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TITLE:

Photodeposition of Pd onto Colloidal Au Nanorods by Surface Plasmon Excitation

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SHORT ABSTRACT:

A protocol for anisotropic photodeposition of Pd onto aqueously-suspended Au nanorods via localized surface plasmon excitation is presented.

LONG ABSTRACT:

A protocol is described to photocatalytically guide Pd deposition onto Au nanorods (AuNR) using surface plasmon resonance (SPR). Excited plasmonic hot electrons upon SPR irradiation drive reductive deposition of Pd on colloidal AuNR in the presence of $PdCl_4^{2-}$. Plasmon-driven reduction of secondary metals potentiates covalent, sub-wavelength deposition at targeted locations coinciding with electric field "hot-spots" of the plasmonic substrate using an external field (e.g., laser). The process described herein details a solution-phase deposition of a catalytically-active noble metal (Pd) from a transition metal halide salt (H_2PdCl_4) onto aqueously-suspended, anisotropic plasmonic structures (AuNR). The solution-phase process is amenable to making other bimetallic architectures. Transmission UV-vis monitoring of the photochemical reaction, coupled with ex situ XPS and statistical TEM analysis, provide immediate experimental feedback to evaluate properties of the bimetallic structures as they evolve during the photocatalytic reaction. Resonant plasmon irradiation of AuNR in the presence of $PdCl_4^{2-}$ creates a thin, covalently-bound Pd^0 shell without any significant dampening effect on its plasmonic behavior in this representative experiment/batch. Overall, plasmonic photodeposition offers an alternative

route for high-volume, economical synthesis of optoelectronic materials with sub-5 nm features (e.g., heterometallic photocatalysts or optoelectronic interconnects).

INTRODUCTION:

Guiding metal deposition onto plasmonic substrates via plasmonic hot carriers generated from a resonant external field could support 2-step formation of heterometallic, anisotropic nanostructures at ambient conditions with new degrees-of-freedom[1–3]. Conventional redox chemistry, vapor deposition, and/or electrodeposition approaches are ill-suited for high-volume processing. This is primarily due to excess/sacrificial reagent waste, low throughput 5+ step lithography processes, and energy intensive environments (0.01-10 Torr and/or 400-1000 °C temperatures) with little or no direct control over resultant material characteristics. Immersion of a plasmonic substrate (e.g., Au nanoparticle/seed) into a precursor environment (e.g., aqueous Pd salt solution) under illumination at the localized surface plasmon resonance (SPR) initiates externally-tunable (i.e., field polarization and intensity) photochemical deposition of the precursor via plasmonic hot electrons and/or photothermal gradients[3, 4]. For example, protocol parameters/requirements for plasmonically-driven photothermal decomposition of Au, Cu, Pb, and Ti organometallics and Ge hydrides onto nanostructured Ag and Au substrates have been detailed[5–9]. However, utilization of femtosecond plasmonic hot electrons to directly photoreduce metal salts at a metal-solution interface remains largely undeveloped, absent processes employing citrate or poly(vinylpyrrolidone) ligands acting as intermediary charge relays to direct nucleation/growth of the secondary metal[2, 10–12]. Anisotropic Pt-decoration of Au nanorods (AuNR) under longitudinal SPR (LSPR) excitation was recently reported[1, 13] where the Pt distribution coincided with the dipole polarity (i.e., the assumed spatial distribution of hot carriers).

The protocol herein expands upon recent Pt-AuNR work to include Pd and highlights key synthesis metrics that can be observed in real-time, showing the reductive plasmonic photodeposition technique is applicable toward other metal halide salts (Ag, Ni, Ir, etc.).

PROTOCOL:

1. Allocation of Au nanorods

NOTE: Cetyltrimethylammonium bromide (CTAB)-covered AuNR may be synthesized by wet-chemistry (step 1.1) or purchased commercially (step 1.2) according to the reader's preference, with each yielding similar results. Results in this work were based on commercially-sourced, AuNR with penta-twinned crystal structure. Impact of AuNR seed crystal structure (i.e., monocrystalline vs. penta-twinned) on ultimate morphology of the secondary metal shell remains unclear within the scope of plasmonic photodeposition, but has been of keen interest in both wet-[14, 15] and similar photo-chemical[12] syntheses. Alternative surfactants to CTAB may be employed so long as Zeta-potential is positive, although final Pd morphology could change.

1.1. Synthesis Techniques: Synthesize aqueously-dispersed AuNR at 0.5 mM Au using the silver-assisted method by Nikoobakht *et al.*[16, 17] (yielding monocrystalline structure) or the surfactant-assisted method by Murphy *et al*.[18, 19] (yielding penta-twinned crystal structure). Wash the AuNR via centrifugation[20, 21] to remove excess, free CTAB to a final concentration of 1-10 mM.

1.2. Commercial Sources: Purchase aqueous AuNR dispersions at 0.5 mM Au with the following specifications: 40 nm diameter, 808 nm LSPR, and CTAB ligand (5 mM concentration) in DI water. Wash the AuNR via centrifugation[20, 21] to remove excess, free CTAB if the CTAB concentration exceeds 1-10 mM upon receipt.

NOTE: Aqueous AuNR dispersions with CTAB surfactant at a variety of sizes, aspect ratios, and particle number densities may be purchased from many commercial vendors and used successfully in this protocol.

2. Plasmonic photodeposition of Pd onto Au nanorods

2.1. Preparation of Pd precursor

2.1.1. Prepare a 20 mM HCl solution. First, make 0.1 M HCl by diluting 830 µL of stock concentrated HCl (37%, 12 M) with water to 100 mL. Second, make 0.02 M HCl by diluting 4 mL of 0.1 M HCl with water to 20 mL.

2.1.2. Pipette 10 mL of 20 mM HCl into appropriate glassware and place in a bath sonicator (no sonication) with water temperature set to 60 °C.

2.1.3. Add 0.0177 g of $PdCl_2$ into the 10 mL of 20 mM HCl and mix via sonication until all $PdCl_2$ is dissolved. The resultant 10 mM H_2PdCl_4 solution should exhibit a dark orange color.

2.2. Preparation of photodeposition reaction mixture

NOTE: The procedure described assumes a 3 mL total volume for use in a cuvette to allow real-time feedback into plasmonic photodeposition process. The cited masses/volumes were selected for compatibility with typical chemicals/materials/reagents while allowing facile washing/recovery of the Pd-decorated AuNR. It is anticipated that similar results may be achieved if scaled to other volumes and/or alternative reaction vessels are used (e.g., glass beaker).

2.2.1. Degas stock AuNR solution and methanol (MeOH) in a bath sonicator for 30 min.

2.2.2. Pipette 2.5 mL of aqueously-suspended AuNR (from step 2.2.1) into a 1 cm path length, macrovolume cuvette with a magnetic stir bar. Place the cuvette on a stir plate.

NOTE: Typical volume of a macrovolume cuvette is 3.5 mL. Quartz may be substituted with UV-transparent plastics.

2.2.3. Pipette 475 µL of degassed MeOH (from step 2.2.1) into the cuvette while gently stirring for approximately 15-30 min. Periodically remove any bubbles by gently tapping the bottom of the cuvette against a rigid surface as needed; removing solvated gasses can prolong the stability of the metal halide salt.

2.2.4. Pipette 5 µL of stock concentrated HCl (37%, 12 M) into the cuvette and let mix for 15 min.

NOTE: Tuning concentration of HCl support could influence final morphology/rate of Pd deposition, but concentrations less than 20 mM in the reaction mixture will allow H_2PdCl_4 to progressively hydrolyze and oxolate, leading to eventual PdO_x formation after ~3 h.

2.3. Plasmonic photoreduction of $PdCl_4^{2-}$ onto AuNR[1, 13]

2.3.1. Inject 25 µL of 10 mM H_2PdCl_4 into the reaction mixture for a 1:5 Pd:Au atomic ratio. Let the solution complex in dark for 1 h while stirring.

NOTE: This quantity may be adjusted according the desired Pd:Au ratio as the expense of altering the final molarities of Au, $PdCl_4^{2-}$, HCl, and MeOH of the reaction mixture. Reference[22] illustrates example Pt-AuNR morphologies at different Pt:Au ratios- similar results can be expected with Pd.

2.3.2. Irradiate the reaction mixture with an un-polarized, 715 nm long-pass filtered tungsten-halogen lamp at 35 mW/cm^2 intensity for 24 h.

NOTE: Different light filters (or sources, e.g., laser) may be chosen according to unique LSPR wavelength for different Au nanostructure seeds. For example, a 420 nm long-pass filter may be used for plasmonic seed structures exhibiting LSPR at 450 nm. Light intensity may be decreased with neutral density filtration at the expense of a slower $PdCl_4^{2-}$ reduction rate, leading to a longer total reaction time. Light intensity may be increased to reduce reaction time at the expense of potential for thermal reduction of $PdCl_4^{2-}$ (onset is ~360 °C via Reference[23]). An appropriate intensity can be calculated *a priori* to mitigate thermal reduction via calculation of nanoparticle surface temperature in isolation and/or collective ensembles[24]. Effects on ultimate Pd-AuNR morphology from varying irradiation intensity have not been explored.

2.3.3. Wash the residual chemicals/reagents from the Pd-AuNR two times, each by: centrifugation at 9000 x *g*, removing the supernatant with a pipette, re-suspending the Pd-AuNR pellet in water, and immersing the vial into a bath sonicator for 1-2 min to disperse[20, 21].

REPRESENTATIVE RESULTS:

Transmission UV-vis spectra, X-ray photoelectron spectroscopy (XPS) data, and transmission electron microscopy (TEM) images were acquired for the CTAB-covered AuNR in the presence/absence of H_2PdCl_4 in dark and under resonant irradiation at their longitudinal SPR (LSPR) to catalyze nucleation/growth of Pd. Transmission UV-vis spectra in **Figure 1** and **Figure 2** provide insights into the reaction dynamics according to changes in: (a) precursor ligand-metal charge transfer (LMCT) feature intensity and wavelength and (b) nanorod SPR intensity, full width at half maximum (FWHM), and wavelength (λ). XPS is used to confirm presence of metallic Pd and covalent Pd-Au bonding. XPS is also used to characterize the composite valence band density-of-states (DOS) of the bimetallic nanostructures, shown in **Figure 3**. TEM images and energy dispersive spectroscopy (EDS) maps in **Figure 4** determine the structural morphology and size distribution of the Pd-decorated AuNR.

Figure 1 shows representative UV-vis-NIR absorbance trends upon sequential, step-by-step addition of each chemical component comprising the reaction mixture, beginning with 2.5 mL of stock 0.5 mM AuNR (dashed black). Addition of 475 µL of MeOH as a sacrificial hole scavenger and 5 µL of 12 M HCl (solid black) decreases absorbance magnitude across the UV and visible spectrum due to simple dilution. A ~5-8 nm blue-shift in the longitudinal SPR (LSPR) wavelength upon HCl addition is typical, which likely arises from screening by the solvated Cl^- anions[25]. Addition of 25 µL of 10 mM H_2PdCl_4 (dashed and solid blue) causes high intensity UV absorbance features to emerge, which correspond to LMCT bands of $[PdCl_4]^{2-}$. LMCT bands are characteristic of metal halide salts[26, 27]. After equilibrating in the dark for 1 h with the CTAB-covered AuNR in 20 mM HCl, the $[PdCl_4]^{2-}$ molecules exhibit LMCT features at approximately 247 nm and 310 nm. Upon light irradiation resonant with the AuNR LSPR (dark red), the $[PdCl_4]^{2-}$ LMCT bands respectively blue-shift to 230 nm and 277 nm within a few minutes, and their molar absorptivity appears to decrease. Absorbance magnitude of the L_πMCT band decreases from 1.7 to approximately 0.47 over the course of 24 h due to progressive photoreduction of $[PdCl_4]^{2-}$ (dark red through yellow) by the excited AuNR via plasmonic hot electrons[1, 13]. Precursor LMCT features in the UV region disappear after 24 h (yellow), which indicates full consumption of $[PdCl_4]^{2-}$. Transverse SPR (TSPR) and LSPR features begin red-shifting as the $[PdCl_4]^{2-}$ LMCT bands lower simultaneously. Temperature of the reaction vessel may be monitored concomitantly (e.g., via thermocouple) to ensure plasmonic photothermal damping does not increase the bulk temperature above the ~360° C onset temperature for $[PdCl_4]^{2-}$ reduction[23]. Typical steady-state temperatures range from 26-32 °C under these experimental conditions without ambient convection.

Figure 2 shows the TSPR and LSPR of the doubly washed particles before (black) and after (red) resonant irradiation in the presence of adsorbed $[PdCl_4]^{2-}$. The LSPR wavelength red-shifts from 807 nm to 816 nm along with a 5% FWHM expansion. The TSPR remains unchanged. Absorbance magnitude at wavelengths below ~400 nm is increased by ~40-55%, due to both changes in and accrued interband metal absorption after apparent photodeposition of Pd.

XPS analysis in **Figure 3A** confirm presence of metallic Pd by the emergence of Pd 3d lines at 335 eV and 340 eV binding energies. Note that Au exhibits convoluting 4d photoelectron line in this binding energy region as well, but is suppressed after photoreduction of $[PdCl_4]^{2-}$ that covers AuNR with Pd. A ~0.5 eV shift in the Au 4f photoelectron lines to lower binding energies in Figure 3B is indicative of covalent Au-Pd interaction[28, 29]. The valence band DOS after Pd photodeposition in Figure 3C exhibit a higher DOS near the Fermi level, E_F (i.e., binding energy of 0 eV) and moves the *d*-band onset toward the E_F [13]. These are typical characteristics of metallic Pd and may be calculated *a priori* using density functional theory (DFT)[13].

TEM analysis in **Figure 4A,B** reveal the respective structural morphologies of the AuNR mixed with H_2PdCl_4 in the dark (**Figure 4A**, blue) and under LSPR irradiation (**Figure 4B**, red). Sharp-tipped Pd-AuNR are observed as a result of Pd photoreduction by plasmonic hot electrons generated under LSPR irradiation. These sharp nanorod tips coincide with the end Au (111) facets that are characteristic of the penta-twinned AuNR seeds[30]. Such exacerbated end facets are not observed for AuNR mixed with H_2PdCl_4 in the dark. Size distribution analysis of rod lengths in **Figure 4C** indicates LSPR irradiation expands mean rod length from 127 nm to 129 nm, due to presence of photoreduced Pd. An apparent sub-2 nm Pd thickness is confirmed in an energy dispersive spectroscopy (EDS) map of a representative Pd-AuNR, shown in Figure 4D. No change in rod diameter is observed (39.1 nm under dark condition versus 39.2 nm under LSPR irradiation). Overall rod AR increases from 3.27 to 3.30 (±0.34) due to the increase in nanorod length. These size population metrics are consistent with the small 7 nm LSPR red-shift measured in Figure 2.

FIGURE AND TABLE LEGENDS:

Figure 1: Transmission UV-vis spectroscopy analysis of the AuNR-H_2PdCl_4 reaction mixture. The spectra showing typical LMCT and SPR absorbance features upon sequential addition of MeOH (solid black) and H_2PdCl_4 (dashed blue) to a stock 0.5 mM AuNR solution (dashed black). After 1 h equilibration in the dark (solid blue), broadband LSPR irradiation with a 715 nm long-pass filter (35 mW/cm^2; red shaded area) catalyzes photoreduction over a 24 h timespan (solid red → yellow, 2 h time-steps). MeOH consumption as the reaction progresses is observable around 950 nm. Arrows guide the eye to show trends in LMCT wavelength shifts with time.

Figure 2: Transmission vis-NIR spectroscopy analysis of SPR modes of doubly washed AuNR before (black) and after addition + photoreduction of H_2PdCl_4 (red). Respective shifts in resonant wavelength (Δ λ) and bandwidth expansion (Δ FWHM) of the TSPR and LSPR modes after photoreduction of H_2PdCl_4 are inset. Accrued interband Pd absorption is evident below ~480 nm.

Figure 3: XPS analysis of AuNR before (black) and after LSPR irradiation in presence of H_2PdCl_4 (red). (A) Au 4d and Pd 3d region showing respective spin-orbit split 5/2 and 3/2 lines. **(B)** Au 4f region showing spin-orbit split 7/2 and 5/2 lines. **(C)** Valence band DOS region, where 0 eV binding energy is the Fermi level (E_F).

Figure 4: TEM analysis of AuNR in the presence of H_2PdCl_4 in dark versus LSPR illumination. (A) TEM micrographs of AuNR mixed with H_2PdCl_4 in dark for 24 h and washed 2x. **(B)** TEM micrographs of AuNR mixed with H_2PdCl_4 under LSPR excitation for 24 h and washed 2x. **(C)** Cumulative distribution function (CDF) of nanorod lengths, where blue and red correspond to the dark and light conditions, respectively. **(D)** EDS mapping of Au (purple) and Pd (green) signals at the tip of on representative nanorod that was resonantly irradiated in the presence of H_2PdCl_4.

DISCUSSION:

Monitoring changes in optical absorbance using transmission UV-vis spectroscopy is useful to assess status of the photocatalytic reaction, with particular attention to the LMCT features of H_2PdCl_4. Wavelength maxima of LMCT features after injection of H_2PdCl_4 at step 2.3.1 (going from solid black to solid blue in **Figure 1**) provide insights into the local "environment" of the $[PdCl_4]^{2-}$ molecules[1] (e.g., electrostatic coordination with N^+ headgroups of CTAB followed by transport to the AuNR surface[1] and/or molecular speciation consequent of hydrolysis and/or oxolation[31–33]). Magnitude of LMCT features during irradiation (dark red through yellow in **Figure 1**) quantifies the concentration of H_2PdCl_4 remaining in solution as the precursor is progressively photoreduced to Pd^0 during LSPR irradiation. If the LMCT features do not decrease in magnitude during irradiation, then the photocatalytic reaction is not taking place (CTAB concentration could be too high and additional washing is recommended). A flattening of the long-wavelength tail on the Lorentzian LSPR feature should occur around 950 nm (see "MeOH consumption" label in **Figure 1**) during LSPR irradiation as a result of the sacrificial MeOH scavenging hot holes at the AuNR surfaces[12] to maintain charge neutrality[1]. The SPR modes may be monitored during the reaction, but their wavelengths and intensities appear to hold little *quantitative* information with regards to the progressive status of the reaction[1]. This is due to the multitude of convoluting effects from parallel changes in (i) the precursor electrolyte environment over time (e.g., effective solvent refractive index and/or tail of precursor d→d band) vs. (ii) morphological changes (e.g., rod elongation). If the solution exhibits a dark brown/orange color after ~3 h with broad, feature-less UV absorbance, then it is likely PdO_x has formed. Any residual, unconsumed H_2PdCl_4 will be evident in XPS analysis where the divalent Pd 3d lines (i.e., Pd^{2+}) will occur approximately 2.5 eV higher in binding energy than the metallic lines shown in **Figure 3**.

Minute changes in final LSPR wavelength after Pd photodeposition, as shown in **Figure 2**, are typical of the plasmonic photodeposition process when using NR seeds[1]. Other seed structures or Pd:Au atomic ratios, however, may result in more drastic shifts and remain to be examined. A core-shell growth mechanism, where LSPR is governed by the overall rod aspect ratio,[1, 34] appears to be responsible for the minutely changed LSPR. For example, a mean length growth of 4.7 nm was recently reported for Pt photodeposited onto AuNR under similar conditions which lead to an AR increase from 4.4 to 4.7 (±1.0) and followed an anisotropic core-shell growth mechanism[1]. This in stark contrast to wet-chemical methods reporting dumbbell-like morphologies that yield 50-250 nm LSPR red-shifts for nanorods[22, 35–37]. Ultimate Pd thickness can be increased by an adding additional H_2PdCl_4 in protocol step 2.3.1 (e.g., total of 62.5 µL of 10 mM H_2PdCl_4 for a 1:2 Pd:Au atomic ratio). FWHM expansions in the LSPR appears to predominantly be consequent of Pd deposition polydispersity[38], as opposed to a damping signature[1].

The penultimate structural morphology resultant from the plasmon-driven photoreduction of metal salts, such as H_2PdCl_4, is hypothesized to be governed by the spatial distribution of plasmonic hot electrons under LSPR excitation whose absorbed energy exceeds the reduction potential of the precursor[1, 22, 39]. Although only yet demonstrated for Pd and Pt[1, 13], the technique is anticipated to be amenable to other metals, such as Ag, Ni, Ir, Cu, Co, Ru, etc. This makes it a potentially powerful and flexible technique for synthesizing heterometallic plasmonic structures with sub-5 nm features- in particular, for plasmonically-sensitized photocatalysts. At its current stage, the technique is limited to solution-phase deposition onto colloidally-suspended plasmonic metals. The potential exists to perform *reductive* plasmonic photodeposition in gaseous-phase environments (e.g., in a chemical vapor deposition furnace) for high-volume processing, but remains to be explored.

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DISCLOSURES:

The authors have nothing to disclose.

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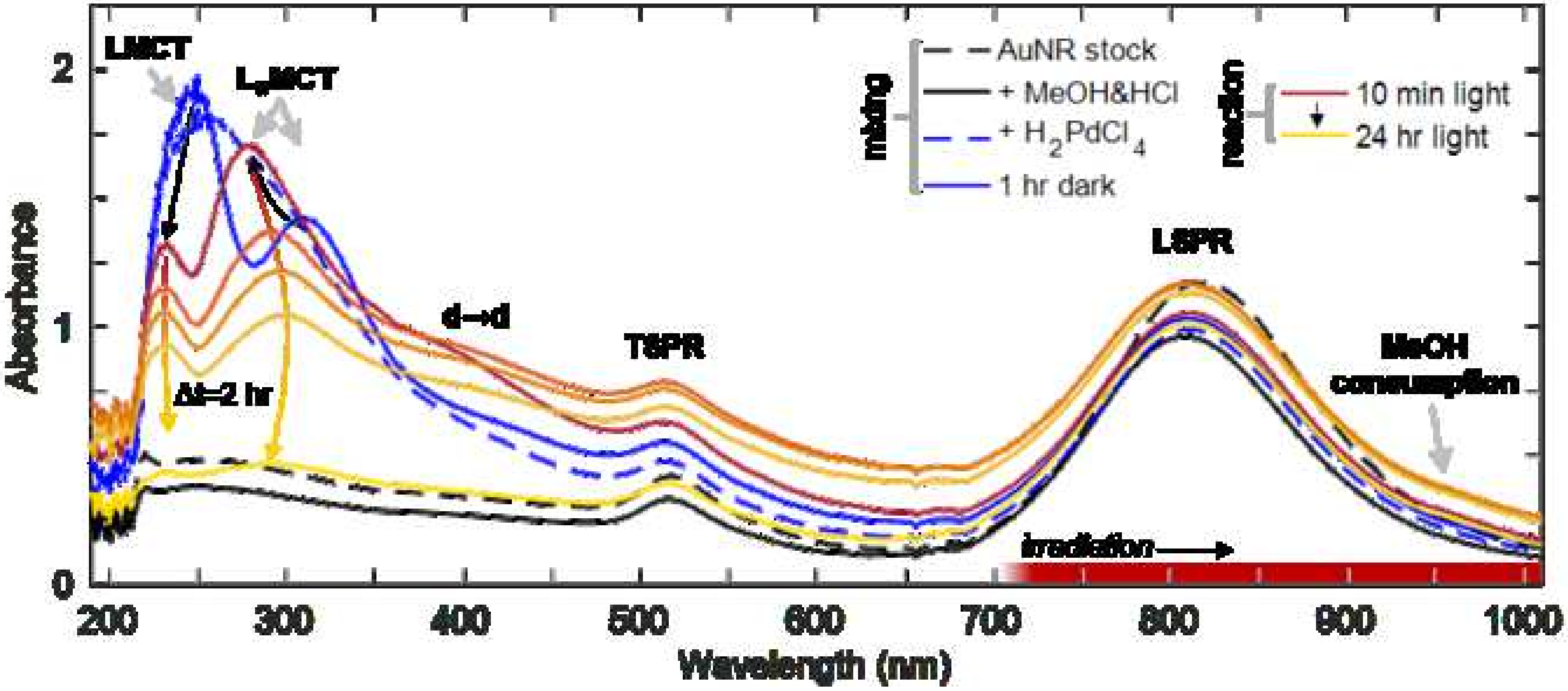
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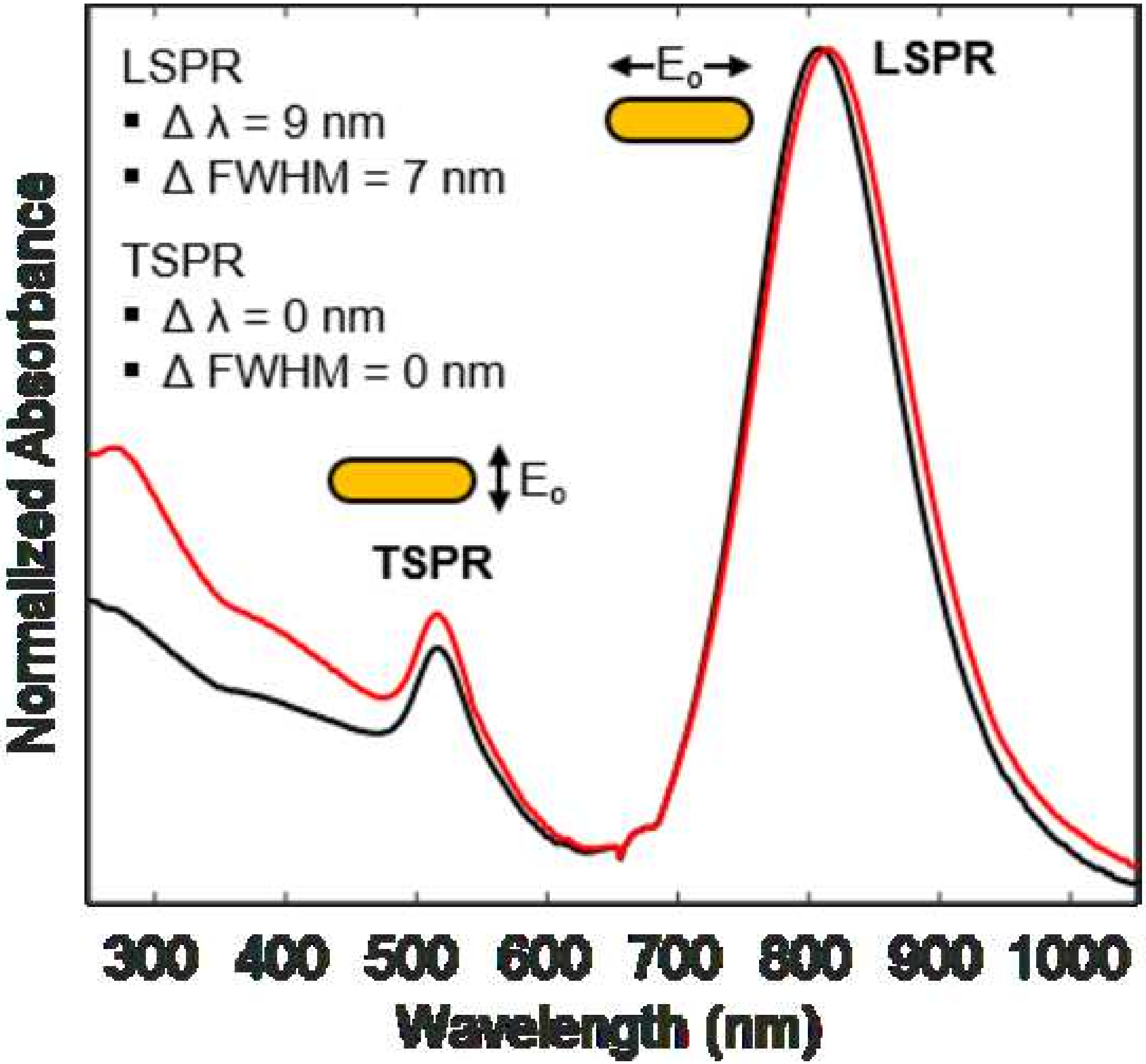
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▪ Δ FWHM = 7 nm
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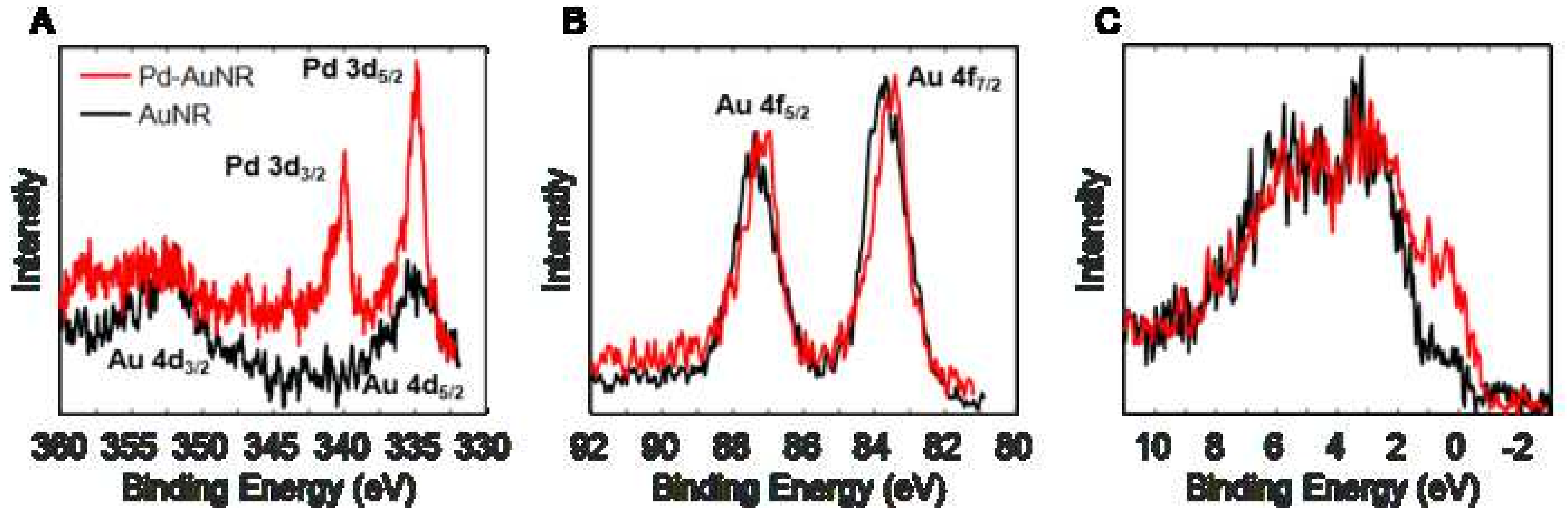
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Au $4f_{7/2}$
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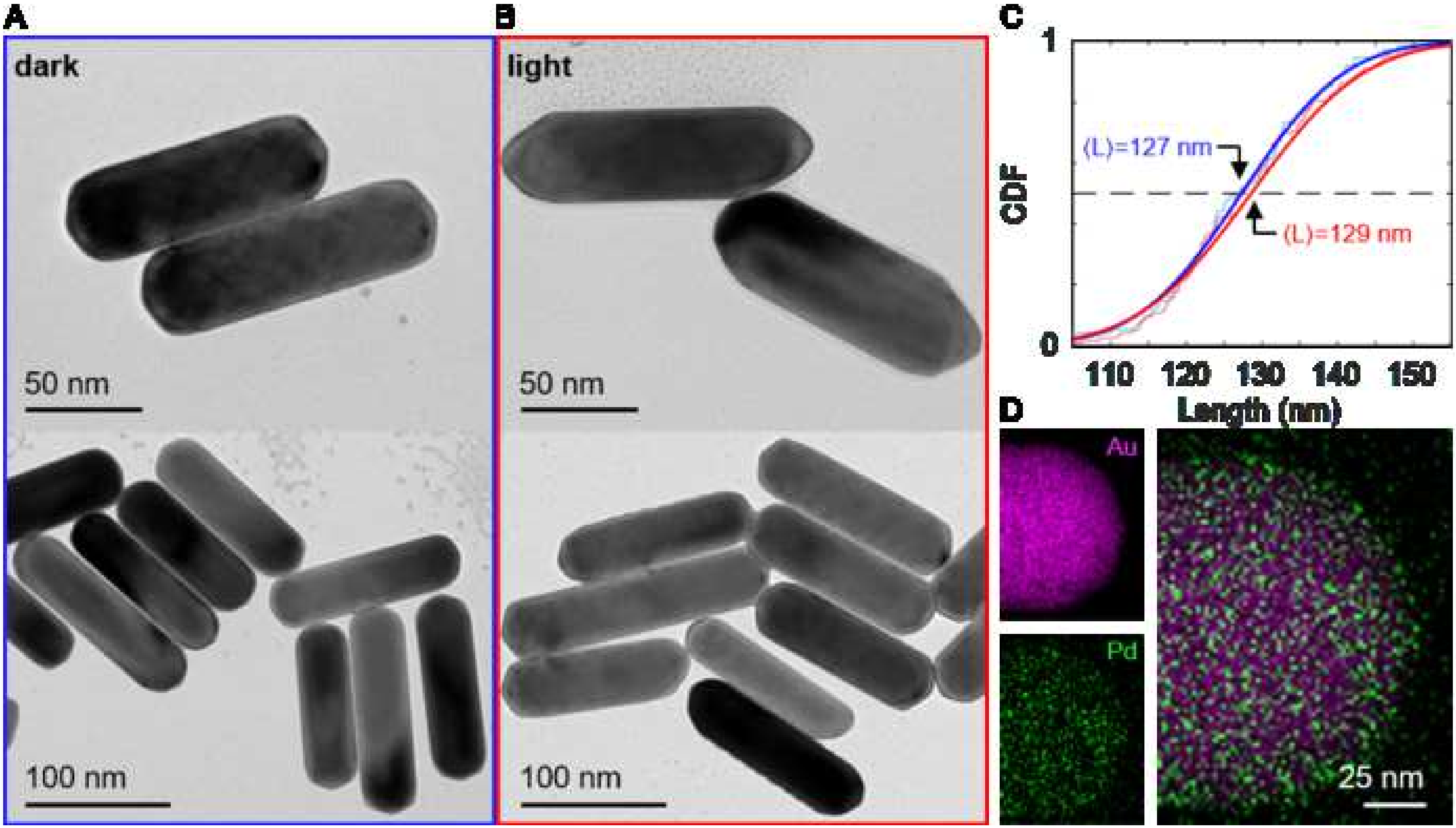
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Name of Material/ Equipment	Company	Catalog Number
Aspheric Condenser Lens w/ Diffuser	Thorlabs	ACL5040U-DG15
Deuterium + Tungsten-Halogen Lightsource	StellarNet	SL5
Gold Nanorods, AuNR	NanoPartz	A12-40-808-CTAB
Ground Glass Diffuser	Thorlabs	DG20-1500
Hydrochloric acid, HCl	J.T. Baker	9539-03
Low Profile Magnetic Stirrer	VWR	10153-690
Macro Disposable Cuvettes, UV Plastic	FireFlySci	1PUV
Methanol, MeOH	J.T. Baker	9073-05
Palladium (II) chloride, $PdCl_2$	Sigma Aldrich	520659
Plano-Convex Lens	Thorlabs	LA1145
Quartz Tungsten-Halogen Lamp	Thorlabs	QTH10
UV-vis Spectrometer	Avantes	ULS2048L-USB2-UA-RS

Comments/Description
f=40 mm, NA=0.60, 1500 grit, uncoated
CTAB surfactant, 808 nm LSPR, 40 nm diameter
1500 grit, N-BK7
concentrated, 37%
10 mm path length
≥99.9%
≥99.9%
f=75 mm, N-BK7, uncoated
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13 May 2019

Bing Wu
Review Editor, Chemistry / Biochemistry
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Re: JoVE60041, rev. 2

Dear Dr. Wu:

Thank you for considering publication of the revised manuscript. The manuscript has been again revised to address the second round of editorial comments. We anticipate these revisions will further increase the value of the manuscript for the readers of the *Journal of Visualized Experiments*. Editorial comments are copied below verbatim and followed by corresponding revisions made to the manuscript.

Editorial Comments

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

> **Author Reply**: The authors confirm the manuscript was proofread to mitigate spelling and/or grammar issues, and none exist to the authors knowledge.

2. The representative results should refer to all figures.

> **Author Reply**: The authors confirm that all figures, including respective parts (i.e., A, B, etc.), from the Representative Results are discussed.

3. Figure 2: Please add a short description of the figure in Figure Legend.

> **Author Reply**: The Figure 2 caption was revised to include a short description: "**Transmission vis-NIR spectroscopy analysis of SPR modes of doubly washed AuNR before (black) and after addition + photoreduction of H_2PdCl_4 (red).** Respective shifts in resonant wavelength (Δ λ) and bandwidth expansion (Δ FWHM) of the TSPR and LSPR modes after photoreduction of H_2PdCl_4 are inset. Accrued interband Pd absorption is evident below ~480 nm.

4. Reference 34: Please do not abbreviate journal titles for references.

> **Author Reply**: The journal title of Reference 24 was un-abbreviated to read "Journal of Materials Chemistry."

I appreciate your consideration of this revised video protocol manuscript.

Sincerely,

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