Nanoengineering Instrumentation to Control the Optical Properties of Plasmonic Nanoparticles for Thin Film Optics

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ABSTRACT

Plasmonic nanoparticles are desirable for a wide range of applications and act as the base nano-building blocks for thin film optics and optical metamaterials. The properties and applicability of plamsonic materials are considerably influenced by their size, shape, charge, and agglomeration, all of which contribute to their optical properties. There is a range of top-down and bottom-up engineering processes now available for synthesizing these nanomaterials. However, the majority of current fabrication methods are thermally based which give rise to broad particle polydisersity and require strong reducing agents. Our research has developed a new nanoengineering instrument that is capable of synthesizing plasmonic nanoparticles to a desired optical specification. This novel synthesizing method provides excellent spatial and temporal control, avoids harmful strong reducing agents, and can be synthesis at room temperature. The underlying technology functionalizes seed nanoparticles and utilizes a photochemical reaction to activate the higher order plasmon modes from a seed nanoparticle solution to finely tailor the morphology of the nanoparticles in order to provide a desired optical response. This is achieved through intramolecular α-hydrogen abstraction of arylcycloalkyl ketones through the Norrish type II reaction. The end product yields a colloidal solution with optical properties that have been tuned and tailored by pure spectral radiation. Utilizing this technology could enable a manufacturing route for optical metamaterial building blocks in a repeatable and reliable fashion that assist hierarchical assembly techniques.

Keywords: Nanoengineering, Plasmonics, Nanoparticles, Optical Properties, Thin Film Optics

1. INTRODUCTION

Due to their high surface area and exceptional electronic, optical, magnetic, and catalytic properties, nanoparticles (NPs) provide an exciting opportunity, with their chemical and physical characteristics differing from their bulk equivalent. A rapidly expanding area of research right now is the creation of useful nanoparticles for specific applications. Due to the persistent and ever-increasing demand for nanomaterials, new and effective synthesis techniques require development. One particular material of choice is silver. Silver nanoparticles (AgNPs) and nanostructures provide valuable properties for many applications and are heavily targeted as a material of choice. Like many nanomaterials, AgNPs are significantly influenced by their size, shape, and optical properties.

AgNPs can be created using a variety of techniques, which can also be used to modify their shape and size. The most available method being thermal synthesis. Although the thermal synthesis of the difference shapes (plates, dodecahedra, rods, etc.) is often quick, it produces a wide range of particle polydispersities, necessitates strong reducing agents, and frequently occurs at high temperatures. Additionally, photochemical techniques have been developed for the synthesis of nanostructures. The benefits of photochemical approaches include superior spatial and temporal control, the avoidance of dangerous and harmful reducing agents, and the fact that they are typically performed at room temperature.

This research progresses current photochemical techniques and introduces a nanoengineering instrumentation to control the optical properties of silver nanoparticles. The procedure outlines a photochemical synthesis of spherically stabilized, citrate-modified AgNPs that are then used to create a variety of nanostructures with predictable and controllable size and morphology when exposed to narrowband LED lighting. The illumination and process is centrally controlled in a close-loop system to actively monitor and adjust the process to stabilize the solution and direct the growth and morphology. The instrument enables a direction to manufacture repeat batches of AgNPs with desired optical properties. The applications are far reaching with this paper demonstrating its usefulness for optical thin film filters and metamaterial building blocks.

2. METHODOLOGY

The synthesis of the fundamental silver ion solution was prepared by mixing together 0.2mM $AgNO_3$, 0.2mM 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (*photo initiator*), and 1mM trisodium citrate. The prepared solution was purged in a Nitrogen environment prior to the exposure of UV light in order to maximize the efficiency of the photo initiator. The seed solution was developed post purge, within the instrumentation presented in this paper, by a collective array of UV LED sources (*270nm, 275nm, 365nm, 380nm, 400nm, and 405nm*) for 10 minutes; which produces a dark yellow coloration salutation due to the dipole absorption of spherical AgNPs. Once the seed solution has been developed within the instrument and confirmed by the optical sensors, the "tuning" LED light source is activated and enables the anisotropic growth of AgNP seeds to alter the resonance and adjust the optical properties to the desired outcome. The instrument environment is air as the reaction requires O_2. This process is simple, quick and enables UV-Vis spectroscopy for real-time kinetics monitoring.

3. NANOENGINEERING INSTRUMENTATION

3.1 Chemistry

The photo initiator has an absorption peak at ~272 nm wavelength that can be excited by a UV light source to produce the AgNP seed solution. Once excited, the photo initiator experiences a Norish II cleavage reaction that yields ketyl radicals and cross decays to a long-lived triplet state. The ketyl radicals action a strong reduction to reduce Ag^+ to Ag^0. The homolytic breakage of the α-cleavage link, which is promoted by alkylation of the 2-hydroxy group, happens in the picosecond time scale following excitation. After the homoglytic bond scission in the first reaction, the substituted benzoyl radical's final outcome is the formation of the corresponding carboxylic acid 4-(2-hydroxyethoxy) benzoic acid; which, through mild binding, aids in the stability of "naked" metal nanoparticles. Naked nanoparticles do not possess any additional stabilizers. There is an apparent impact of light on the morphology of AgNP during Ag^0 seed development. The result is that different nanostructures with shape and size control are photo generated during the ripening of small spherical AgNP (5nm) seeds, depending on the excitation wavelength from a single or multi-wavelength narrowband light emitting diode illumination source. The electromagnetic field created in the vicinity of AgNP is particularly high, which is related to the size and shape control on the AgNP creation. Work presented by Maillard et al., stated that the synthesis of Ag nanoparticles becomes nonlinear at high light intensities that correspond to the aggregation/coalescence mechanism.

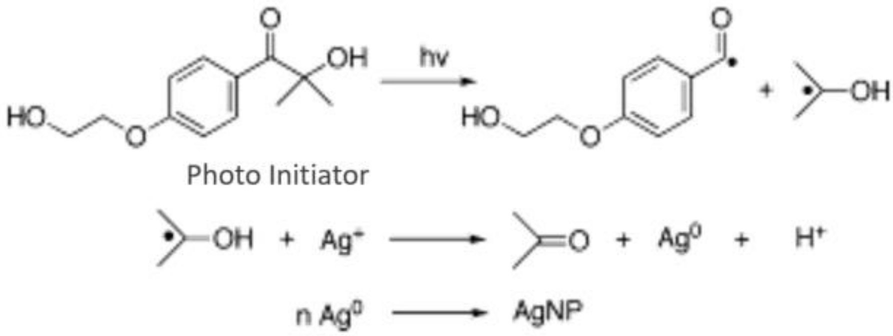

Figure 1. The mechanism for AgNP formation starting from the photo induced bond cleavage of 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone.

3.2 Instrumentation

The development of tuned optical responses from plasmonic nanoparticles relies on the execution of a control system with a feedback loop to take the output response (*optical*) into consideration. This enables the system to adjust its performance to meet the desired output response. The instrumentation relies on an input selection of single or multiple resonance wavelength from the operator. The feedback loop then intermittently monitors the optical absorption of the AgNP solution and actively selects the associated LED source and controls the forward current for a finely tuned wavelength selection. Additionally, the time and thermal response are monitored. Figure 2 illustrates the process for a given light source to interact with the silver seed solution to alter and adjust the growth rate and nanoparticle shape in order to provide a given optical response.

The system is split into two close-loop systems with a single input referring to the desired optical peak absorption wavelength. Once the desired response has been inputted, the system will run a timed cycle to develop the seed solution (*error = actual time – 10 minutes*). Once the 10 minute timer has completed and the spectral response confirms the seed solution, the system will continue to colloidal nanoengineering stage. The optical sensor would monitor the actual optical absorption response and compare it with the input reference. The error signal (*error = required optical response – actual optical response*) is amplified by the controller, and the controller output makes the necessary adjustments. For example if the peak optical response is at 460nm, with a 530nm input, the controller unit may adjust the illumination wavelength or exposure time. Likewise, if the engineered solution is close to the input wavelength it may stop the process so it does not over expose.

The closed-loop configuration is characterized by the feedback signal, derived from the sensor in the system. The magnitude and polarity of the resulting error signal would directly relate to the difference between the required optical response and the actual optical response. Additionally, since the close-loop system has some knowledge of the output condition, through the sensor, it is better prepared to handle any system disturbance or changes in the condition which may reduce its ability to complete the desired task. For example, if the system was started without the chemical solution, the deviation between the absorption is detected by the feedback sensor and the control unit would stop the process. In a closed-loop control system the error signal, which is the difference between the input signal and the feedback signal, is fed to the controller to reduce the systems error and bring the output of the system back to a desired value.

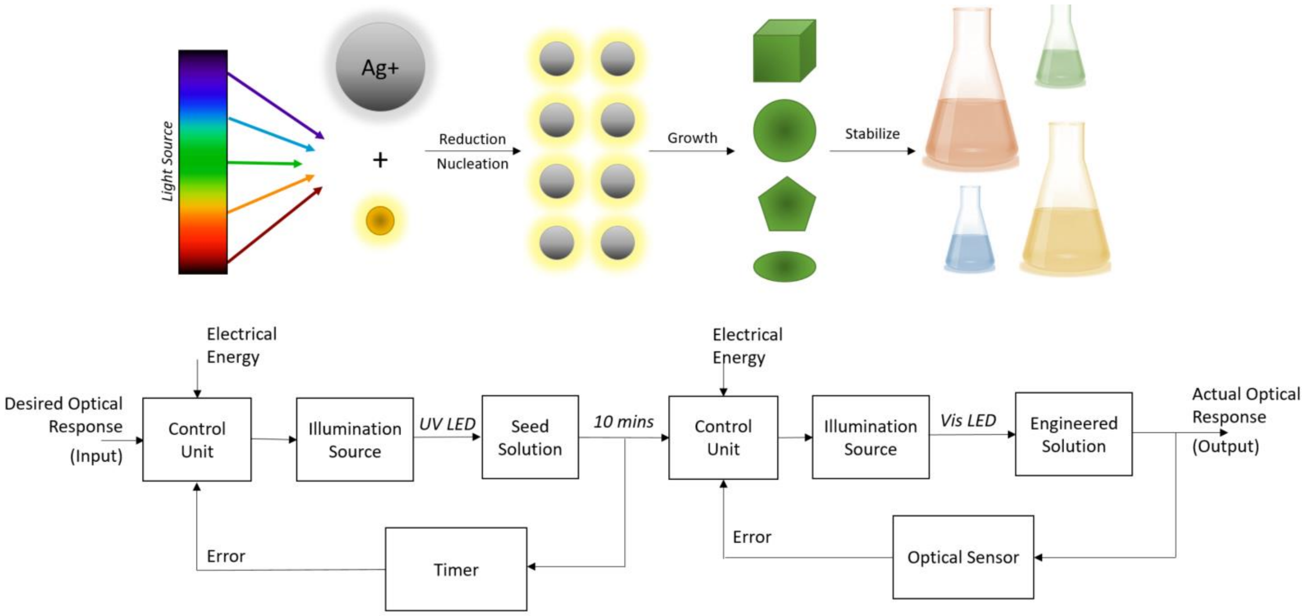

Figure 2. Block diagram for the closed-loop system process to tune the nanoparticle optical response.

The instrument design is based off an integrating sphere design to uniformly reflect the light and concentrates it on the silver colloidal solution situated at the base of the sphere. The system consists of a hollow spherical cavity with an internal aluminium reflective coating. The top of the sphere contains the LED array with 15 different targeted wavelengths, spanning the visible spectrum (*400-700nm*) with four LEDs reserved for the UV range (*270-380nm*). The optical sensor intermittently activates a white light source with its path traversing through the solution to the optical receiver where the absorption spectrum is taken by a spectrometer that feeds into the control unit.

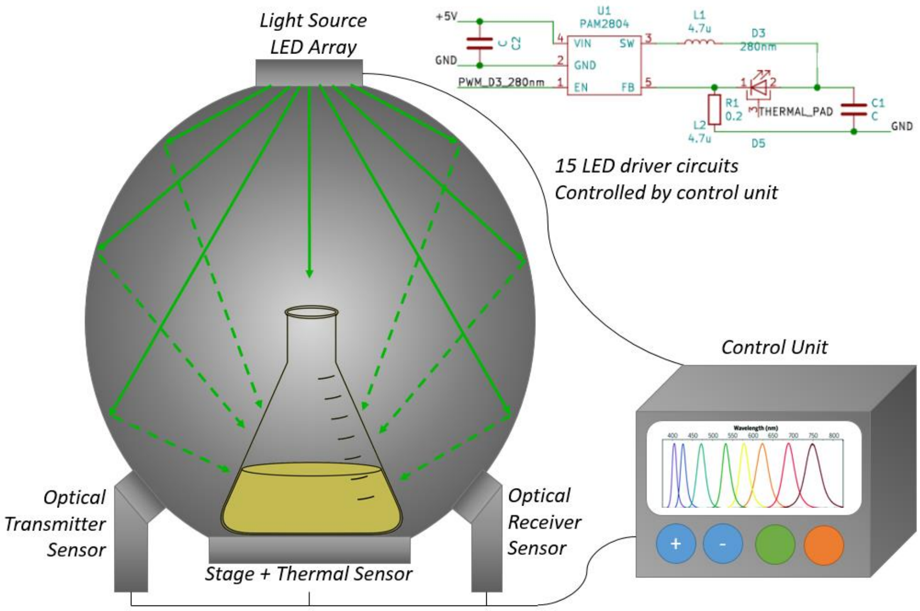

Figure 3. Schematic diagram of the nanoengineering instrumentation based off an integrating sphere.

The instrument has been built through fused deposition 3D printing technology using Polyactic Acid filament material due to its high strength and low thermal expansion with a internal reflective coating. Figure 4 shows the instrument test unit operating at a low voltage (*8.78V:28mA*) for the entire system. The LED wavelength in figure 4 has a peak intensity of 505nm to provide the silver nanoparticles with an optical resonance of 550nm, as inputted into the control unit. This is demonstrated with the figure 4 (*right*) where the seed solution with its distinctive yellow coloration, due to the short wavelength resonance, converts and grows into a pinkish/red color after the peak 505nm LED exposure, due to the red-shift in resonance to ~550nm.

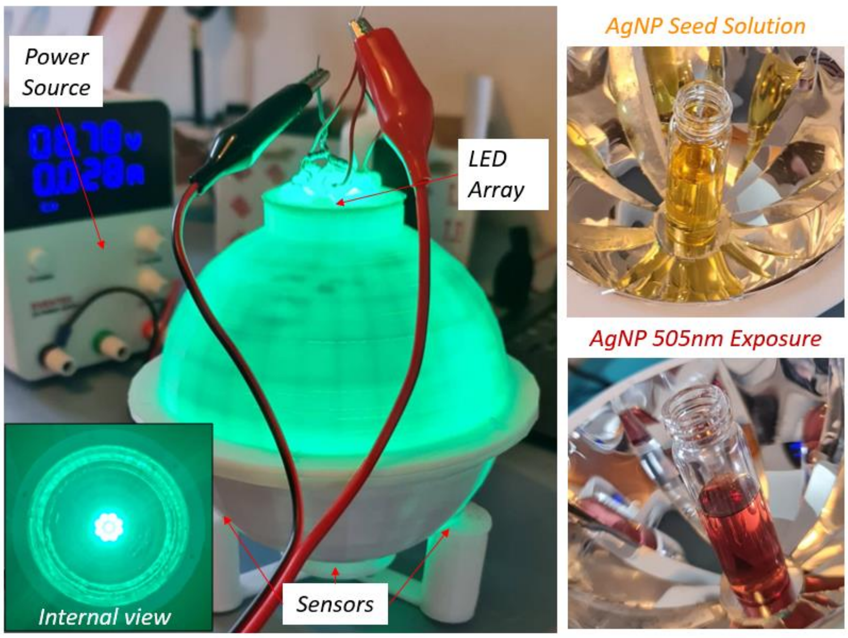

Figure 4. (*Left*) The physical instrument printed by FDM technology and demonstrating the operation at a low voltage. (*Insert*) Show the internal illumination source. (*Right-top*) Picture of the AgNP seed solution after UV exposer. (*Right-bottom*) Picture of the AgNP solution after peak 505nm LED exposure.

3.3 Optical Properties

Mie theory serves as the primary framework for understanding optical absorption and scattering processes. As described by Mie theory, plasmonic nanoparticles have distinctive optical properties depending on the near-field enhancement, size, shape, composition, and surrounding medium, allowing them to be modified to maximize performance for specific applications without altering the material's chemical makeup.

Optical absorption describes how electromagnetic radiation takes up a photon's energy and transforms it into internal energy. Attenuation in light wave intensity as it travels through the medium is a prominent effect of absorption. With far-field effects combining transmission, reflection and absorption, understanding the absorption will enable a description of the transmission for a given material, with the transmitted light through the colloidal solution appearing as the complementary color to the absorption. For example, the absorption of blue light will lead to a yellow-colored solution. Nanoparticle dispersion color can be adjusted by varying the absorption wavelength.

By examining the polarizability, it is possible to comprehend the plasmon resonance of the free electrons in the metal nanoparticle. The polarizability is related to how easily charges, like conduction electrons, can undergo charge dispersion and form partial dipoles on the surface of metal nanoparticles. The quasi-static polarizability of the nanoparticle if given by the following equation.

$$\alpha = (x)\frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + p\varepsilon_2} \qquad (1)$$

Where x is a function of the particle shape, ε_1 is the wavelength dependent permittivity function of the metal nanoparticle and ε_2 is the permittivity function of the surrounding medium, and p is a condition when the particle is driven into resonance resulting in a strong increase in absorption.

Equation (1) provides the foundations to derive the peak absorption wavelength with dependence on the particle shape. As previously discussed, the particle shape and size is formally driven by the illumination wavelength. Thus, a linear estimation for the resonant wavelength can be concluded by the LED peak wavelength.

$$\lambda_{res} = 1.5638\lambda_{LED} - 229.76 \qquad (2)$$

Where λ_{res} is the estimated resonant wavelength and λ_{LED} is the peak wavelength of the illumination LED.

The presence of other plasmonic nanoparticle proximity can affect the optical characteristics of the colloidal solution. Surface plasmons pair when two or more plasmonic nanoparticles are in close proximity to one another due to the collective oscillation of the conduction electrons on each particle surface. Plasmon coupling causes oscillating electrons to assume the lowest energy state, which causes the plasmon resonance wavelength of the connected particles to red-shift to longer wavelengths. This effect is comparable to molecular orbital theory. When nanoparticles aggregate to form the shape, this coupling effect causes the noticeable hue of the plasmonic nanoparticle solution to shift dramatically.

The irradiation of AgNP seeds with three different illumination peak wavelengths has been demonstrated in figure 5a. The LED wavelength results in the spectral change due to the in-plane dipole and weakens the bands below 400nm due to the in-plane and out-of-plane quadrupole plasmon modes. Figure 5b demonstrates the relation to equation (2). The absorption spectra of the different exposed nanoparticles exhibit a broadening absorption at longer wavelengths. It is attributed to the aggregated forms during the photo-conversion.

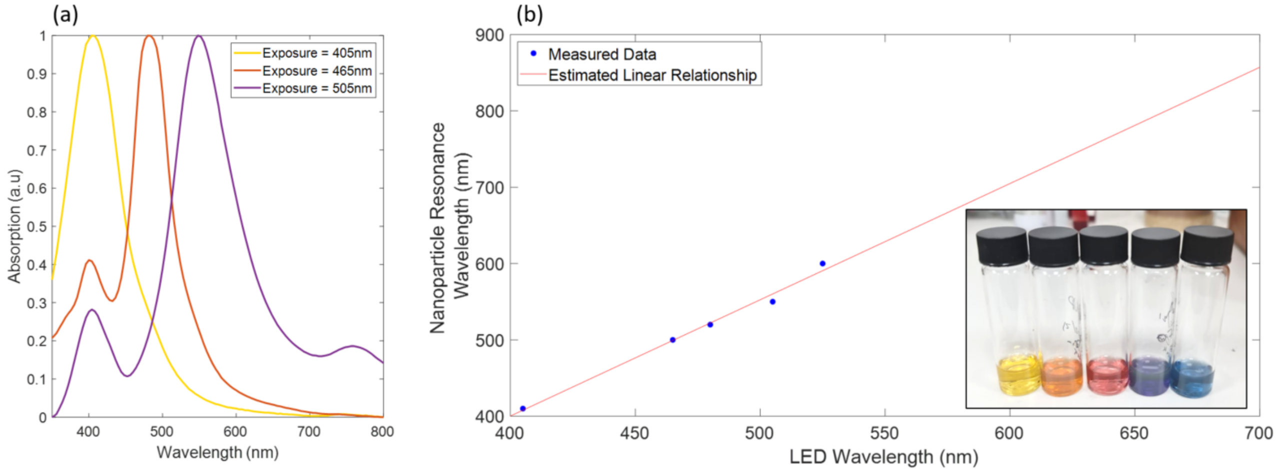

Figure 5. (a) Three examples of colloidal engineered solutions obtained from expose

4. APPLICATIONS

Noble metal nanoparticles have been widely used in a variety of applications due to their distinctive optical characteristics that result from their interaction with an incident light. The realization of precision controlled plasmonic nanoparticle provides applications in biomedicine, nanosurgery, cancer treatment, imaging, color engineering, solar cells, spectroscopy, displays, optics, and more. The rapid advancement in technologies is likely to find many more applications in the coming years for plasmonic nanoparticles. One of the more recent advancements has been in optical metamaterials and thin films.

Metamaterials are composite materials that have been purposely engineered to provide material properties that are not otherwise attainable with ordinary materials. Unlike conventional materials and composites that get their optical properties from their chemistry, metamaterials have an additional design freedom with their optical properties arising from the combination of the chemistry and its physical structures. Metamaterials consist of periodically arranged building blocks called meta-atoms.

Traditionally, thin film dielectric stacks have formulated the solution for filtering light in a multitude of fashions. However, in recent years it has been shown that optical metamaterials could also provide a solution for filtering light. Dielectric thin film filters are an excellent technology that will not be surpassed with ease. Nonetheless, they do have some drawbacks; more noticeably their ability to shift to short wavelengths as the angle of incidence increase. This can be used as an advantage for a lot of technology including chemical sensing. However, it does provide a problem for applications such as laser protection where filtering is required from all angles of incidence.

The effects that dominate angular sensitivity and polarization stability at optical frequencies rely on the materials ability to create a strong electric resonance which in turn creates circulating currents to efficiently drive a magnetic response. The strong electric and magnetic responses lead to an impedance mismatch and angular stability and can be driven by absorption. Therefore the requirement to engineer nanoparticles absorption responses become necessary to solve such solutions and to formulate the metamaterials building blocks.

Figure 6 demonstrates a theoretical example thin film metamaterial design using nanoengineered plasmonic silver particles. The colloidal solution would be subjected to 602nm wavelength illumination source, followed by polymerization and spin coated into a thin film on a glass substrate. The thin film configuration consists of four layers, a low (L), high (H) and medium (M) index dielectric layers that acts as an anti-reflection coating to the metamaterial thin film (E_{MM}).

$$Air \mid LHM(E_{MM}) \mid Glass$$

The theoretical transmission response provides an optical notch filter at 532nm. Unlike conventional dielectric thin film filters, the metamaterial with nanoengineered particles remains shift free for all angles of incidence as demonstrated in figure 6b. This example establishes an application requirement for precision nanoengineering instruments that are capable of tailoring the optical responses to a desired output.

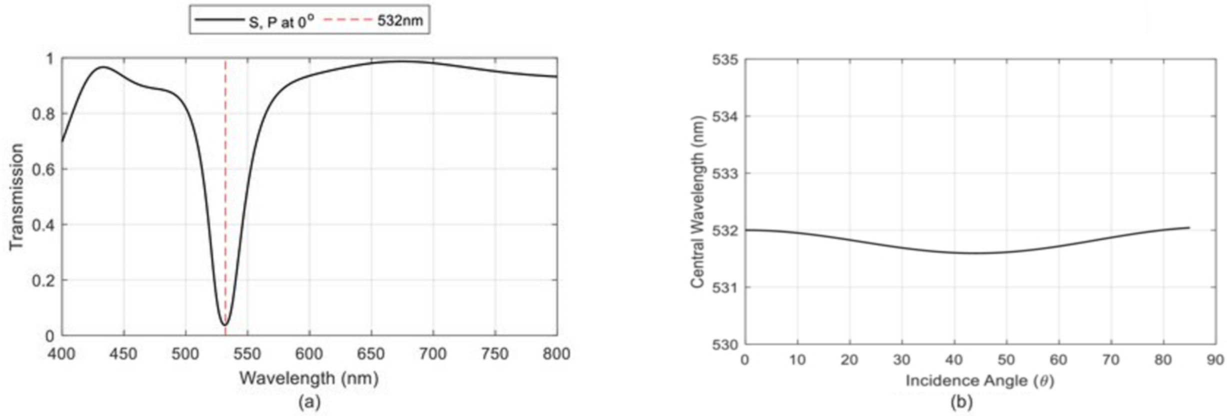

Figure 6. (a) The transmission response for the nanoengineering thin film at normal incidence. (b) The central notch location for all incidence angles.

5. CONCLUSION

In conclusion, this research demonstrates a nanoengineering instrument for controlling the desirable optical properties of silver nanoparticles through a novel photochemical synthesis method that generates a AgNP colloidal seed solution that grows via photo generation of nanostructures with controlled size and morphology. The cost-effective production of a variety of particles with predicable and controllable optical absorption properties across the whole visible range is made possible with the discussed nanoengineering instrumentation that centers around a closed-loop system to control an array of narrowband LED illumination sources. By using the powerful emission of light emitting diodes and the plasmon absorption of AgNPs, photochemically produced AgNP seeds may quickly and precisely control the morphology and optical properties of the nanoparticles. The applications for the accurately controlled production of nanoparticles is vastly growing in demand. This technology aids the rapid expansion and research into optical metamaterials by providing the control assessment over the production of metamaterial building blocks for the visible spectrum.

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