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# Engineering the Optical Properties of Gold Nanorods: Independent Tuning of Surface Plasmon Energy, Extinction Coefficient, and Scattering Cross Section

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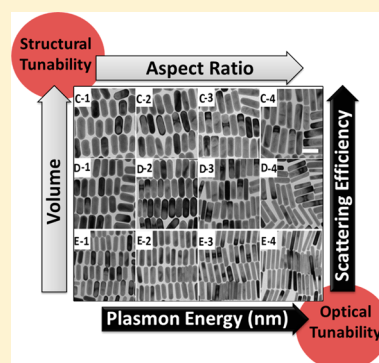
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## Supporting Information

**ABSTRACT:** The future integration of plasmonic nanoparticles, such as gold nanorods (Au NRs), into applications requires the ability to tune the components of their optical properties to optimize performance for the underlying technology. Verifying techniques that model the resonance energy and associated extinction, scattering, and absorption cross sections necessitate experimental data from series of Au NRs where structural features are independently tuned. Here, the extinction cross section and scattering efficiency are presented for Au NR series with high compositional and structural purity where effective volume, aspect ratio, length, and diameter are independently varied by factors of 25, 3, 2, and 4, respectively. The extinction cross sections quantitatively agree with prior calculations, confirming that the volume of the rod is the dominant factor. Comparisons of the scattering efficiency however are less precise, with both quantitative and qualitative differences between the role of rod volume and aspect ratio. Such extensive experimental data sets provide a critical platform to improve quantitative structure–property correlations, and thus enable design optimization of plasmonic nanoparticles for emerging applications.



## INTRODUCTION

The interaction between light and noble metal nanoparticles is one of the most efficient in the physical world, with a ratio of extinction cross section to physical cross section greater than 1.<sup>1</sup> The optical properties of noble metal nanoparticles arise from localized surface plasmon resonances (LSPRs), which are broadly tunable through manipulation of size, structure, and composition. This provides avenues to manipulate and focus electromagnetic fields at the nanoscale, and thus these nanoparticles and their clusters are many times thought of as nanoantennas.<sup>2</sup> Such characteristics have attracted attention in numerous fields including sensing, imaging, medical diagnostics, therapeutics, and energy harvesting.<sup>1,3–5</sup> However, as one would for a macroscopic antenna, independent tuning of different structural parameters is still a challenge despite recent advances in fabrication. As such, it is also challenging to quantitatively verify not only the energy, but also the magnitude of the optical response predicted by different levels of modeling.

The optical response at the LSPR (extinction cross section) is determined by the strength of both scattering (radiative) and absorptive (nonradiative) processes.<sup>6,7</sup> Nonradiative decay occurs on the order of 10–100 femtosecond (fs), and is due to the creation of electron–hole pairs via either intraband excitations within the conduction band or interband transitions from lower-lying d-bands to the sp-conduction band. The

energy, its dispersion, and the dissipation rate of these nonradiative processes depend mainly on nanoparticle composition and volume. In contrast, radiative decay occurs on the order of tens of fs and arises from the coherent oscillation of electrons. The characteristics of these radiative oscillations depend on volume, shape, and surface features. The cross sections for these processes increase with particle size, but with different dependencies, absorption depends on volume ( $C_A \approx r^3$ ,  $r$  is the particle radius), whereas scattering depends on volume squared ( $C_S \approx r^6$ ).<sup>8,9</sup> This suggests that larger nanoparticles would be preferred for plasmon enhanced fluorescence and imaging applications where the scattering component is critical. In contrast, smaller particles optimize the effectiveness of nonradiative processes, such as photothermal conversion for therapeutics.<sup>10–12</sup> More quantitative design tools and the complementary ability to tailor the relative contribution from absorption and scattering, as well as tune the energy of the plasmon resonance, however are central to the realization of the aforementioned technologies.

In the case of Au NRs, various models of increasing complexity, such as Mie–Gans theory,<sup>13</sup> effective medium theory,<sup>14</sup> and various numerical techniques (discrete dipole

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approximation (DDA), finite-difference time-domain method (FDTD), and T-matrix method<sup>15–20</sup>) enable prediction of these optical characteristics based on the nanoparticle structure (size and shape). These predictions include the energy, magnitude, and dispersion of the LSPR, as well as near field enhancement, far-field scattering magnitude, and heat generation. Confirming assumptions and improving the accuracy of the computational models essentially require reliable experimental data. Predictions of how the energy of the LSPR depends on nanorod features are well validated, having been experimentally confirmed by numerous techniques, including ensemble spectral extinction measurements (UV–vis–NIR spectroscopy),<sup>21</sup> single particle spectral scattering,<sup>22,23</sup> near-field optical microscopy,<sup>24</sup> and electron energy loss spectroscopies.<sup>25</sup> In contrast, quantitative comparisons of the magnitude (strength) of the resonance (i.e., extinction cross section) are not as readily available due to the lack of sufficient experimental data. For example, studies of Au NRs using DDA and FDTD showed that the extinction cross section scales with the volume of the rod for constant aspect ratio ( $L/D$ ;  $L$ , length of the rod;  $D$ , diameter of the rod).<sup>16,17</sup> However, results depend on initial model parameters, whose selection is generally guided heuristically. Calculations have shown that the extinction cross section depends on rod aspect ratio for constant rod volume, in a manner analogous to the energy of the longitudinal resonance.<sup>26</sup> Other studies, even using the same DDA method, have argued that the dependency of extinction coefficient on aspect ratio is more profound for larger particles.<sup>9,16</sup> Similarly, calculations of scattering efficiency by DDA and FDTD reveal increasing scattering efficiency with rod volume; however, they differ quantitatively, predicting different aspect ratio dependencies.<sup>9,16,17</sup>

The lack of experimental reports is mainly due to challenges obtaining and verifying a series of compositionally pure, nanorod dispersions with independent variation of particle volume and aspect ratio. For example, validated analytical procedures to independently measure the Au NR molar concentration or efficiency of gold precursor incorporation into the Au nanoparticle product are lacking or not used in common practice.<sup>33</sup> Thus, most experimental reports on Au NRs only provide a relative extinction cross section. Furthermore, rarely are independent measurements of the magnitude of the component absorption and scattering reported. A notable exception is the work by Ungureanu et al. on gold nanospheres and nanoshells using differential path length spectroscopy to measure scattering.<sup>27,28</sup> Recently, He et al. successfully measured scattering loss and discussed the ratio of scattering to extinction; however, the examined range of Au NR sizes was very limited.<sup>29</sup> In general, the limited availability of robust experimental data sets that encompass a large range of structural parameters has hindered the optimization of computational models, and the detailed understanding of the relationship between structure, scattering, and absorption cross sections.<sup>16,22–26</sup>

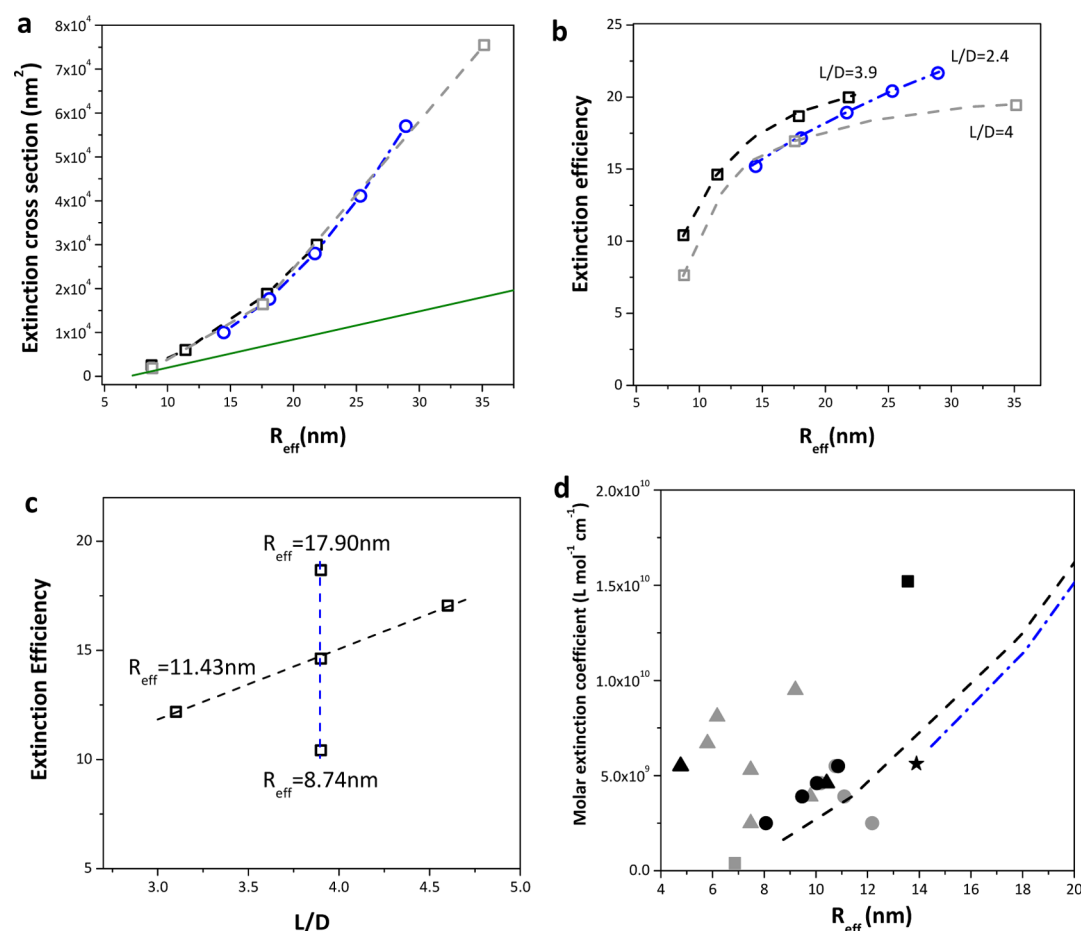
Herein, we address this challenge of verifying relationships for the extinction and scattering cross sections at the LSPR by bringing together synthetic procedures that provide independent tuning of the Au NR structure with robust characterization of composition and structural purity. Specifically, a set of well-defined Au NRs were fabricated via a simple modification of existing seed-mediated growth method, followed by depletion-induced purification.<sup>30</sup> Structure and composition were quantified via statistical analysis of TEM images and inductively

coupled plasma optical emission spectroscopy (ICP-OES). The effective volume, aspect ratio, length, and diameter of the Au NRs were independently varied by factors of 25, 3, 2, and 4, respectively. The extinction coefficient (0.1–1 nM) was deconvoluted into scattering and absorption components by measuring the absorption cross section with an integrating sphere.<sup>31</sup> Overall, these preparations enabled us to generate a large data set of the absolute magnitude of the extinction cross section. The results increase with rod volume for constant aspect ratio ( $L/D$ ) in quantitative agreement with prior predictions. Additionally, the measurements show no significant difference in extinction efficiency as the aspect ratio increases at similar volume. Hence, the volume of the rod is the dominant factor determining extinction cross section. As for the relative scattering contribution, the measurements also confirm theoretical predictions that the ratio of scattering to extinction cross section increases linearly with the volume of the rods for similar rod aspect ratio. The impact of aspect ratio on scattering however exhibits a more complex relationship with rod volume, in general being greatest for  $1 < L/D < 3$  (sphere to short rod) but relatively invariant for longer rods ( $L/D > 3$ ).

## ■ EXPERIMENTAL METHODS

**Materials.** Hexadecyltrimethylammonium bromide (CTAB) (98%), benzyldimethylammonium chloride hydrate (BDAC) (98%), and L-ascorbic acid were purchased from Tokyo Chemical Industry. Chloroauric acid ( $\text{HAuCl}_4$ ) (99.999%) and sodium borohydride ( $\text{NaBH}_4$ ) (>95%) were purchased from Sigma-Aldrich. Silver nitrate ( $\text{AgNO}_3$ ) (electrophoresis grade) was purchased from ACROS. All chemicals were used as received without further purification. ICP gold standard solution (100 ppm) was purchased from Inorganic ventures for the calibration of ICP-OES. Deionized water (18.2 M $\Omega$ ), obtained from a Milli-Q water purification system, was used in all of the experiments.

**Synthesis of Au NRs: Increasing Volume at a Constant Aspect Ratio.** Au NRs were synthesized by the seed-mediated growth process in CTAB solutions in the presence of  $\text{AgNO}_3$ , as reported previously. To ensure reproducibility of the subsequent steps, we set the temperature at 25 °C for all reactions. The seed solution was prepared by dissolving  $\text{HAuCl}_4$  (0.025 mL, 0.1 M) in an aqueous solution of CTAB (10 mL, 0.1 M). A freshly prepared, ice-cold  $\text{NaBH}_4$  solution (0.6 mL, 0.01 M) was then added into the mixture under vigorous stirring (1 min). The seed solution was aged for 10 min before being added into the growth solution. The growth solution was prepared by mixing  $\text{HAuCl}_4$  (0.5 mL, 0.1 M),  $\text{AgNO}_3$  (0.08 mL, 0.1 M), and CTAB (100 mL, 0.1 M) followed by addition of the ascorbic acid solution (0.55 mL, 0.1 M) as a mild reducing agent. The prepared solution was divided into five vials, each containing 20 mL of growth solution. Varied volume of seed solution (8, 16, 32, 80, and 160  $\mu\text{L}$ ) was added into each vial, and the solution was gently shaken for 30 s. The volume of seed solution was normalized based on the smallest volume (8  $\mu\text{L}$ ) and described as  $S_N = 1, 2, 4, 10$ , and 20. As  $S_N$  increases, for a given reaction yield, decreasing the amount of Au precursor per seed particle will result in a smaller average rod volume. The as-made Au NR solution was kept at 25 °C for 24 h to ensure the complete growth. To obtain the series of rods with increasing volume at larger aspect ratio, varied concentration of BDAC was added to the growth solution. For example, to obtain a series of larger aspect ratio rods ( $L/D = 4$ –5) with increasing volume, 4.95 g of BDAC was



**Figure 1.** The effect of effective radius ( $R_{\text{eff}}$ ) on extinction cross section of Au NRs. (a) Computational calculations showing the relationship between the size of Au NRs and extinction cross section. Mie–Gans calculation<sup>35</sup> (green —) was done by fixing the width of the rods (10 nm) and increasing the length for larger volume and aspect ratio ( $L/D = 2.5$ –8). DDA calculations ( $\square$ ,<sup>16</sup> and gray  $\square$ ,<sup>36</sup>) were performed for a series of nanorods with increasing volume at a fixed aspect ratio ( $L/D = 3.9$ ,<sup>16</sup> and 4<sup>36</sup>). FDTD calculation<sup>17</sup> (blue  $\circ$ ) was for  $L/D = 2.4$ . Dashed line depicts fit to DDA and FDTD results to convey trend. (b) The extinction cross section is converted to extinction efficiency to reveal model's different predictions of size and aspect ratio ( $L/D$ ). (c) Dependency of extinction efficiency on effective radius (blue —) and aspect ratio (—) at constant  $L/D$  and  $R_{\text{eff}}$  respectively. (d) Compilation of experimental data for molar extinction coefficients of Au NRs.  $\bullet$ ,<sup>37</sup> gray  $\bullet$ ,<sup>26</sup>  $\blacksquare$ ,<sup>27</sup>  $\star$ ,<sup>38</sup> gray  $\blacktriangle$ ,<sup>35</sup> and  $\blacktriangle$ .<sup>19</sup> The dashed line shows the representative computational extinction coefficients from (a). Note that  $\bullet$  and gray  $\bullet$  are plotted from the same experimental extinction data with different reported structural parameters that result in an opposite trend as a function of Au NR size.

added to the surfactant solution (resulting concentration of CTAB is 0.1 M and BDAC is 0.125 M in 100 mL of water).

**Synthesis of Au NRs: Increasing Aspect Ratio at a Constant Volume.** To obtain a series of rods with increasing aspect ratio at a constant volume, the concentration of BDAC as a cosurfactant to the growth solution was varied. The seed solution was prepared as described previously. The growth solution was prepared by mixing  $\text{HAuCl}_4$  (0.5 mL, 0.1 M),  $\text{AgNO}_3$  (0.08 mL, 0.1 M), and CTAB (100 mL, 0.1 M) followed by addition of the ascorbic acid solution (0.55 mL, 0.1 M) as a mild reducing agent. The prepared solution was divided into four vials, each containing 25 mL of growth solution. Varied amount of BDAC (to make final concentration of BDAC at 0, 0.03, 0.06, and 0.08 M) was added into each vial, and the solution was sonicated for 5 min. 20  $\mu\text{L}$  of seed solution (corresponding to  $S_N = 1$ ) was added to each vial, and the solution was gently shaken for 30 s. The as-made Au NR solution was kept at 25  $^\circ\text{C}$  for 24 h to ensure the complete growth. To obtain the series of rods with increasing aspect ratio at smaller volume, the volume of the seed solution was varied from  $S_N = 2$  to 4.

**Purification of Au NRs.** As-made solution obtained from the synthetic routes described above contains 10–20% of isotropic particles as byproducts. To remove those byproducts and obtain the rods with high purity, depletion-induced separation method was adopted.<sup>30</sup> Briefly, the concentration of CTAB or BDAC was increased until one species with larger contact area formed flocculation. Within 24 h, sediment that is comprised of flocculates of those particles formed on the bottom of vials. The concentration of surfactant can be determined on the basis of the calculation of contact energy between resulting rods and byproducts to induce the aggregation of one species. For example, consider Au NRs synthesized in CTAB growth solution (0.1 M) with  $S_N = 2$ . A stable colloidal dispersion of relatively short NRs ( $L/D \approx 2.9$ ,  $D \approx 18$  nm) was obtained with large polycrystalline particles ( $D \approx 60$  nm). By increasing CTAB concentration to 0.25 M, the number of surfactant micelles became sufficient to induce an attractive potential energy between the large spherical particles resulting in sediment after 24 h. The supernatant containing rods was collected and centrifuged at 7500 rpm for 1 h to



remove excess stabilizers and was redispersed in Milli-Q water for the characterization.

**Optical and TEM Characterization.** Ensemble extinction spectra were acquired with a Cary 5000 UV–vis–NIR spectrophotometer (Agilent) from 200 to 1350 nm. The absorption spectra were obtained by attaching diffuse reflectance accessories (integrating sphere) from 350 nm to 900 nm. The scattering spectra were calculated by subtracting the absorption from the extinction for each sample measurement. Morphology and mean size of Au NRs were determined by TEM (Philips CM200 LaB6 at 200 kV). For each sample, more than 500 particles were measured to obtain the average size and the size distribution (Image J, NIST).

**ICP-OES Analysis.** The calibration was conducted with various concentrations of gold solution ranging from 0.0001 to 0.001 M prepared from ICP gold standard solution (100 ppm). Au NR samples (9 mL) were added to a mixture of concentrated nitric acid (0.5 mL) and concentrated hydrochloric acid (0.5 mL) in a Teflon tube and microwave digested using EPA method 3015A.<sup>32</sup> The sample from microwave (Microwave Digester, serial no.: MD5280) is analyzed for total gold followed by inductively coupled plasma optical emission spectrometry (ICP-OES, serial no.: 080N5082901). The efficacy of this sample preparation procedure was verified by EPA Method 3015A<sup>32</sup> (USEPA 1997). The lower detection limit for ICP-OES was  $7 \mu\text{g L}^{-1}$ .<sup>33</sup>

To confirm the necessity of both acid and microwave digestion for accurate ICP measurements of Au NR solutions, control solutions were prepared and analyzed with and without microwave digestion (see Supporting Information, Table S.3). The control solutions include  $5 \times 10^{-4}$  M  $\text{HAuCl}_4$ , a mixture of  $\text{HAuCl}_4$  ( $5 \times 10^{-4}$  M) and CTAB (0.1 M), as-made Au NRs, and purified Au NR solutions. For  $\text{HAuCl}_4$  solutions, the additional use of microwave digestion does not significantly affect results. However, when only acid digestion was used for preparation of CTAB– $\text{HAuCl}_4$  solution, the measured Au concentration was less than the actual concentration. Additional microwave digestion was necessary to detect all of the Au in these mixed solutions. This is due to the existence of metallomicelles containing CTA– $\text{AuBr}_4$  complex,<sup>34</sup> which cannot be fully digested via acid. In parallel, it was found that without microwave digestion, Au content in Au NR solution was underestimated, also indicating incomplete digestion when acid-only preparation procedures are used.

## RESULTS AND DISCUSSION

Figure 1 provides a compilation of theoretical and empirical extinction cross sections<sup>16,17,35,36</sup> reported for Au NRs at the frequency of the longitudinal surface plasmon resonance as a function of effective radius,  $R_{\text{eff}} = (3V/4\pi)^{1/3}$ .  $R_{\text{eff}}$  is the radius of a sphere having a volume,  $V$ , equal to that of the nanorod. In addition to cross section, it is also useful to consider the efficiencies of extinction, absorption, and scattering. These values are obtained by dividing the cross sections by the geometric cross section,  $\pi r^2$ , where  $r$  is the radius (or effective radius for nonspherical particle). Extinction efficiency greater than 1 means the optical species has an extinction cross section larger than its physical cross section. Finally, extinction cross section is commonly expressed experimentally as the molar extinction coefficient ( $\text{L mol}^{-1} \text{cm}^{-1}$ ).<sup>16</sup> The DDA and FDTD calculations shown in Figure 1a and b were performed for a series of nanorods with increasing volume at a fixed aspect ratio ( $L/D = 2.4, 3.9$ , and 4). For the Mie–Gans calculation, the

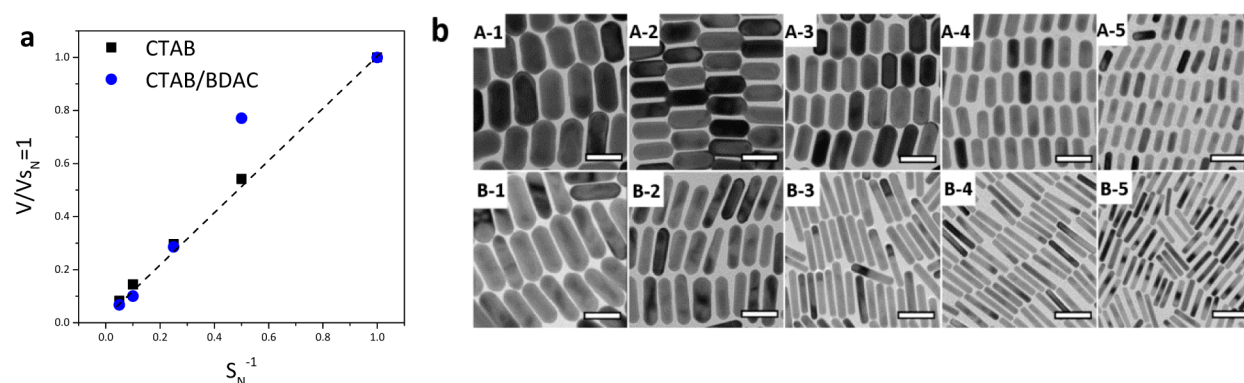
width of the rods was fixed (10 nm) and the length increased for larger volume and aspect ratio ( $L/D = 2.5$ –8). Details of the Mie–Gans, DDA, and FDTD calculations can be found in the Supporting Information.

With respect to theories, Figure 1a and b reveals a quasi-linear increase of extinction cross section with  $R_{\text{eff}}$  (5–35 nm). Consistent with prior observations by El Sayed and co-workers for nonisotropic optical particles, the extinction coefficient of different aspect ratios collapses to a general scaling with  $R_{\text{eff}}$  (Figure 1a).<sup>9</sup> The calculation based on Mie–Gans theory is only valid for small particles where retardation effects are negligible, and corresponds to a size regime  $\leq 0.02\lambda$  (i.e.,  $R_{\text{eff}} \approx 5$ –10 nm for  $\lambda \approx 500$ –1000 nm). When accounting for physical size, the extinction efficiency levels off for the largest particles (Figure 1b).

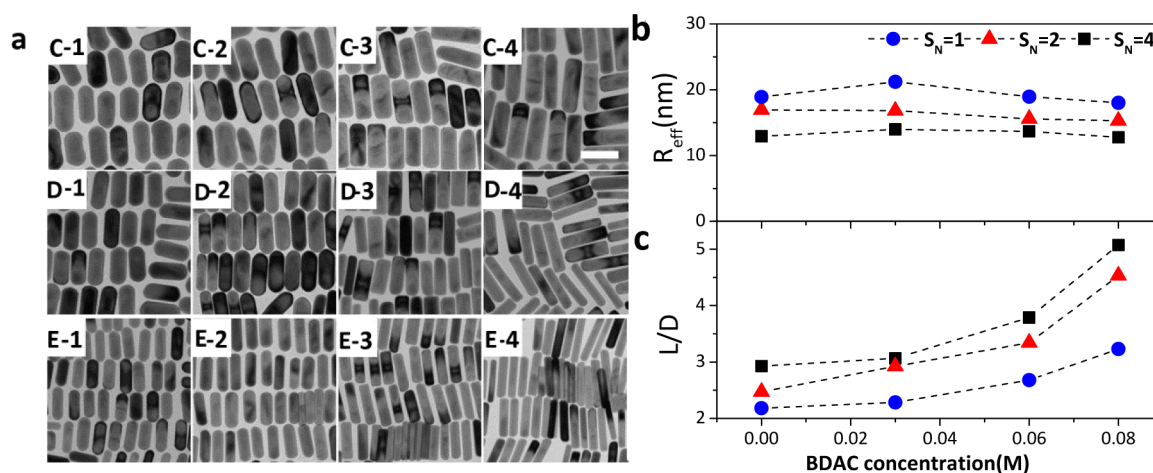
Overall, their magnitudes are much greater than 1 (5–25), consistent with the notion that Au NRs can strongly concentrate electromagnetic fields in the vicinity of their physical boundary. In other words, the field near the surface for a particle can exceed the average incident field in the medium.<sup>8</sup>

Qualitatively, FDTD and DDA show good agreement with respect to extinction cross section. However, quantitative differences are seen<sup>16,20</sup> when accounting for the particle size (Figure 1b). The disagreement is also seen between DDAs from different reports, which is most likely due to the difference in number of dipoles used in the calculation.<sup>39</sup> Finally, Figure 1c summarizes DDA results indicating a linear increase in extinction efficiency with respect to aspect ratio ( $L/D$ ) at constant volume.<sup>12</sup> As the rod elongates from  $L/D = 3.1$ –4.6 at the same volume ( $R_{\text{eff}} = 11.9$  nm), the extinction efficiency increases about 17%. A similar increase can be achieved by increasing the effective radius by 2.7 nm at constant  $L/D$ .

In contrast to the relative consistency of the models, experimental data<sup>26,27,35,38,37</sup> are sparse and only available for a limited range of Au NR effective radii (4–14 nm). Whether considered within a study or collectively, the data do not even yield a qualitative trend, let alone verify the calculations (Figure 1d). Note that in the aforementioned models, the magnitude of the extinction cross section of the LSPR is determined for a single Au NR oriented such that the long axis of the rod is parallel to the polarization of incident light. To directly compare with dilute solution data, this must be rescaled to account for the random orientation of the Au NRs in the experimental ensemble<sup>38</sup> (Figure 1d dashed line and dashed dotted line; Supporting Information). In general, the vast majority of the experimental molar extinction coefficients are greater than the theoretical estimate. The major sources of experimental uncertainty have been ascribed to a broad distribution of Au NR size, and to the presence of a significant fraction (>10%) of gold nanospheres.<sup>40</sup> These factors however should cause an underestimate of the molar extinction coefficient. The presence of byproducts will result in an overestimation of the number of nanorods, and because the molar extinction coefficient is obtained by dividing the optical density by the number of Au NRs, this will result in an underestimate of the molar extinction coefficient. Rather, the overestimation of extinction coefficient is mostly likely due to an uncertainty in the Au NR concentration caused by the uncertainty in Au NR yield relative to the initial concentration of Au-salt precursor ( $\text{HAuCl}_4$ ). Determination of the final Au content after purification is not trivial. For example, variations in sample preparation, digestion procedure, and measuring condition for ICP are known to significantly affect the final



**Figure 2.** The effect of seed concentration on the volume of resulting Au NRs. The normalized seed concentration ( $S_N$ ) was changed from  $S_N = 1$  to 20 (detailed in method). (a) As the seed concentration increases ( $S_N = 1, 2, 4, 10$ , and 20), the volume of the nanorods decreases. When  $S_N = 1$ , the average rod volume was  $5.6 \times 10^4 \text{ nm}^3$  for CTAB-based synthesis and  $3.5 \times 10^4 \text{ nm}^3$  for CTAB/BDAC-based synthesis. (b) TEM images of resulting nanorods with  $S_N$  increasing from left to right. Set A was prepared in CTAB solution (0.1 M), and set B was prepared in CTAB/BDAC binary solution (0.1 M/0.125 M). The scale bar is 50 nm.



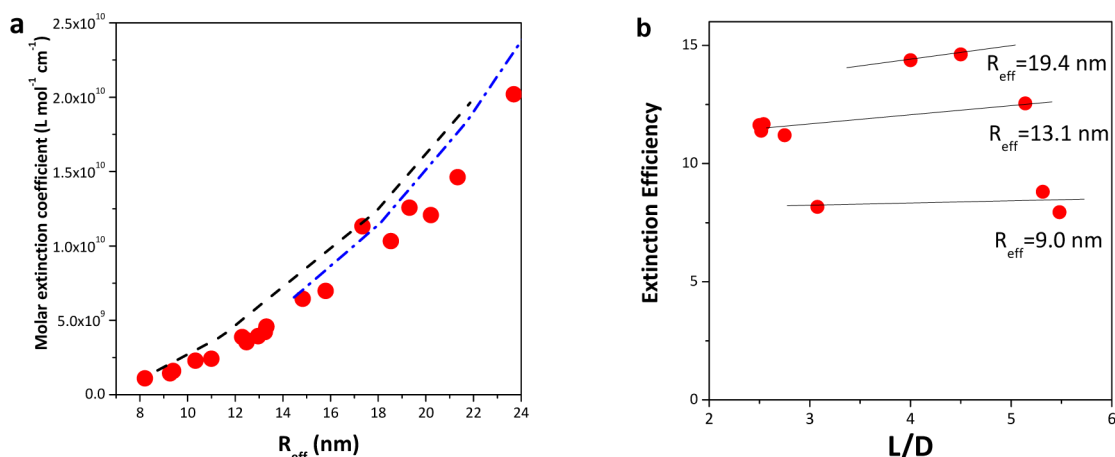
**Figure 3.** The effect of cosurfactant (BDAC) on tuning the aspect ratio of nanorods. (a) TEM images of nanorods when BDAC concentration was changed from 0 to 0.08 M at different normalized seed concentration ( $S_N$ ). C, D, and E correspond to  $S_N = 1, 2$ , and 4, respectively. The scale bar is 50 nm. (b) The effective radius of the resulting nanorods as a function of BDAC concentration. Regardless of BDAC concentration, the volume of the rods was similar at given seed concentration. (c) The aspect ratio of the resulting nanorods as a function of BDAC concentration.

determination of metal concentration.<sup>41</sup> Unfortunately, a standard procedure for the digestion of Au nanoparticles has yet to be established. Incomplete digestion of the Au NR would underestimate Au concentration, and thus result in an overestimate the molar extinction coefficient. This highlights the critical need for improved standard characterization of Au NR products.

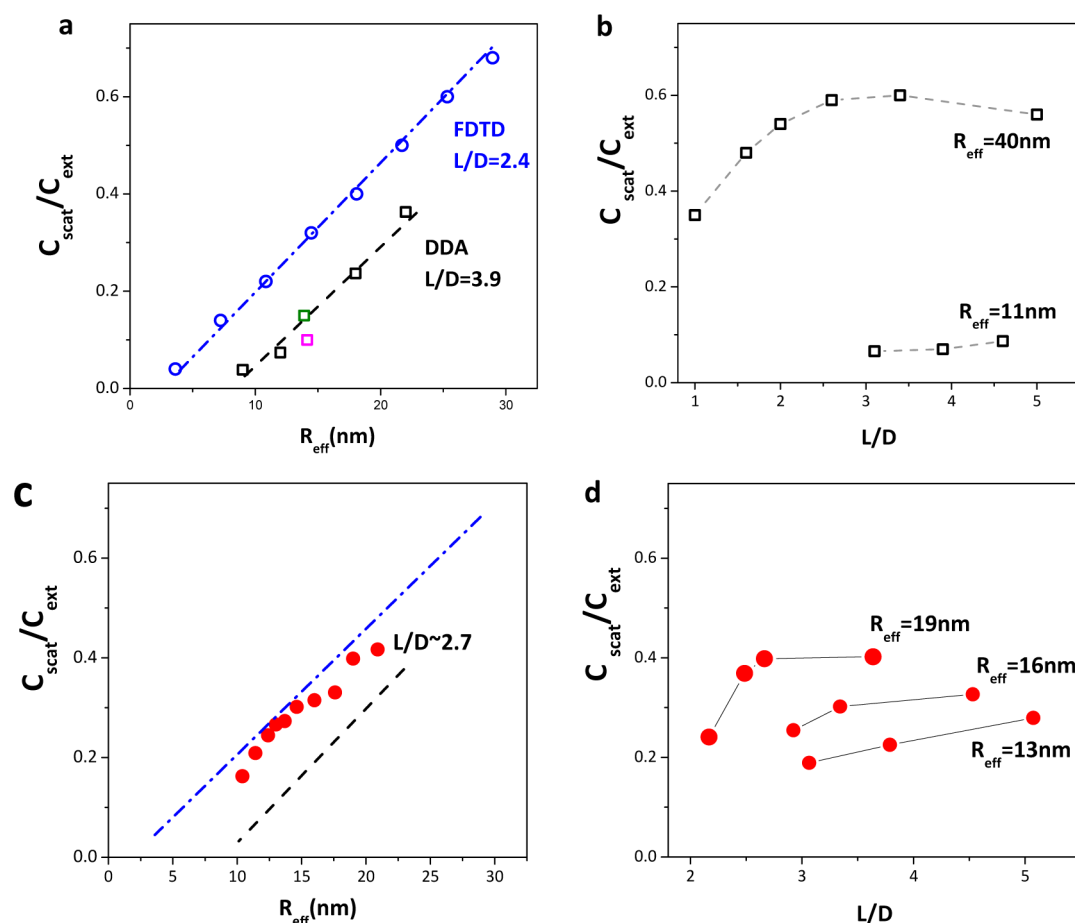
The recently established understanding of factors that control seed-mediated growth of Au NRs<sup>29,30,42–44</sup> provides routes to achieve the precision necessary to fabricate the requisite systematic series to compare with models. Mechanistically, the final morphology of the Au NRs is determined early in the growth reaction by the adsorption of surfactant micelles onto the coarsening seeds (<5 nm). The relative stability of the subsequent surfactant bilayer on different crystal facets mediates the evolution of the particle morphology. As such, aspect ratio is controlled by surfactant concentration and composition, whereas particle volume is independently tuned by controlling the ratio of seed particle to Au(III) precursor.

Figure 2 demonstrates this tunability. The Experimental Methods section provides detailed experimental conditions. The average volume of the resulting NR is inversely

proportional to the normalized seed concentration (Figure 2a), irrespective of the surfactant composition. Assuming complete conversion, the average volume per rod is the total volume of Au-atoms ( $nv_0$ , where  $n$  is the total number of Au atoms, each of volume  $v_0$ ) divided by the number of seeds ( $N$ ). For a given reaction yield, decreasing the amount of Au precursor per seed particle will result in a smaller average rod volume. By increasing the seed concentration 20-fold for 0.1 M CTAB (cetyl trimethyl ammonium bromide) in the growth solution, the average  $R_{\text{eff}}$  decreases from 24 to 10 nm ( $L/D \approx 2–3$ ). A similar effect is observed for cosurfactant growth (0.1 M CTAB, 0.125 M BDAC (benzyl dimethyl hexadecylammonium chloride)). The cosurfactant systems provide higher aspect ratios ( $L/D \approx 4–5.5$ ). Increasing seed concentration however also reduces the average  $R_{\text{eff}}$  from 20 to 8 nm. The reason for the formation of higher aspect ratio when BDAC is used as a cosurfactant is related to a reduced micelle size.<sup>45,46</sup> Smaller micelles passivate the (110) and (100) surfaces at earlier times. The reduced rate of Au addition on these smaller crystalline facets leads to anisotropic growth at earlier stages, resulting in longer Au NRs with smaller diameter (Supporting Information Table S.2). TEM images of the products show the



**Figure 4.** (a) Experimentally obtained extinction coefficients as a function of effective radius as compared to DDA (—) and FDTD (blue - · -). (b) The effect of aspect ratio on the extinction efficiency. Three sets of Au NRs with increasing aspect at similar effective radius were examined showing that increasing aspect ratio does not significantly impact the extinction efficiency.



**Figure 5.** (a) Calculated scattering efficiencies ( $C_{\text{scat}}/C_{\text{ext}}$ ) showing the effect of effective radius. DDA ( $\square$ ,<sup>16</sup> pink  $\square$ ,<sup>29</sup> and green  $\square$ <sup>38</sup>) and FDTD (blue  $\circ$ <sup>17</sup>) calculations from various groups. (b) DDA calculation of scattering efficiencies showing the effect of aspect ratio. (c) Experimentally obtained scattering efficiency as a function of effective radius for aspect ratio  $\sim 2.7$ . Dashed line is from DDA calculation, and dashed dotted line is from FDTD calculation showing qualitatively good agreement with experimental result. (d) Experimentally obtained scattering efficiency as a function of aspect ratio for three different effective radii.

high uniformity and purity of the resulting Au NRs. For the conditions used, all of the nanorods exhibit a spherocylinder shape (Figure 2b).

Using these techniques, Figure 3 summarizes three sets of nanorods with a prescribed set of diameter–length–volume–

aspect ratio. Au NRs were grown by increasing BDAC concentration at the normalized seed concentrations of 1, 2, and 4 (corresponding TEM images of C, D, and E, respectively). At a given normalized seed concentration, and regardless of BDAC concentration, the effective radius was



similar (Figure 3b). When the concentration of BDAC increased, the aspect ratio of the resulting nanorods increased (Figure 3c). Removal of nonrod product was achieved using the previously reported depletion technique.<sup>30</sup> A complete list of the dimensions and molar extinction coefficients of the Au NRs can be found in Tables S.1 and S.2 of the Supporting Information.

The extinction coefficients were experimentally determined using Beer–Lambert equation,  $A = \epsilon \cdot l \cdot c$ , where  $A$  is the optical density of the solution,  $l$  is the light path length, and  $c$  is the Au NR concentration determined by ICP-OES analysis. As noted above, ICP is one of the most powerful methods for trace element analysis; however, only a handful of reports are available that describe procedures for sample preparation, digestion, and measurement of Au nanoparticles.<sup>41,47</sup> Without calibration, changes in any of these procedures are known to greatly affect the final measurement.<sup>41,48</sup> For consistency, our preparation and calibration procedure is detailed in the Experimental Methods. In brief, ICP-OES analysis of aqueous solutions containing Au precursor, as well as Au precursor with surfactant (0.0005 M HAuCl<sub>4</sub>, 0.1 M CTAB), was used to understand the role of surfactant and verify the measurement and digestion procedures. For complete particle digestion, we demonstrated that the EPA standard digestion procedure for Ag nanoparticles, which combines acid digestion with microwave, provides reproducible, quantitative results (Experimental Methods and Supporting Information Table S.3).<sup>32,33</sup> With this improved ICP analysis, we were able to evaluate the fraction of gold precursor ions that were incorporated into the final nanoparticle product (yield). The maximum theoretical yield is determined by the stoichiometric ratio between reducing agent (ascorbic acid) and Au precursor (HAuCl<sub>4</sub>). In our case, a ratio of 1.1 was used to ensure slow growth of well-shaped spherocylinder nanorods. This gives a maximum theoretical yield of 73%. Our ICP-OES analysis of as-made Au NR solution revealed an experimental yield of ~70%, in good agreement with calculations and further confirming the validity of ICP-OES procedure on solutions of Au NR. Note that previously reported reduction yields are significantly low (~15%), which was ascribed to the addition of AgNO<sub>3</sub>.<sup>49</sup>

Figure 4 compares the molar extinction coefficient and extinction efficiency of this series to DDA and FDTD calculations. The agreement with respect to particle volume ( $R_{\text{eff}}$ ) is very good (Figure 4a). Deviation between data and calculations increases with particle volume (5–25%), where the experimental extinction coefficients are less than the calculations. This is likely due to the impact of polydispersity of the Au NR dimension, which broadens the shape of LSPR peak and suppresses the magnitude of the ensemble.<sup>36</sup> The extinction efficiency is seen to slightly increase with aspect ratio at constant particle volume (Figure 4b), which is similar to that predicted by Jain et al.<sup>16</sup> As the rod elongates from  $L/D = 2.8$  to 5.1 at the same volume ( $R_{\text{eff}} = 13.1$  nm), the extinction efficiency increases about 11%.

The increment however is slightly lower than theoretical prediction. As a note, the difference between Figure 1d and Figure 4a emphasizes the crucial importance of correctly measuring Au concentration and achieving high structural purity when experimental quantification of optical performance is required.

Figure 5 summarizes the trending of the absorption and scattering components of the extinction by comparing the measured scattering efficiencies to those from DDA and FDTD

calculations. The scattering efficiency ( $\eta$ ) is defined as the ratio of the scattering cross section ( $C_{\text{scat}}$ ) to the total extinction cross section ( $C_{\text{ext}}$ ) at the resonance and is expressed as:<sup>9</sup>

$$\eta = \left| \frac{C_{\text{scat}}}{C_{\text{ext}}} \right|_{\text{Res}} \quad (1)$$

DDA and FDTD calculations (Figure 5a) indicate that the scattering efficiency increases linearly with effective radius for intermediate aspect ratios ( $L/D \approx 3.9$ <sup>12</sup> and  $2.4$ <sup>13</sup>) due to the rapid scaling of  $C_s \propto R_{\text{eff}}^6$ . However, for the same particle volume, the absolute scattering efficiency is greater for FDTD than DDA, even though the FDTD report was for rods with slightly smaller  $L/D$ . This discrepancy can be attributed to different model parameters due to an absence of common experimental data to calibrate the initial dipole density of mesh size.

With regard to the impact of  $L/D$  at fixed volume (Figure 5b), only DDA studies have been reported.<sup>9,15</sup> For small effective radii ( $R_{\text{eff}} = 11.43$  nm), Jain et al.'s calculations imply that the aspect ratio (ranging from 3.1 to 4.6) does not have a substantial effect on scattering efficiency. This is the same as they concluded for the extinction cross section.<sup>16</sup> He et al. later confirmed this trend with two datum.<sup>29</sup> For larger effective radii ( $R_{\text{eff}} = 40$  nm), however, Lee et al. predicted an almost 2-fold increase of  $\eta$  for elongation of a sphere ( $\eta = 0.346$ ) to a rod of aspect ratio of 3 ( $\eta = 0.603$ ). Further elongation of the rod leads to a decrease in the scattering efficiency. This optimum arose from an increase in the imaginary part of the dielectric function, and thus increased absorption cross section, as the resonance peak shifted into the infrared.<sup>9</sup> Thus, a large range in particle size and aspect ratio is required to understand the competing factor contributing to the scattering efficiency of a given metal nanoparticle.

Figure 5c summarizes the experimental scattering efficiency for increasing particle volume ( $R_{\text{eff}} = 10$ –21 nm) at similar aspect ratio ( $L/D \approx 2.7$ ). The scattering spectrum of the dilute Au NR solutions was determined by subtracting the absorption spectra, measured with an integrating sphere from the extinction spectra.<sup>31</sup> This simple and reliable approach was calibrated with polystyrene beads (pure scattering) and different size Au nanospheres with known optical properties (Supporting Information Figure S.2). The scattering efficiency at similar aspect ratio (Figure 5c) linearly increases with particle volume ( $R_{\text{eff}}$ ), which is in good agreement qualitatively with available FDTD predictions.

Figure 5d shows a much more complex dependency of scattering efficiency on aspect ratio ( $L/D = 2.3$ –5) at constant particle volume ( $R_{\text{eff}} = 13, 16, 19$  nm). The upper limit of aspect ratio examined was determined by the available detection range of the spectrophotometer (<900 nm). Overall, increasing aspect ratio at constant volume results in an increased scattering efficiency. For the smallest nanorods ( $R_{\text{eff}} = 13$  nm), the scattering efficiency linearly increases within the range of aspect ratios. As the rods get larger, the scattering efficiency plateaus at smaller aspect ratios. For example, scattering efficiency rapidly increases to  $L/D \approx 3.4$  for  $R_{\text{eff}} = 16$  nm, but only to  $L/D \approx 2.7$  for  $R_{\text{eff}} = 19$  nm. Further increase of aspect ratio at these larger particle volumes does not appreciably change the efficiency. Qualitatively, these trends are reminiscent of the DDA calculations for considerably larger rods ( $R_{\text{eff}} = 40$  nm) where the scattering efficiency increases to aspect ratio of 3 (Figure 5b). Further theoretical calculations



are necessary to elucidate the factors underlying this dependency of scattering efficiency on aspect ratio at constant volume.

## CONCLUSION

Herein, we report the optical extinction, absorption, scattering, and their relative contributions for Au NRs across a wide range of volume and aspect ratio by bringing together synthetic procedures that provide independent tuning of the Au NR structure (effective volume, aspect ratio, length, and diameter range of 25×, 3×, 2×, and 4×, respectively) with robust characterization of the composition and structural purity. This provides a more extensive comparison of experimental measurements and theoretical calculations than previously reported. The comparison quantitatively verifies predictions that the extinction cross section and the relative contribution of scattering depend on both rod dimensionality and aspect ratio. The total extinction increases linearly with increasing Au NR volume. In contrast, aspect ratio for Au NRs with the same volume has a negligible impact on extinction. On the other hand, the relative enhancement of scattering efficiency increases with increasing aspect ratio, but saturates at intermediate values. Additionally, results such as ours provide the solid reference set to validate the accuracy of simulations and fine-tune the assumptions and input parameters. DDA and FDTD are two of the most common methods to simulate optical responses of Au NRs, but are rarely compared against each other or with a number of extensive data sets from different laboratories. Additional extended sets of experimental data are crucial to validate design tools to enable Au NR and Au NR cluster engineering. Coupled with synthetic procedures to independently tune particle characteristics, optical performance such as maximal near field enhancement, far-field scattering magnitude, or heat generation can then be optimized for each application under consideration.

## ASSOCIATED CONTENT

### Supporting Information

Additional information on the compilation of theoretical extinction cross sections, measurement of scattering efficiency, and detailed size measurement of experimentally obtained Au NRs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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