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Title: Preparation of Silver-Palladium Alloyed Nanoparticles for Plasmonic Catalysis Under Visible-Light Illumination

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Author Questionnaire

1. Microscopy: Does your protocol demonstrate the use of a dissecting or stereomicroscope for performing a complex dissection, microinjection technique, or similar? **N**

2. Software: Does the part of your protocol being filmed demonstrate software usage? **N**

3. Filming location: Will the filming need to take place in multiple locations (greater than walking distance)? **N**

Protocol Length
Number of Shots: **54**

Introduction

1. Introductory Interview Statements

REQUIRED:

1.1. **Pedro H. C. Camargo**: This protocol represents the synthesis of silver-palladium alloy nanoparticles supported on zirconium dioxide and facilitates the harvesting of energy from visible light irradiation to accelerate and control molecular transformations **[1]**.

1.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

REQUIRED:

1.2. **Erandi Peiris**: This method allows the merging of plasmonic and catalytic properties in a single nanoparticle to enable light-driven transformations in catalytic metals that do not have plasmonic properties **[1]**.

1.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

OPTIONAL:

1.3. **Pedro H. C. Camargo**: This protocol can give insights into nanocatalysis, nanoparticle synthesis, and supported catalyst synthesis and can be applied to other molecular transformations and nanoparticle compositions **[1]**.

1.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera *Videographer: Can cut for time*

Protocol

2. Silver-Palladium/Zirconium Dioxide ($Ag\text{-}Pd/ZrO_2$) Nanoparticle (NP) Synthesis

2.1. To fabricate silver-palladium zirconium dioxide nanoparticles, add 50 milliliters of silver nitrate and 9.71 milliliters of potassium tetrachloroplatinate to a 250-milliliter beaker containing 1 gram of zirconium dioxide **[1]**.

2.1.1. WIDE: Talent adding silver nitrate to flask, with $AgNO_3$, K_2PdCl_4 and ZrO_2 containers visible in frame *Videographer: Important step*

2.2. Mix the solutions under vigorous magnetic stirring at 500 revolutions per minute at room temperature for 5 minutes **[1]** before adding 10 milliliters of lysine to the beaker **[2]**.

2.2.1. Solution being stirred

2.2.2. Talent adding lysine to beaker, with lysine container visible in frame

2.3. After 20 minutes, add 10 milliliters of a freshly prepared sodium borohydride solution to the mixture dropwise at a rate of 1 milliliter/minute **[1]**.

2.3.1. Talent adding drops of solution to beaker, with solution container visible in frame *Videographer: Important step*

2.4. Continue to stir the mixture for an additional 30 minutes at room temperature **[1]**. Then allow the reaction to settle overnight **[2]**.

2.4.1. Mixture being stirred
2.4.2. Talent stopping stirring

3. Catalyst Separation and Purification

3.1. The next morning, split the suspension between several centrifuge tubes **[1]** and separate the solids from the mixture by centrifugation **[2-TXT]**.

3.1.1. WIDE: Talent adding suspension to tube(s)
3.1.2. Talent adding tube(s) to centrifuge **TEXT: 10 min, 3260 x g, RT**

3.2. Use a pipette to carefully remove the supernatant **[1]** and add 15 milliliters of deionized water to the tubes **[2]**.

3.2.1. Talent removing supernatant
3.2.2. Talent adding water to tube(s)

3.3. Shake vigorously until the solid has been thoroughly dispersed **[1]**, placing the tubes in a vortex for 1 minute to fully resuspend the material as necessary **[2]**.

3.3.1. Talent shaking tube
3.3.2. Vortex mixing

3.4. Repeat the centrifugation, wash, and resuspension two more times as demonstrated, using 15 milliliters of deionized of the second wash and ethanol for the third **[1]**.

3.4.1. Talent adding water or ethanol to tube, with ethanol container visible in frame

3.5. After removing the ethanol from the last wash, dry the solid in a 60-degree Celsius oven for 24 hours **[1]** before characterizing the silver-palladium zirconium dioxide preparation by standard microscopy, elemental, and spectroscopic techniques **[2]**.

3.5.1. Talent placing sample into oven *Videographer: Important step*
3.5.2. Shot of dried solid *Videographer: Important step* NOTE: 2 shots were taken (shot 1: Dried solid without a label, shot 2: dried solid with a label

4. Ag/ZrO_2 NP Synthesis

4.1. To produce silver zirconium dioxide nanoparticles, add 50 milliliters of silver nitrate to a 250-milliliter beaker containing 1 gram of zirconium dioxide powder under vigorous magnetic stirring at room temperature **[1]**.

4.1.1. WIDE: Talent adding $AgNO_3$ to beaker, with $AgNO_3$ and ZrO_2 container visible in frame

4.2. Add 10 milliliters of lysine to the beaker **[1]** and continue to stir the mixture for an additional 20 minutes **[2]**.

4.2.1. Lysine being added to beaker
4.2.2. Mixture being stirred

4.3. At the end of the incubation, add 10 milliliters of freshly prepared sodium borohydride to the solution as demonstrated for a 30-minute stirring incubation at room temperature **[1]**.

4.3.1. Talent adding drops of $NaBH_4$ to beaker, with $NaBH_4$ container visible in frame

5. Catalyst Separation and Purification

5.1. For separation and purification of the catalyst, split the solution between several centrifuge tubes **[1]** and collect the solids by centrifugation **[2]**.

5.1.1. WIDE: Talent adding solution to tube(s)
5.1.2. Talent adding tube(s) to centrifuge

5.2. Use a pipette to carefully remove the liquid phase **[1]** and add 15 milliliters of deionized water to the tubes to allow a vigorous resuspension of the solids **[2-TXT]**.

5.2.1. Liquid being removed
5.2.2. Water being added to tube **TEXT: Mixing in vortex to dissolve solid as necessary**

5.3. Centrifuge the resulting solution **[1]** for one additional wash with distilled water and one with ethanol as demonstrated **[2]**.

5.3.1. Talent placing tube(s) into centrifuge
5.3.2. Talent shaking tube with water, with ethanol container visible in frame

5.4. After removing the ethanol, dry the solid in a 60-degree Celsius oven for 24 hours **[1]** before characterizing the silver zirconium dioxide nanoparticles by a variety of standard microscopy, elemental, and spectroscopic techniques **[2]**.

5.4.1. Talent placing solid into oven
5.4.2. Shot of dried solid NOTE: 2 shots were taken (shot 1: Dried solid without a label, shot 2: dried solid with a label)

6. Plasmonic Catalytic Performance Investigation with and without Localized Surface Plasmon Resonance (LSPR) Excitation

6.1. To investigate the performance of the plasmonic catalyst under light illumination, add 30 milligrams of catalyst to a 25-milliliter round bottom flask with a magnetic stir bar **[1]** and add 5 milliliters of a 0.03-mole/liter nitrobenzene in isopropyl alcohol solution **[2]**.

6.1.1. WIDE: Talent adding catalyst to flask and stir bar *Videographer: Important step*
6.1.2. Talent adding solution to flask, with solution container visible in frame *Videographer: Important step*

6.2. Add 11.22 milligrams of potassium hydroxide powder to the flask **[1]** and bubble the suspension with an argon flow for 1 minutes to purge the reactor **[2]**.

6.2.1. Talent adding powder to flask
6.2.2. Flask contents being bubbled

6.3. Immediately after purging, place the sealed flask in a 70-degree Celsius oil bath above a temperature-controlled magnetic stirrer at 500 revolutions per minute **[1]**.

6.3.1. Talent placing flask into bath above stirrer

6.4. Use four LED (L-E-D) lamps with a 427-nanometer wavelength and a 0.5 Watts/square centimeter light intensity placed exactly 7 centimeters away from the flask to irradiate the solution **[1]** and let the reaction proceed for 2.5 hours at 70 degrees Celsius under vigorous magnetic stirring **[2]**.

6.4.1. Talent turning on lamps around flask *Videographer: Important/difficult step*
6.4.2. Flask contents being stirred *Videographer: Important/difficult step*

6.5. At the end of the incubation, turn off the lights **[1]** and use a syringe and a needle to collect a 1-milliliter sample from the open reactor **[2]**.

6.5.1. Talent turning off lights
6.5.2. Sample being collected

6.6. Then strain the sample through a 0.45-micron filter into a gas chromatography vial to remove the catalyst particulate **[1]**.

6.6.1. Sample being filtered

6.7. To investigate the performance of the plasmonic catalyst in the absence of light irradiation, perform the analysis as just demonstrated **[1]** but with the reaction container wrapped with aluminium foil to protect it from light **[2]**.

6.7.1. Talent adding catalyst to flask
6.7.2. Talent wrapping flask with foil

7. Gas Chromatography (GC) Analysis

7.1. For gas chromatograpic analysis, prepare 10 milliliters of isopropyl alcohol solution containing approximately 30 millimoles/liter of nitrobenzene, 30 millimoles/liter of

aniline, and 30 millimoles/liter of azobenzene **[1]** and run gas chromatography analysis on the solution according to standard protocols **[2]**.

7.1.1. WIDE: Talent adding NB to container (volumetric flask with IPA), with NB, AN, AB, and IPA containers (volumetric flasks) visible in frame
7.1.2. Talent adding sample to GC instrument

7.2. The selected method should be able to separate the peaks **[1]** corresponding to isopropyl alcohol **[2]**, nitrobenzene **[3]**, aniline **[4]**, and azobenzene in the minimum period of retention time as illustrated **[5]**.

7.2.1. LAB MEDIA: Figure 5A or Figure 5B
7.2.2. LAB MEDIA: Figure 5A or Figure 5B *Video Editor: please emphasize PriOH peak*
7.2.3. LAB MEDIA: Figure 5A or Figure 5B *Video Editor: please emphasize nitrobenzene peak*
7.2.4. LAB MEDIA: Figure 5A or Figure 5B *Video Editor: please emphasize aniline peak*
7.2.5. LAB MEDIA: Figure 5A or Figure 5B *Video Editor: please emphasize azobenzene peak*

7.3. Once the method has been selected, prepare individual sets of solutions of 50-, 25-, 10-, 5- and 2.5-millimolar nitrobenzene, aniline, or azobenzene in isopropyl alcohol **[1]**.

7.3.1. Talent adding NB to IPA in volumetric flask, with NB, AN, AB, NB-IPA, AN-IPA, and AB-IPA containers (volumetric flasks) visible in frame

7.4. Then run a gas chromatography analysis of each of the prepared solutions **[1]**.

7.4.1. Talent adding sample to instrument

7.5. Each chromatogram should present two peaks **[1]**, with the higher peak corresponding to isopropyl alcohol **[2]** and the lower peak corresponding to nitrobenzene, aniline, or azobenzene as appropriate **[3]**.

7.5.1. LAB MEDIA: 7.5.1. LAB MEDIA.pdf
7.5.2. Use 7.5.1. *Video Editor: please emphasize higher peak*
7.5.3. Use 7.5.1. *Video Editor: please emphasize lower peak*

7.6. For each chromatogram, note the retention time **[1]** and peak area of each peak **[2]**.

7.6.1. Use 7.5.1. *Video Editor: please emphasize retention time for all peaks*
7.6.2. Use 7.5.1. *Video Editor: please emphasize peak for all peaks*

7.7. Then plot the concentration versus peak area of each sample to trace the calibration curve to determine the concentration of each solvent t **[1]**.

7.7.1. LAB MEDIA: 7.7.1. LAB MEDIA.pdf

Protocol Script Questions

A. Which steps from the protocol are the most important for viewers to see?

2.1., 2.3., 3.5., 6.1., 6.4.

B. What is the single most difficult aspect of this procedure and what do you do to ensure success?

6.4. Keep the LED lamps in exact distance from the reaction flask and seal the reaction flask properly to ensure there is no leak of hydrogen gas.

Results

8. Results: Representative Ag-Pd/ZrO_2 NP Plasmonic Catalysis

8.1. Zirconium dioxide does not display bands in the visible range and therefore should not contribute to any photocatalytic activity **[2]**.

8.1.1. LAB MEDIA: Figure 1B
8.1.2. LAB MEDIA: Figure 1B *Video Editor: please emphasize black data line*

8.2. A signal centered at 428 nanometers can be detected for the silver zirconium dioxide nanoparticles **[1]** while the silver-palladium zirconium dioxide nanoparticles display a peak centered at 413 nanometers **[2]**.

8.2.1. LAB MEDIA: Figure 1B *Video Editor: please emphasize red peak at 428*
8.2.2. LAB MEDIA: Figure 1B *Video Editor: please emphasize*

8.3. It is difficult to identify silver-palladium nanoparticles by scanning electron microscopy **[1]** but the formation of nanoparticles with a mean particle size of around 10 nanometers can be visualized by transmission electron microscopy **[2]**.

8.3.1. LAB MEDIA: Figure 2A
8.3.2. LAB MEDIA: Figure 2B *Video Editor: please emphasize small spheres and/or add/emphasize arrows emphasizing small spheres*

8.4. After the reaction, the conversion and selectivity for the formation of azobenzene and aniline can be measured by gas chromatography **[1]**.

8.4.1. LAB MEDIA: Figure 5

8.5. In the absence of catalysts **[1]**, no nitrobenzene conversion is detected in the presence or absence of light illumination **[2]**.

8.5.1. LAB MEDIA: Figure 6 and Table 1
8.5.2. LAB MEDIA: Figure 6 and Table 1 *Video Editor: please emphasize Blank data row*

8.6. For silver zirconium dioxide nanoparticles, no conversion is detected in the dark **[1]**, while a 36% conversion is observed under LSPR (L-S-P-R) excitation **[2]**.

8.6.1. LAB MEDIA: Figure 6 and Table 1 *Video Editor: please emphasize red Dark data bar in Figure 6A and Ag/ZrO2 Dark Condition and Conversion data cells*
8.6.2. LAB MEDIA: Figure 6 and Table 1 *Video Editor: please emphasize red Light data bar in Figure 6A and Ag/ZrO2 Light Condition and Conversion data cells*

8.7. A 56% selectivity towards azobenzene is also detected **[1]**, indicating that the silver alone can catalyze this reaction under LSPR excitation **[2]**.

8.7.1. LAB MEDIA: Figure 6 and Table 1 *Video Editor: please emphasize red Azobenzene data bar and Ag/ZrO2 Light Azobenzene data cell*
8.7.2. LAB MEDIA: Figure 6 and Table 1

8.8. For the bimetallic silver-palladium zirconium dioxide nanoparticles, no significant conversion is detected under dark conditions **[1]**.

8.8.1. LAB MEDIA: Figure 6 and Table 1 *Video Editor: please emphasize blue Ag-Pd/ZrO2 data bar and AgPd/ZrO2 Dark Condition Conversion data cells*

8.9. Interestingly, under LSPR excitation, the conversion is 63% **[1]** with a 73% selectivity towards azobenzene **[2]**, demonstrating the potential of the bimetallic configuration to not only increase conversion under LSPR excitation but to also control reaction selectivity **[3]**.

8.9.1. LAB MEDIA: Figure 6 and Table 1 *Video Editor: please emphasize blue Light data bar and AgPd/ZrO2 Light Condition Conversion data cell*
8.9.2. LAB MEDIA: Figure 6 and Table 1 *Video Editor: please emphasize blue Ag-Pd/ZrO2 Azobenzene data bar and AgPd/ZrO2 Light Azobenzene data cell*
8.9.3. LAB MEDIA: Figure 6 and Table 1

Conclusion

9. Conclusion Interview Statements

9.1. **Pedro H. C. Camargo**: This reaction is catalytically driven by palladium and plasmonically enhanced by silver under visible-light irradiation. Therefore, controlling the nanoparticle synthesis and selecting the light wavelength for catalysis are important **[1]**.

9.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera (6.4)

9.2. **Erandi Peiris**: The catalytically active metal, palladium, and plasmonically active metal, silver, can be replaced with other combinations of materials to target different types of industrially important transformations **[1]**.

9.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera *Videographer: Can cut for time*