at 4-8°C
-I have not tried to scale this up or down.
-you can add less aliquots for smaller particles
*I have not tried to grow bigger nanoparticles, but if you want to try it, I recommend increasing the amount of sodium citrate added at the beginning

[5] Geitner, NK; Marinakos, SM, Guo, C; O'Brien, N; and Wiesner, MR. "Nanoparticle Surface Affinity as a Predictor of Trophic Transfer," *Environ. Sci. Technol.* **2016**, *50*, 6663-6669.

Modification of 40-nm citrate-stabilized gold nanoparticles

*for the modification listed here, you can centrifuge once to purify – if you centrifuge more than once, they usually don't stay stable

Gold nanoparticles, 40-nm, PAH-coated (PAH=polyallylamine hydrochloride)
50 ml of 40-nm Au-CIT, stirred
+ 50 mg of PAH(70K)
-stir overnight
-centrifuge one time at 5,000 x g for 20 min, resuspend in water
-store at 4-8°C [5]
DO NOT FREEZE, DO NOT DRY
*you should be able to use this same procedure to coat 40-nm Au-CIT NPs with other polymers

[5] Geitner, NK; Marinakos, SM, Guo, C; O'Brien, N; and Wiesner, MR. "Nanoparticle Surface Affinity as a Predictor of Trophic Transfer," *Environ. Sci. Technol.* **2016**, *50*, 6663-6669.

Gold nanoparticles, 8-nm, PVP-coated (Au-PVP)
*this is the gold counterpart to 8-nm AgPVP(55K)

-in a 1-L Erlenmeyer flask, dissolve 1.5 g of PVP (MW 55,000) in 288 ml of water
+ 3 ml of 0.1 M hydrogen tetrachloroaurate, stir for 5 min
+ 9 ml of 0.1 M ice-cold sodium borohydride all at once
-centrifuge at 112,000 x g for 1 h three times and resuspend in water
-store at 4-8°C

Gold nanorods, CTAB-stabilized, ~250-300 nm in length, ~25 nm in diameter

This procedure is based on a seeded, step-wise growth [6] and results in a small amount of long gold rods, with the bulk of the suspension consisting of spheres and short rods. However, the long rods are easily separated from the spheres and short rods.
*you must heat the CTAB solution in order to dissolve the CTAB. In order to keep the CTAB dissolved throughout the reaction, place all solutions containing CTAB in a water bath at 29°C

Synthesis of gold seed suspension
9 ml of water, stir
+ 0.25 ml of 0.01 M $HAuCl_4$

+ 0.25 ml of 0.01 M sodium citrate
+ 0.25 ml of cold 0.1 M sodium borohydride
-continue stirring for 30 sec, then set aside

Synthesis of rods
-prepare 3 solutions as described below and place in a water bath at 29°C
solution A: 4.5 ml of 0.1 M CTAB + 0.125 ml of 0.01 M $HAuCl_4$ + 25 µl of 0.1 M ascorbic acid + 25 µl of 0.1 M NaOH
solution B: 45 ml of 0.1 M CTAB + 1.25 ml of 0.01 M $HAuCl_4$ + 250 µl of 0.1 M ascorbic acid + 250 µl of 0.1 M NaOH
solution C: 450 ml of 0.1 M CTAB + 12.5 ml of 0.01 M $HAuCl_4$ + 2.5 ml of 0.1 M ascorbic acid + 2.5 ml of 0.1 M NaOH
-add 0.5 ml of gold seed suspension to solution A, cap and invert 5 times
-immediately add solution A to solution B, cap and invert 5 times
-immediately add solution B to solution C, swirl to mix well, and incubate in the water bath at 29°C overnight
-the next day, decant the purple suspension from solution C (the purple suspension contains spheres and short rods)
-add a small amount of water to the settled brown residue left behind, and swirl to resuspend. This brown suspension contains the long nanorods.
-centrifuge the brown suspension at 2500 x g for 10 min two times, resuspend in water
-if you want to keep the spheres/short rods, you can centrifuge the purple suspension at 5000 x g for 20 min two times and resuspend in water

[6] Jana, NR; Gearheart, L; and Murphy, CJ. "Wet Chemical Synthesis of High Aspect Ratio Cylindrical Gold Nanorods," *J. Phys. Chem. B* **2001**, *105*, 4065-4067.

Gold nanorods, CTAB-stabilized, bone shaped, ~50 nm in length, ~20 nm in diameter across the middle

This procedure is based on a seeded growth [7] and results in bone-shaped gold rods.
*you must heat the CTAB solution in order to dissolve the CTAB. In order to keep the CTAB dissolved throughout the reaction, place all solutions containing CTAB in a water bath at 29°C

Synthesis of gold seed suspension
5 ml of 0.2 M CTAB in water, stir
+ 5 ml of 0.5 mM $HAuCl_4$
+ 0.6 ml of ice cold 0.1 M sodium borohydride
-continue stirring for 30 sec, heat gently for 5 min, then set aside
-should be light brown

Synthesis of rods
50 ml of 0.2 M CTAB, placed in a water bath at 29°C
+ 200 µl of 0.04M $AgNO_3$, swirl
+ 50 ml of 1 mM $HAuCl_4$, swirl
+ 0.56 ml of 0.1M ascorbic acid, swirl → should turn colorless because the ascorbic acid reduces Au^{3+} to Au^{1+}, but is not strong enough to reduce to Au^0 without the presence of a seed.
+ 120 µl gold seed
-cap and leave undisturbed overnight at 29°C
-heat to 37°C to keep CTAB dissolved during purification
-centrifuge at 5000 x g for 15 min two times

[7] Nikoobakht, B; El-Sayed, MA. "Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method," *Chem. Mater.* **2003**, *15*, 1957-1962.

Silver nanoparticles, ~25 nm, citrate-stabilized (Ag-CIT) *results in very polydisperse particles if you don't use tannic acid

Silver nanoparticles are synthesized by sodium citrate reduction of silver nitrate in water at reflux [8].
In a round-bottom flask equipped with a condenser, bring 1 L of 1 mM silver nitrate in water to reflux while stirring. Add 10 mL of 1 M sodium citrate all at once, and continue heating and stirring for 30 min. Remove the yellow suspension from heat, and continue stirring until cool. Store covered at 4-8°C.
DO NOT FREEZE, DO NOT DRY
Purification is not recommended because removal of citrate can result in irreversible aggregation of the particles.

[8] P.C. Lee and D. Meisel. "Adsorption and Surface-Enhanced Raman of Dyes on Silver and Gold Sols," *J. Phys. Chem.* **1982**, *86*, 3391-3395.

Silver nanoparticles, ~25 nm, citrate-stabilized with a small amount of tannic acid added (Ag-CIT/TA)

-heat 80 ml of 0.74 mM silver nitrate to 60°C, stir
+ 20 ml of 6.8 mM sodium citrate / 3 uM tannic acid
-once the suspension starts to turn yellow, increase heat and boil for 20 min, then turn off heat and stir until cool. Store covered at 4-8°C. [9]
DO NOT FREEZE, DO NOT DRY
Purification is not recommended because removal of citrate can result in irreversible aggregation of the particles.

[9] T. Dadosh. "Synthesis of uniform silver nanoparticles with a controllable size," *Materials Letters* **2009**, *63(26)*, 2236-2238.

Silver nanoparticles, 40-nm, PVP-coated (Ag-PVP55K)

These particles are synthesized using the polyol method. [10,11]
-dissolve 20 g of PVP (MW 55,000) in 50 ml of ethylene glycol (put these in a beaker the day before, stir with a glass pipet to mix well, allow to sit overnight to dissolve)
-transfer the PVP solution in ethylene glycol to a 250-ml round-bottom flask with a stir bar
+ 0.75 g of silver nitrate, stir until dissolved (it takes about 30 min because the solution is very viscous
-attach a reflux condenser and heat in an oil bath to 140°C for 24 h. You can monitor the temperature by placing a thermometer in the oil bath (make sure it is not touching any of the glass)
-turn off heat, stir until cool, or cool in an ice bath (only do this if using pyrex glassware, and even then, do it behind the sash/windows of a hood – warning – it is VERY hot, handle only at the neck)
-dilute 1:10 with water
-centrifuge at 10,000 x g for 1 h three times and resuspend in water [10,11]
-store covered at 4-8°C
*I've found that decreasing the heat results in smaller NPs

[10] Silvert et al. *J. Mater. Chem.*, 1996, 6, 573-577.
[11] Silvert et al. *J. Mater. Chem.*, 1997, 7, 293-299.

Silver nanoparticles, 8-nm, PVP-coated (Ag-PVP)

***can use either MW 55,000 or MW 10,000 PVP**

-in a 1-L Erlenmeyer flask, dissolve 1.5 g of PVP in 282 ml of water
+ 9 ml of 0.1 M silver nitrate, stir for 5 min
+ 9 ml of 0.1 M ice-cold sodium borohydride all at once
-centrifuge at 112,000 x g for 1 h three times and resuspend in water [12]
-if the suspension is really cloudy, or if there is visible white solid settling at the bottom, centrifuge at 3000 x g and discard precipitate
-store covered at 4-8°C

[12] Ma et al. "Size-Controlled Dissolution of Organic-Coated Silver Nanoparticles," *Environ. Sci. Technol.* **2012**, *46*, 752-759.

Silver nanoparticles, 8-nm, amine-modified (Ag-NH2)

first make 8-nm AgPVP(55K)
-in a 1-L Erlenmeyer flask, dissolve 1.5 g of PVP in 282 ml of water
+ 9 ml of 0.1 M silver nitrate, stir for 5 min
+ 9 ml of 0.1 M ice-cold sodium borohydride all at once
-centrifuge at 112,000 x g for 1 h three times and resuspend in water [12]
-if the suspension is really cloudy, or if there is visible white solid settling at the bottom, centrifuge at 3000 x g and discard precipitate
-store covered at 4-8°C until further use

then displace some of the PVP with aminohexanethiol
*from a modified published procedure [13]
-dilute the 8-nm AgPVP(55K) to 100 ppm
100 ml of 100 ppm 8-nm AgPVP(55K), stir
+ 1 ml of 0.1 M aminohexanethiol in ethanol
+ 2.5 ml of 1 M acetic acid
-continue stirring for 2 days
-centrifuge at 112,000 x g for 1 h one time and resuspend in water
-store covered at 4-8°C
-confirm positive charge with zeta potential measurement
-can also confirm presence of amine with FT-IR
*I have not tried it in this procedure, but stirring for longer may result in increased displacement of PVP by aminohexanethiol (and thus, greater positive charge)
*you should be able to use this procedure to displace the PVP with other thiols, but I have not tried it

[12] Ma et al. "Size-Controlled Dissolution of Organic-Coated Silver Nanoparticles," *Environ. Sci. Technol.* **2012**, *46*, 752-759.
[13] Johnston et al. “Impact of As-Synthesized Ligands and Low-Oxygen Conditions on Silver Nanoparticle Surface Functionalization,” *Langmuir* **2016**, *32*, 3820-3826.

Silver nanoparticles, 25-nm, gum arabic-coated (Ag-GA)

-in a 1-L Erlenmeyer flask, add 304 ml of water, stir
+ 60 ml of 10 g/L gum arabic
+ 30 ml of 0.1 M silver nitrate, stir for 10 min
-heat to boiling on a hot plate
+ 6 ml of 1 M sodium citrate all at once
-continue boiling and stirring for 10 min
-dilute 1:2 with water
-centrifuge at 10,000 x g for 1 h three times and resuspend in water
-store covered at 4-8°C [14]

[14] Yin, L., et al. "More than the Ions: The Effects of Silver Nanoparticles on Lolium multiflorum," *Environmental Science & Technology*, **2011**, *45(6)*, 2360-2367.

Silver nanoparticles, 6-nm, gum arabic-coated (Ag-GA)

-in a 1-L Erlenmeyer flask, add 273 ml of water
+ 9 ml of 10 g/L gum arabic
+ 9 ml of 0.1 M silver nitrate, stir for 5 min
+ 9 ml of 0.1 M ice-cold sodium borohydride all at once
-centrifuge at 112,000 x g for 1 h three times and resuspend in water
-store covered at 4-8°C [14]

[14] Yin, L., et al. "More than the Ions: The Effects of Silver Nanoparticles on Lolium multiflorum," *Environmental Science & Technology*, **2011**, *45(6)*, 2360-2367.

Silver sulfide nanoparticles, 20-nm, gum arabic-coated (Ag2S-GA)

first make 6-nm AgGA
-in a 1-L Erlenmeyer flask, add 273 ml of water
+ 9 ml of 10 g/L gum arabic
+ 9 ml of 0.1 M silver nitrate, stir for 5 min
+ 9 ml of 0.1 M ice-cold sodium borohydride all at once, stir for 5 min [14]

then sulfidize the 6-nm AgGA
+ 5 ml of 0.2 M thioacetamide
-cover flask with a Kimwipe and rubber band to keep dust out, and stir overnight
-centrifuge at 10,000 x g for 1 h three times and resuspend in water
-store at 4-8°C [15]

[14] Yin, L., et al. "More than the Ions: The Effects of Silver Nanoparticles on Lolium multiflorum," *Environmental Science & Technology*, **2011**, *45(6)*, 2360-2367.
[15] Djokovic, V., et al. "Adsorption of sulfur onto a surface of silver nanoparticles stabilized with sago starch biopolymer." *Colloids Surf B Biointerfaces* **2009**, *73(1)*, 30-35.

Silver sulfide nanoparticles, 45-nm, PVP(55K)-coated (Ag2S-PVP)

first make 40-nm AgPVP(55K)

-dissolve 20 g of PVP (MW 55,000) in 50 ml of ethylene glycol (put these in a beaker the day before, stir with a glass pipet to mix well, allow to sit overnight to dissolve)
-transfer the PVP solution in ethylene glycol to a 250-ml round-bottom flask with a stir bar
+ 0.75 g of silver nitrate, stir until dissolved (it takes about 30 min because the solution is very viscous
-attach a reflux condenser and heat in an oil bath to 140°C for 24 h. You can monitor the temperature by placing a thermometer in the oil bath (make sure it is not touching any of the glass)
-turn off heat, stir until cool, or cool in an ice bath (only do this if using pyrex glassware, and even then, do it behind the sash/windows of a hood – warning – it is VERY hot, handle only at the neck)
-dilute 1:10 with water
-centrifuge at 10,000 x g for 1 h three times and resuspend in water [10,11]
-store covered at 4-8°C

then sulfidize the 40-nm AgPVP(55K)
-dilute the AgPVP to a concentration of 3 mM Ag (you should confirm the stock concentration with ICP so you know how much to dilute it)
500 ml of purified 3 mM AgPVP
+ 15 ml of 0.2 M thioacetamide
-cover flask with a Kimwipe and rubber band to keep dust out, and stir for 3 days
-centrifuge at 10,000 x g for 1 h three times and resuspend in water
-store at 4-8°C [15]

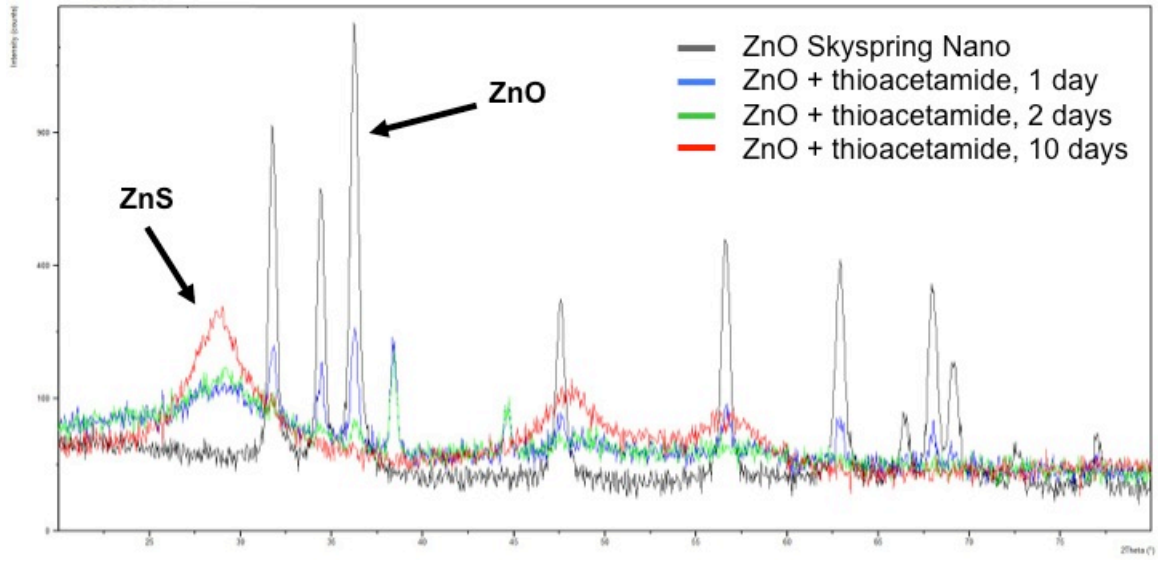
[10] Silvert et al. *J. Mater. Chem.*, 1996, 6, 573-577.
[11] Silvert et al. *J. Mater. Chem.*, 1997, 7, 293-299.
[15] Djokovic, V., et al. "Adsorption of sulfur onto a surface of silver nanoparticles stabilized with sago starch biopolymer." *Colloids Surf B Biointerfaces* **2009**, *73(1)*, 30-35.

Zinc sulfide nanoparticles, ZnS, ~100 nm

Nano Zinc Sulfide is synthesized by sulfidizing the commercial ZnO material from Skyspring Nano.
*the 100-nm particles will consist of small primary particles <10 nm
*this procedure will probably work for other ZnO samples, but I have only tried it with the Skyspring Nano ZnO

-disperse 100 mg of ZnO nanopowder (Skyspring Nano) by probe-sonicating in 80 ml of water at 50% power (~60W) for 10 min
-divide the dispersion into two 50-ml centrifuge tubes
-while stirring, add 7 ml of a 0.2 M aqueous solution of thioacetamide to each tube, and stir the dispersion for 10 days

*you can monitor the progression of the conversion to the sulfide during the 10-day time period with X-ray diffraction
-purify the ZnS by centrifuging 3 times at 5000 x g for 15 min.
*complete conversion may take less than 10 days. If you are monitoring it with XRD, and the XRD pattern matches that of ZnS, then you can stop early and purify the particles.
example of XRD patterns showing the progression of the conversion of ZnO to ZnS



Nano-Selenium, BSA-coated, 20 nm (Se-BSA)

BSA-stabilized selenium nanoparticles are synthesized according to a modified published procedure [16].

-while stirring, add 10 ml of 25 mM sodium selenite to 40 ml of 25 mM glutathione containing 50 mg BSA
-adjust the pH with the addition of 1.4 ml of 1 M sodium hydroxide (the suspension will turn red when you add the NaOH)
-continue stirring for 15 min, and then centrifuge the suspension for 1 h at 112,000 x g
-resuspend in water, and cover and store at 4-8°C until further use

[16] Zhang, J-S, et al. "Biological effects of a nano red elemental selenium." *Biofactors* **2001**, *15*, 27-38.

CeO2 modified with fluorescein

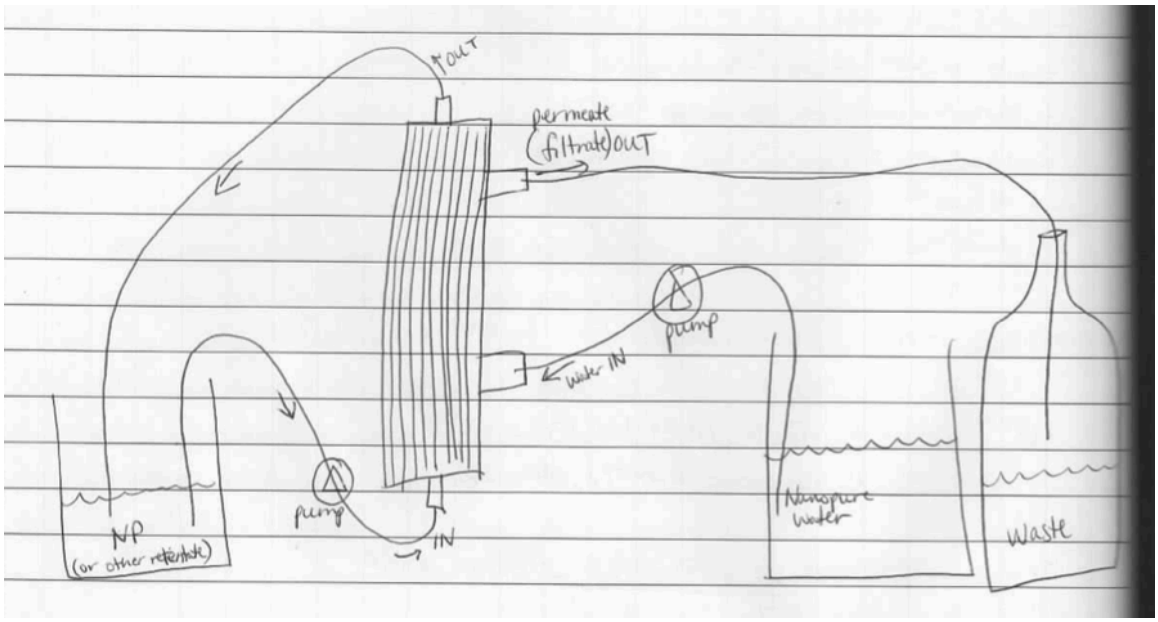
This is a slight modification of a published procedure [17]
-in a vial, disperse 10 mg of commercial CeO2 in 15 ml of ethanol by bath sonicating for 10 min
+ 2.5 µl of 3-aminopropyltriethoxysilane (neat), stir overnight

*3-aminopropyltriethoxysilane should be stored in the refrigerator. Prior to using, remove from fridge and allow to warm to room temperature before opening bottle. It will polymerize over time, so if there is a lot of polymer around the top of the bottle, you should probably order a fresh one (Gelest is my favorite supplier of silanes)
-transfer to a centrifuge tube, and centrifuge at 5000 x g for 10 min 3 times
-resuspend to 12.5 ml with ethanol
+ 2.5 ml of 1 mg/ml fluorescein isothiocyanate in ethanol
-cover with foil and stir overnight
-centrifuge at 10,000 x g for 15 min 3 times
-transfer to a pre-weighed tube and freeze-dry (cover tube with foil, cover top of tube with tissue and rubber band)
**once you introduce the fluorescein, keep the sample covered as much as possible to avoid photobleaching*
*this will work for TiO_2 as well, should work for other bare metal oxides but I have not tried it
*you can use this procedure to modify with any functionalized silane, or anything you can react with the amine group of the aminosilane

[17] Xia, T, et al. "Comparison of the Mechanism of Toxicity of Zinc Oxide and Cerium Oxide Nanoparticles Based on Dissolution and Oxidative Stress Properties." *ACS Nano* **2008**, *2(10)*, 2121-2134.

Copper sulfide nanoparticles, <10 nm, PVP(55K)-coated (CuS-PVP)

*this procedure has not been published
-in a 1-L flask (to avoid bubbling over), add 250 mg of PVP(55K) to 150 ml of water and stir until dissolved
+25 ml of copper (II) chloride dihydrate
+50 ml of 0.2M thioacetamide
+25 ml of 0.2M sodium borohydride all at once (this is when you will see the bubbles because sodium borohydride reacts vigorously with the copper chloride, kind of like what happens when you add alka seltzer to water)
-continue stirring for 3 days
-purify by dialysis, using a medical dialysis fiber membrane (for example, we use Optiflux F200NR Fresenius Polysulfone Dialyzer, Fresenius Medical Care) – the suspension is pumped through the fibers, while water is pumped through the cassette outside of the fibers. Adjust the sample pump speed to be higher than the water pump speed, and the pressure will be such that the impurities, as well as some water, will move through the pores from the sample inside the fibers to the water outside of the fibers (see figure below)
-adjust the pump speeds so that you can concentrate the sample. Once you have concentrated it to a few ml (or <10% of original volume), dilute it with water and concentrate 2 additional times



Copper hydroxide rods, $Cu(OH)_2$

*copper hydroxide is a known hazard (see the SDS on the Sigma Aldrich website http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=289787&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F289787%3Flang%3Den) . Wear appropriate personal protective equipment.
$Cu(OH)_2$ rods are synthesized using a published procedure. [18]

-stir 50 ml of a 0.2M solution of copper (II) chloride dihydrate
+50 ml of a 0.5M solution of NaOH ***dropwise*** (you can use an addition funnel so that you don't have to do this manually)
-you will see some blue material appear where the NaOH hits the $CuCl_2$ solution, and the suspension will get more viscous as more and more $Cu(OH)_2$ forms
-keep an eye on it and increase the speed of stirring if necessary
-when all of the NaOH has been added, ***immediately*** filter the bright blue suspension using a Buchner funnel (or other rigid filtration device) and filter paper
-wash the solid twice by disconnecting the vacuum, adding water, stirring it with a glass rod or spatula, and reconnecting the vacuum
-***immediately*** transfer the blue product to a tube and freeze, then freeze-dry for a minimum of 3 days
-confirm composition with XRD (if you don't add enough NaOH, you will end up with Cu(OH)Cl)
*if possible, complete this synthesis, purification, freezing, and set up in freeze-dryer all in the same day. You might be able to freeze overnight and put in freeze-dryer the next day
**if you see any brown color, it's too late! It has already started to convert to CuO, so you might as well dispose of it in a chemical waste bottle and start over

*the $Cu(OH)_2$ rods will convert to CuO over time. You may be able to prevent this transformation for a longer time period if you fill the tube with nitrogen gas before capping – do this in a hood. Alternatively, you can cap with a septum and fill with nitrogen using a syringe needle (make sure you also use a second needle for a vent)

[18] Singh, DP, et al. "Synthesis of Different Cu(OH)2 and CuO (Nanowires, Rectangles, Seed-, Belt-, and Sheetlike) Nanostructures by Simple Wet Chemical Route." *J. Phys. Chem C* **2009**, *113*, 3409-3418.

Copper oxide rods, CuO

first synthesize copper hydroxide rods, as described above
then either

1) heat the freeze-dried material at 80°C until it turns brown, OR
2) after filtering and washing, resuspend in water and wait a few days – it will transform to CuO on its own (eliminate freezing and freeze-drying, or freeze and freeze-dry after the transformation has taken place, if you want a powder)

Copper hydrogen phosphate hydrate plates

From a modified published procedure [19]

40 ml of 0.5M Na2HPO4, stir
+2.5 ml of 3M copper (II) chloride dihydrate
-stir 10 min
-centrifuge at 5000 x g for 5 min three times
-freeze and freeze-dry
-confirm composition with XRD
*when I followed the procedure in the paper, using triethanolamine resulted in a smaller primary particle size, but a lot of aggregation, and ball milling did not work to reduce particle size or break up aggregates – but you might have better luck!

[19] Laha, D, et al. "Evaluation of copper iodide and copper phosphate nanoparticles for their potential cytotoxic effect." *Toxicol. Res.* **2012**, *1*, 131-136.