

Quantifying the role of redox thermodynamics in the shape-controlled synthesis of gold nanobipyramids

Dong He^{1,2}, Xing Zhang^{1,3}, Thomas Egan¹, Yiteng Tang^{4,5}, Gang Chen^{1,4,5} (✉)

¹ Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA

² State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, Jilin 130012, China

³ National Key Laboratory of Opto-Electronic Information Acquisition and Protection Technology, Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China

⁴ Department of Biochemistry, Chemistry and Physics, Georgia Southern University, GA 30458, USA

⁵ Center for Advanced Materials Science, Georgia Southern University, GA 30458, USA

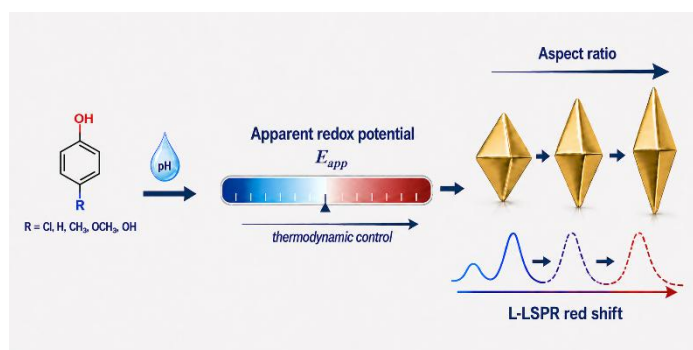
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This study demonstrated that the dimension and L-LSPR peak of as-synthesized Au NBPs is quantitatively related to the reaction potential of the synthesis system but not to the chemical identity of the reductants, which is important not only for understanding the mechanism of synthesis of metallic NPs but for improving its reproducibility and reliability.

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⁴ Department of Biochemistry, Chemistry and Physics, Georgia Southern University, GA 30458, USA

⁵ Center for Advanced Materials Science, Georgia Southern University, GA 30458, USA

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 Address correspondence to gchen@georgiasouthern.edu

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ABSTRACT: The colloidal synthesis of nanoparticles is governed by both thermodynamic and kinetic factors, yet the role of reduction potential, a key thermodynamic parameter, remains underexplored. In this study, we systematically investigate how the reduction potential of phenol derivatives affects the seed-mediated growth of gold nanobipyramids (Au NBPs). Four structurally similar 4-substituted phenols with varying electron-donating or withdrawing groups (-Cl, -H, -CH₃, -OCH₃) were used as reductants. Their reduction potential was modulated by adjusting the pH of the growth solution, enabling a controlled investigation of redox thermodynamics on product morphology and plasmonic properties. For each reductant, there exists a specific pH window where high-quality Au NBPs are formed, with the longitudinal localized surface plasmon resonance (L-LSPR) peak red-shifting as pH increases. While these effective pH ranges differ across reductants, plotting L-LSPR peak positions against the calculated reduction potentials (via the Nernst equation) collapses all data onto a single trend. This demonstrates that the reaction outcome under the investigated conditions and for the tested reductants is governed by reduction potential, not the identity of the reductant. Further validation using hydroquinone, a structurally distinct reductant with a two-electron oxidation, yields consistent results, underscoring the generality of this relationship. Our findings establish reduction potential as a potential dominant descriptor for guiding the shape-controlled synthesis of Au NBPs, offering a pathway to improve reproducibility and rational design in colloidal nanomaterial synthesis.

KEYWORDS: gold nanobipyramids, localized surface plasmon resonance, seed-mediated growth, phenol derivatives, pH value, reduction potential

1 Introduction

Metallic nanoparticles (NPs) have emerged as a central class of nanomaterials, with broad applications in catalysis, photonics, electronics, biomedicine, and data storage [1-4]. Among them, plasmonic NPs, particularly those composed of Au, Ag, and Cu, have garnered significant attention due to their unique optical properties, which arise from localized surface plasmon resonance (LSPR) [5-10]. LSPR results from the collective oscillation of conduction electrons in response to light, enabling plasmonic NPs to efficiently absorb and scatter light and generate strong local electromagnetic fields and hot carriers [6, 11, 12]. These properties are highly sensitive to NP size, shape, composition, and surface environment, making precise control over morphology a central goal in plasmonic nanomaterial synthesis [13-19]. Among the various plasmonic NPs reported, one-dimensional Au NPs, including Au nanorods (NRs) and Au nanobipyramids (NBPs), have attracted the most attention because they support two distinct LSPR modes, with the

longitudinal resonance closely tied to the particle aspect ratio [3, 5, 9, 20, 21]. This feature allows their plasmonic response to be extended deep into the NIR region, enabling efficient harvesting of a wide portion of the solar spectrum. Compared to the more extensively studied Au NRs, Au NBPs, characterized by their pentatwin structure and sharp tips, feature significantly narrower linewidths, stronger local electric field enhancement at their sharp tips, and superior shape and size uniformity [22-30].

Chemical reduction in aqueous solution is a widely used strategy for synthesizing one-dimensional Au NPs due to its simplicity and scalability. Over the past decade, numerous studies have demonstrated shape- and size-controlled synthesis of plasmonic NPs by tuning experimental parameters such as temperature, surfactants, pH, metal precursors, and reductants [31-40]. However, many synthesis protocols remain empirical, lacking a detailed mechanistic understanding at the molecular level [41]. This gap contributes to poor reproducibility and limits the

rational design of nanostructures for targeted applications.

To address these limitations, it is essential to interpret NP formation in terms of fundamental thermodynamic and kinetic parameters [42, 43]. Seed-mediated growth, a commonly used approach to improve product uniformity by decoupling nucleation and growth, is influenced by both thermodynamic factors (e.g., reduction potential, surface binding energies) and kinetic factors (e.g., reactant concentration, diffusion, and temperature) [44-47]. A better understanding of how these parameters interact and govern nanostructure formation is critical for advancing the precision and reliability of colloidal synthesis.

Our previous work on the pH-regulated synthesis of Au NRs and Au NBPs, has highlighted the importance of pH in dictating product morphology when phenolic compounds are used as reductants [31, 34, 35, 48, 49]. Notably, while various phenols (phenol, resorcinol, hydroquinone, phloroglucinol) enabled high-yield synthesis of Au NBPs, each required a different pH window, suggesting a link between product morphology and the redox environment of the reaction [50-52].

In this study, we hypothesize that the reduction potential, a key thermodynamic parameter, plays a fundamental and quantifiable role in determining the geometry and optical properties of Au NBPs. To test this hypothesis, we selected a series of 4-substituted phenol derivatives with varied electron-donating or withdrawing groups (-Cl, -H, -CH₃, -OCH₃) as reductants. These compounds with similar structures but different standard reduction potentials were used to synthesize Au NBPs at a series of solution pH. By correlating the reduction potential (calculated using the Nernst equation) with the dimensions and LSPR properties of the resulting Au NBPs, we demonstrate a consistent, reductant-independent relationship that confirms reduction potential as a dominant descriptor for the tested reductants. This finding provides a mechanistic framework that not only deepens our understanding of shape-controlled growth but also facilitates rational design and reproducibility in NP synthesis.

2 Experimental

2.1 Materials

Tetrachloroauric acid (HAuCl₄, ≥99.9%), citric acid (≥99.5%), sodium borohydride (NaBH₄, ≥99.99%), silver nitrate (AgNO₃, ≥99%), sodium carbonate (≥99.0%), sodium bicarbonate (99.5-100.5%), 4-chlorophenol (≥99.0%), and 4-methylphenol (≥99.0%) were purchased from Sigma-Aldrich. Phenol (≥99.0%) was purchased from Fisher. Hexadecyltrimethylammonium chloride (CTAC, >98%), hexadecyltrimethylammonium bromide (CTAB, >98%), and 4-methoxyphenol (>99%) were purchased from TCI. All chemicals were used without further purification. Ultrapure water (resistivity 18.20 MΩ·cm at 25 °C) was used in all the experiments.

2.2 Synthesis of seed solution

The seeds solution was prepared by using the thermally induced method [35, 44, 53]. Briefly, adding 3.5 mL of deionized water into a 20 mL scintillation vial, and followed by adding 25 μL of 100 mM HAuCl₄ solution while vigorous stirring with a magnetic stir bar at room temperature. Then 5 mL of 100 mM CTAC solution and 1 mL of 50 mM citric

acid solution were added as a subsequence. After the solution turned amber yellow, added 250 μL of 25 mM freshly prepared NaBH₄ solution with 2 min vigorous stirring while the solution turned from amber yellow to brownish. Then the vial was sealed and heated in a water bath at 80 °C for 90 min under gentle stirring. Finally, the solution becomes light red and stored at room temperature.

2.3 Synthesis of Au NBPs

All the synthesis was conducted in 20 mL glass vials, the 5 mL of 0.1 M CTAB solution, 50 μL of 50 mM HAuCl₄ solution, 100 μL of 0.01 M AgNO₃ solution (freshly prepared), variable amount of base (see corresponding tables depending on reducing agent used), and 75 μL of 0.1 M reducing agent solution (4-chlorophenol, phenol, 4-methylphenol, and 4-methoxyphenol) were added into the vials in subsequence under vigorous stirring at room temperature. When the solutions turned clear, revealing the reduction from Au(III) to Au(I), 35 μL of seeds solution were added into the growth solution under vigorous stirring at room temperature. Then, the vials were capped and left with gentle stirring at 30 °C for 7 h. Finally, the solutions were then centrifuged at 8000 rpm (6595 rcf) for 15 minutes at 25 °C and washed twice with 10 mL of CTAB (1mM).

2.4 Reference pH solution

A reference solution was made to test the initial pH value of the growth solution for various amounts of acid or base added. For the reference solution the same amount of 0.1 M CTAB, 50 mM HAuCl₄, 0.01 M AgNO₃ and 0.1 M reducing agent was used as in the growth solution (note: seeds were not used). At different amounts of base, the pH was measured (see corresponding tables in the Electronic Supplementary Material (ESM) for amounts and values). All measurements were made using a Thermo Scientific Orion Star A211 that was calibrated before use.

2.5 Instrumentation

Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100Plus (JEOL, Ltd., Japan) microscope operating at 110 kV. The copper grids were treated by glow discharge to improve their hydrophilicity at 15 mA for 25 s in order to obtain the best performance. We randomly measured at least 100 particles to determine the length, width, and aspect ratio of products using ImageJ software (the National Institutes of Health) and the data was reported as average ± standard deviation. Optical extinction spectra were measured with a BioTek Synergy H1 Multimode Reader (Agilent Technologies, Inc., USA). All the pH values were measured on a Thermo Scientific Orion Star A211 instrument (Thermo Fisher Scientific, USA).

3 Results and discussion

3.1 Effect of pH on the structure of Au NBPs synthesized from different phenol derivatives

Au NBPs were synthesized following our previously reported seed-mediated method using thermally treated seeds [35, 44, 53]. To investigate the effect of pH, we tested a series of 4-substituted phenol derivatives (4-chlorophenol, phenol, 4-methylphenol, and 4-methoxyphenol) as reductants under various pH conditions. To facilitate the comparison, the pH here is referred to as the initial pH value of the growth solution which can be adjusted easily using sodium carbonate or sodium bicarbonate enabling fine

control without strongly perturbing the system [31]. The initial pH was measured using identically prepared seed-free growth solutions because the seed solution constituted less than 0.7% of the total reaction volume and was therefore expected to have a negligible effect on the initial bulk pH. Because pH was not monitored during the subsequent

growth process, the reported values and calculated reduction potentials should be interpreted as estimates based on the initial reaction conditions.

The products synthesized at different pH were characterized by

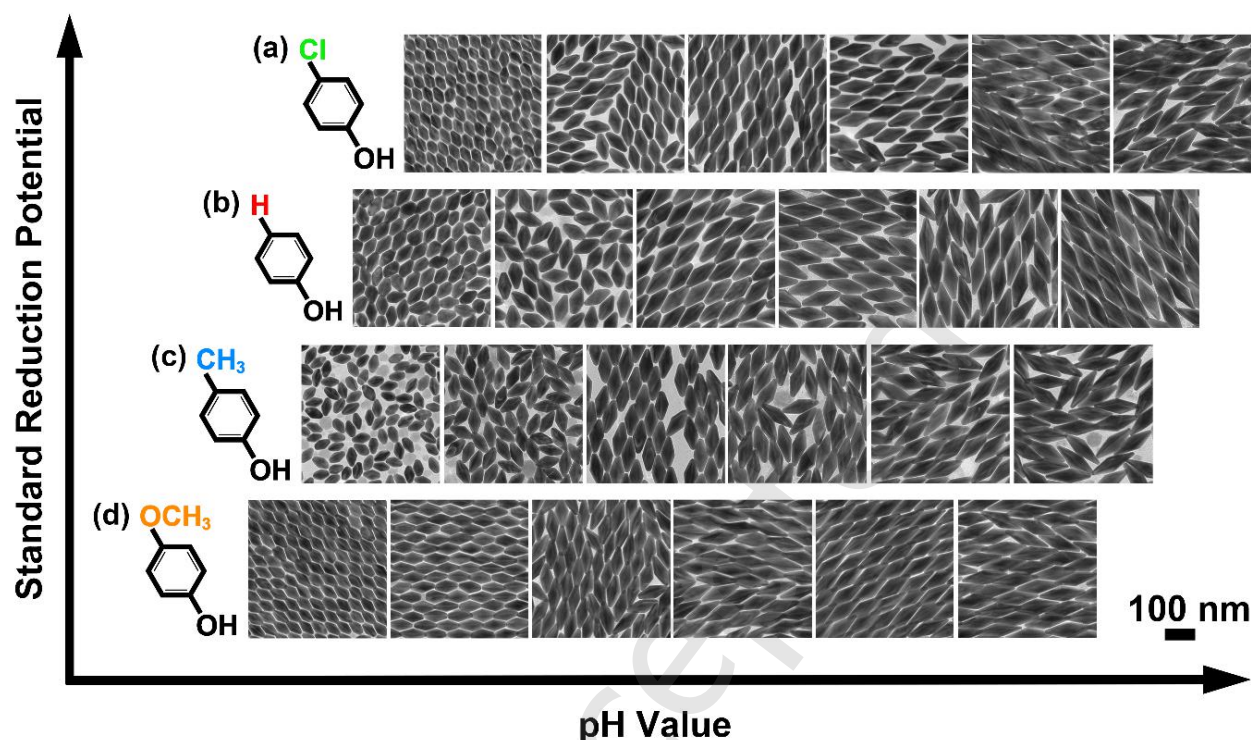


Figure 1. TEM images of the Au NBPs synthesized from various phenol derivatives at different pH values. (a) 4-chlorophenol, (b) phenol, (c) 4-methylphenol, (d) 4-methoxyphenol. Scale bar: 100 nm.

TEM and the results revealed that increasing the pH of the growth solution led to progressively elongated and sharper nanostructures, evolving from spheroidal shapes to well-defined bipyramids, as summarized in Fig. 1. For instance, with 4-chlorophenol as reductant, increasing pH from 7.42 to 10.57 resulted in an increase in particle length from 54.80 ± 3.41 nm to 166.85 ± 3.81 nm and width from 33.44 ± 2.39 nm to 54.90 ± 3.31 nm, leading to a corresponding aspect ratio increase from 1.31 ± 0.32 to 3.05 ± 0.19 . Similar trends were observed for other tested phenol derivatives (phenol, 4-methylphenol, 4-methoxyphenol). More TEM images (Figs. S1, S3, S5, and S7) and the size statistics of Au NBPs in these images (Tables S1-S4) can be found in the ESM.

Table 1. The literature half-wave oxidation potential ($E_{1/2}$) of different phenol derivatives and their corresponding pH range for the synthesis of Au NBPs.

Reductant	$E_{1/2}$ (V) vs. SCE	$E_{1/2}$ (V) vs. SHE	pH Range
4-chlorophenol	0.653	0.894	7.42-10.57
Phenol	0.633	0.874	6.88-9.19
4-methylphenol	0.541	0.784	6.22-7.44
4-methoxyphenol	0.406	0.647	4.81-6.14

To more clearly illustrate the influence of pH on Au NBP dimensions, the average length, width, and aspect ratio of the NPs synthesized with various phenol derivatives were plotted as a function of the initial pH of the growth solution (Figs. 2a-c). All four reductants exhibited a consistent trend:

as pH increased, the Au NBPs became larger and more anisotropic, with all these dimensional parameters (average length, width, and aspect ratio) increasing in a similar manner. However, the effective pH range for Au NBP formation varied depending on the substituent on the phenol ring, as summarized in Table 1. Phenol derivatives containing electron-withdrawing groups (e.g., -Cl) required higher pH values for Au NBP formation, whereas those with electron-donating groups (e.g., -CH₃, -OCH₃) were effective at lower pH compared to unsubstituted phenol (-H). Detailed statistical data from TEM analyses and the corresponding pH values are provided in Tables S1-S4 in the ESM. These observations are consistent with our previous findings using phenolic compounds bearing different numbers of hydroxyl groups as reductants in Au NP synthesis [31, 35].

3.2 Effect of the growth pH on the plasmonic properties of Au NBPs

Since the plasmonic properties of Au NPs are highly dependent on their shape and size, the pH-caused geometric changes observed in Au NBPs synthesis are expected to manifest in their LSPR absorption. To assess this, UV-Vis spectroscopy was performed on Au NBPs synthesized at various pH values using different phenol derivatives as reductants. As shown in Fig. 3, all spectra display two distinct plasmon bands corresponding to the transverse and longitudinal LSPR modes. While the transverse peak exhibits minimal shifts (<20 nm) with increasing pH, the longitudinal peak undergoes a pronounced red shift, moving from approximately 600 nm to 900 nm. This shift correlates with

the increased aspect ratio of the Au NBPs shown in Fig. 2c, indicating anisotropic growth. Notably, this trend was consistently observed across all four phenol derivatives tested. The corresponding UV-Vis spectral data and initial pH values are summarized in Tables S1-S4 in the ESM, and two-dimensional representations of the spectra are also available in the ESM (Figs. S2 for 4-chlorophenol, S4 for phenol, S6 for

4-methylphenol, and S8 for 4-methoxyphenol).

To further compare the pH dependence of the Au NBPs synthesis among the different reductants, the L-LSPR peak positions were plotted as a function of pH (Fig. 4a). Although the trend in L-LSPR shift with increasing pH is nearly identical for all compounds, each derivative operates within a distinct effective

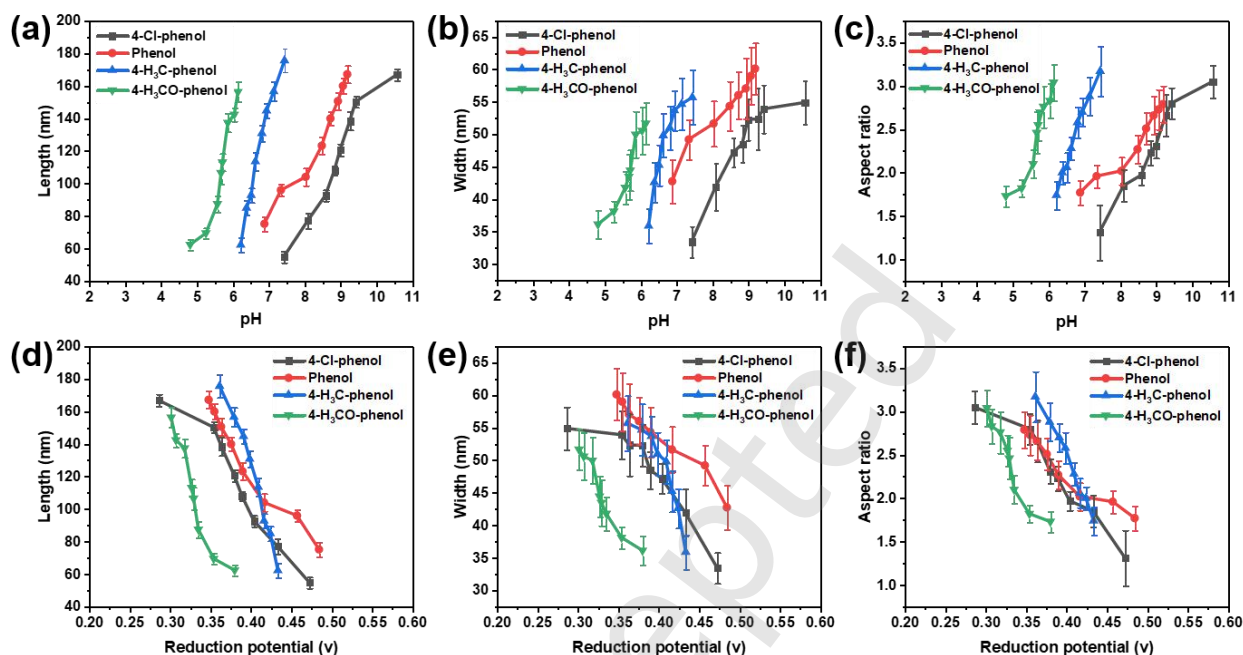


Figure 2. The variation of the dimensions and aspect ratios of Au NBPs synthesized from different phenol derivatives. (a-c) Length, width, and aspect ratio change of Au NBPs with the pH value of the growth solution. (d-f) Length, width, and aspect ratio change of Au NBPs with the reduction potential of the reductants.

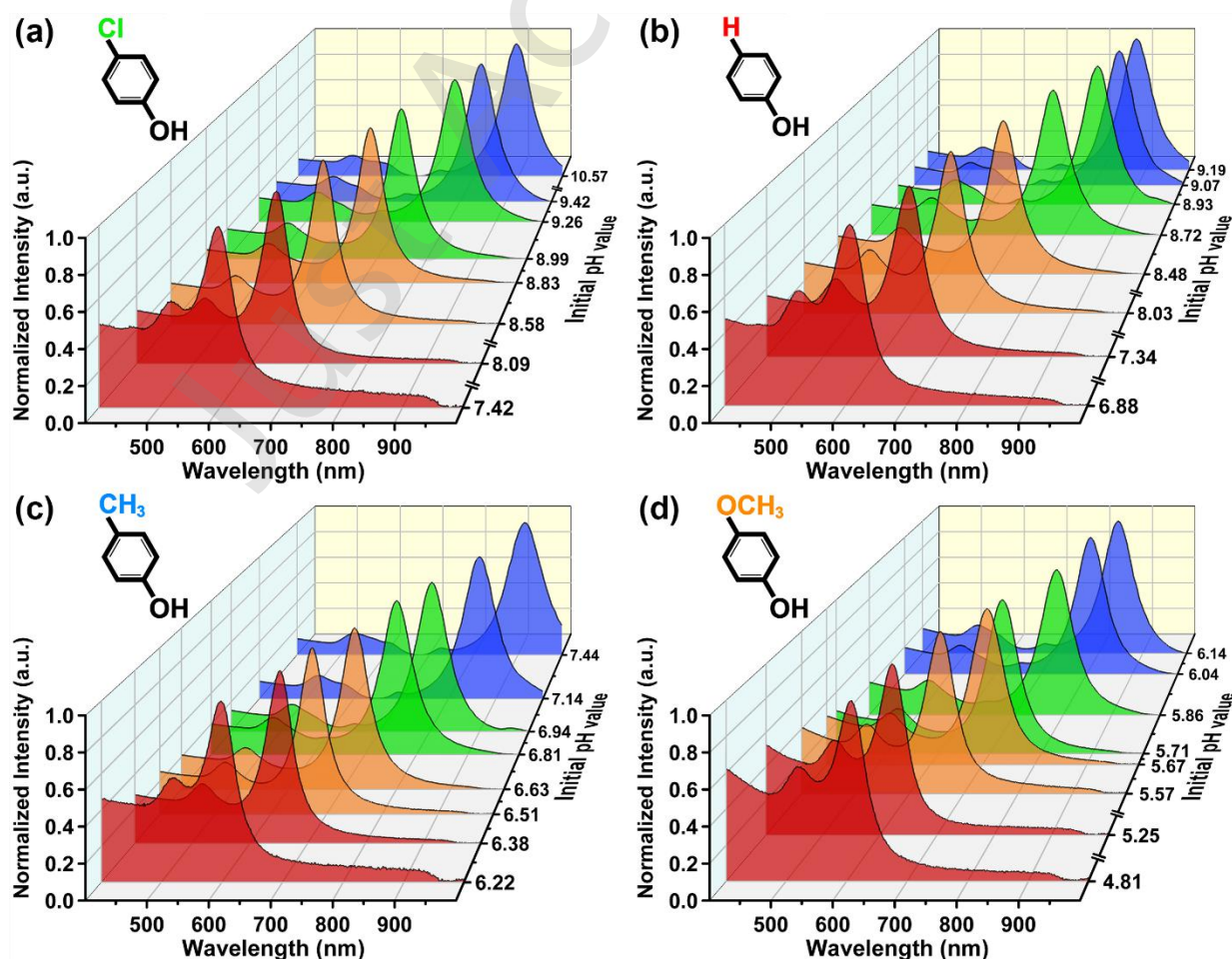


Figure 3. UV-Vis spectra of the Au NBPs synthesized from various phenol derivatives at different pH value. (a) 4-chlorophenol, (b) Phenol, (c) 4-methylphenol, (d) 4-methoxyphenol.

pH range: 4.81-6.14 for 4-methoxyphenol, 6.22-7.44 for 4-methylphenol, 6.88-9.19 for phenol, and 7.42-10.57 for 4-chlorophenol. This systematic variation reflects the electronic nature of the substituents: phenol derivatives

with electron-donating groups require lower pH values to achieve Au NBPs with equivalent L-LSPR peaks compared to those with electron-withdrawing groups.

3.3 Dependence of reduction potential on pH

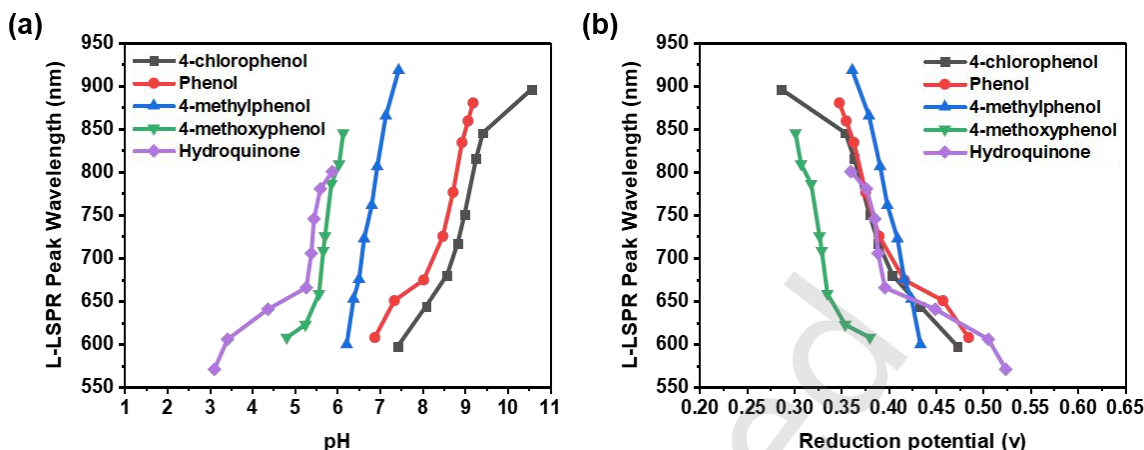
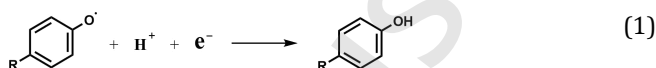


Figure 4. The variation of the peak wavelength of the L-LSPR band of Au NBPs synthesized from different phenol derivatives with the pH value of the growth solution (a) and their corresponding reduction potential (b). The data of hydroquinone was reproduced with permission from ref. 35.

To understand the influence of pH on Au NBP synthesis, as observed in Figs. 2a-c and 4a, it is essential to consider the redox reaction between the gold precursor and the phenol derivatives. The formation of Au NBPs involves a reduction-oxidation process in which phenol derivatives reduce HAuCl_4 , depositing gold atoms onto the seed particles. Whether this redox reaction proceeds depends on the overall reaction potential, defined as the difference between the reduction potentials of the two half-reactions. Assuming the reduction potential of the gold precursor remains relatively constant over the tested pH range, we focus on the oxidation half-reaction of the phenol derivatives. The more negative the reductant's reduction potential, the greater the overall reaction potential ($E = E_{\text{Au}} - E_{\text{PD}}$), and thus the more favorable the reduction of gold ions.



$$E_{\text{PD}} = E_{\text{PD}}^0 + 0.05916 \times \left(\log \frac{[\text{Ox}]}{[\text{Red}]} - \text{pH} \right) \quad (2)$$

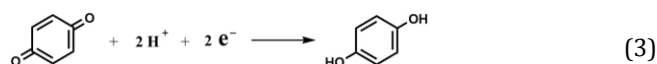
The generalized half-cell equation for the oxidation of phenol derivatives (Eq. (1)) involves the generation of a proton, directly linking the reaction to pH [54, 55]. According to the Nernst equation (Eq. (2)), the reduction potential of the phenol derivatives (E_{PD}) decreases with increasing pH. As a result, the overall redox potential increases ($E = E_{\text{Au}} - E_{\text{PD}}$), facilitating gold reduction and NP growth. This mechanistic insight explains the experimental observation in Figs. 3 and 4a, where the L-LSPR peak redshifts with increasing pH, reflecting the formation of higher aspect ratio Au NBPs. It also accounts for the presence of a minimum effective pH, below which the reductant's potential is insufficient to reduce gold ions efficiently or the reaction proceeds sluggishly.

3.4 Correlation Between L-LSPR peak position and reduction potential of phenol derivatives

The Nernst equation not only qualitatively describes how reduction potential varies with pH but also enables quantitative calculation of a reductant's reduction potential at a given pH, provided its standard electrode potential (E^0) and the concentrations of the redox species are known. In this study, the half-wave potentials ($E_{1/2}$) reported by Suatoni et al. [56] were used, instead of E^0 , for the phenol derivatives examined: 0.894 V for 4-chlorophenol, 0.874 V for phenol, 0.784 V for 4-methylphenol, and 0.647 V for 4-methoxyphenol (see Table 1). These $E_{1/2}$ values were obtained from cyclic voltammetry and represent the average of the anodic and cathodic peak potentials, offering a reliable experimental approximation of E^0 [57]. As expected, substituents on the phenol ring significantly influence $E_{1/2}$ values: electron-withdrawing groups (e.g., $-\text{Cl}$) increase $E_{1/2}$, while electron-donating groups (e.g., $-\text{CH}_3$, $-\text{OCH}_3$) decrease it. ⁵⁶ This trend is consistent with basic principles of organic chemistry, where electron-donating groups enhance the electron density of the hydroxyl group, increasing the compound's reducing power, whereas electron-withdrawing groups have the opposite effect [58].

By substituting the $E_{1/2}$ values, the initial pH of the growth solution, and the concentrations of the reductant and its oxidation product into Eq. (2), we calculated the reduction potentials for each phenol derivative under experimental conditions. When the L-LSPR peak positions of the synthesized Au NBPs were plotted against these calculated potentials (Fig. 4b), the curves for all these phenol derivatives nearly overlapped, with only a slight deviation observed for 4-methoxyphenol. This overlap indicates a universal quantitative relationship between the reduction potential of the reductant and the L-LSPR peak position (reflecting NP aspect ratio) regardless of the reductant's chemical identity. This finding strongly supports the role of reduction potential as a dominant descriptor in Au NBP synthesis and underscores its importance in mechanistic models. The small deviation observed for 4-methoxyphenol

may arise from the fact that, within its working pH range, the pH-dependent change in the reduction potential of the gold precursor may no longer be negligible. In such cases, the reductant's potential alone may not fully represent the net reaction potential. Importantly, this relationship also extends to NP size. As shown in Figs. 2d-f, plots of the average length, width, and aspect ratio versus reduction potential for all four phenol derivatives similarly converge, further validating the reduction potential as a key descriptor.



$$E_{HQ} = E_{HQ}^0 + \frac{0.05916}{2} \times (\log \frac{[Ox]}{[Red]} - 2 \times pH) \quad (4)$$

To evaluate the generality of this correlation, we analyzed data from our previously published work using hydroquinone as the reductant [35]. Unlike the monosubstituted phenol derivatives, hydroquinone features two hydroxyl groups and undergoes a two-electron oxidation (Eq. (3)) [59]. Its pH-dependent reduction potential was calculated using a modified Nernst equation (Eq. (4)), which includes a $2 \times pH$ term to reflect the release of two protons per molecule oxidized. The standard reduction potential of hydroquinone (E_{HQ}^0) is reported as 0.643 V [51, 59]. Using this value, the pH, and concentrations of hydroquinone and its oxidation product (1,4-benzoquinone), we calculated E_{HQ} and plotted the corresponding L-LSPR peak positions. Remarkably, the curve for hydroquinone nearly overlapped with those of the phenol derivatives, despite its structural and redox differences. This further demonstrates that the observed correlation between reduction potential and Au NBP morphology is broadly applicable and not limited to a specific reductant that we tested.

4 Conclusions

This study demonstrates that the reduction potential of the reductant is a dominant descriptor governing the shape-controlled synthesis of Au NBPs. By employing a series of phenol derivatives with tunable redox properties, we show that the aspect ratio and corresponding L-LSPR peak wavelength of Au NBPs can be quantitatively linked to the calculated reduction potential of the growth solution, regardless of the reductant's molecular structure. The convergence of data from various reductants, including hydroquinone, onto a single trend highlights the generality of this relationship under the investigated conditions. These insights offer a mechanistic basis for understanding and predicting NP morphology in seed-mediated syntheses. Incorporating reduction potential into the design framework enables improved reproducibility and facilitates the rational selection of reductants for targeted NP geometries and optical properties. This concept is broadly applicable to other colloidal systems and offers a valuable strategy for advancing the precision and reliability of nanomaterial synthesis.

Electronic Supplementary Material: Supplementary material (TEM images, UV-Vis spectra, and tables of the statistical data of the products from different reductants) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909130>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

D. H.: Conceptualization, data curation, formal analysis, methodology, visualization, writing – original draft. X. Z.: Conceptualization, data curation, methodology, writing – review & editing. T. E.: data curation, validation. Y. T. T.: data curation, validation. G. C.: Conceptualization, formal analysis, funding acquisition, methodology, project administration, resources, supervision, writing – review & editing. All the authors have approved the final manuscript.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

During the preparation of this work, the authors used ChatGPT for language editing and the TOC creation. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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Electronic Supplementary Material

Quantifying the role of redox thermodynamics in the shape-controlled synthesis of gold nanobipyramids

Dong He^{1,2}, Xing Zhang^{1,3}, Thomas Egan¹, Yiteng, Tang^{4,5}, and Gang Chen^{1,4,5}  

¹ Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA

² State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, Jilin 130012, China

³ National Key Laboratory of Opto-Electronic Information Acquisition and Protection Technology, Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China

⁴ Department of Biochemistry, Chemistry and Physics, Georgia Southern University, GA 30458, USA

⁵ Center for Advanced Materials Science, Georgia Southern University, GA 30458, USA

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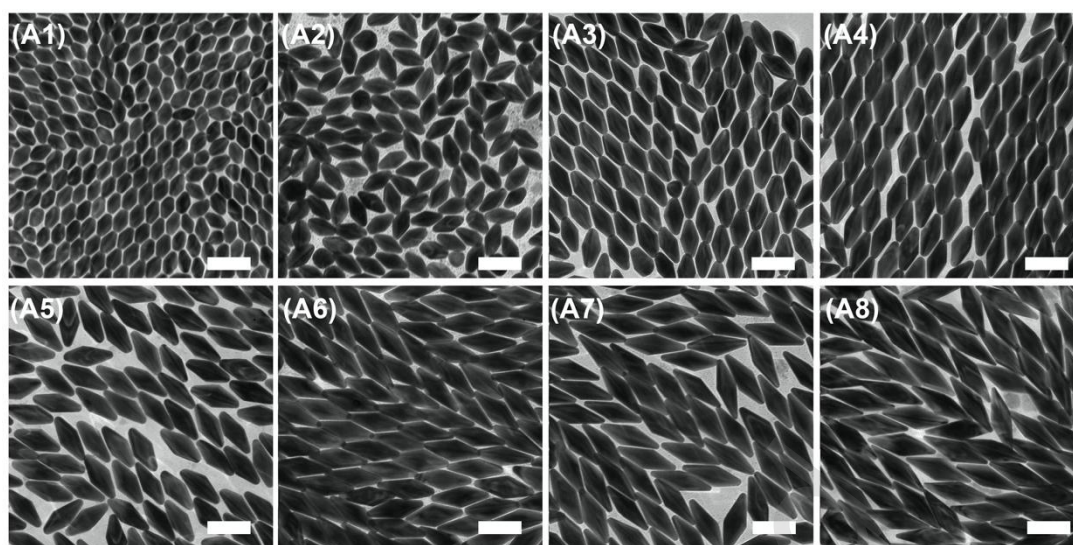


Figure S1. The TEM images of Au NPs prepared from 4-chlorophenol at different pH values (7.42, 8.09, 8.58, 8.83, 8.99, 9.26, 9.42, and 10.57). Scale bar: 100 nm.

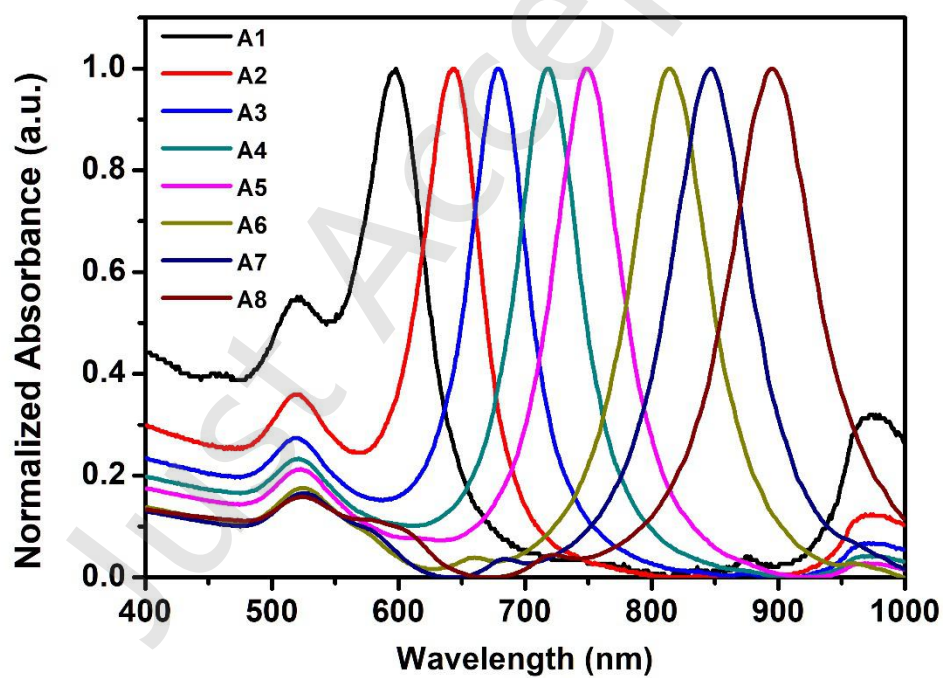


Figure S2. The normalized UV-Vis spectra of Au NPs prepared from 4-chlorophenol at different pH values (7.42, 8.09, 8.58, 8.83, 8.99, 9.26, 9.42, and 10.57).

Table S1. Dimensions, aspect ratios, and LSPR of the Au NBPs prepared from 4-chlorophenol at different pH values.

Sample	^[a] Na ₂ CO ₃ (μL)	pH	Length (nm)	Width (nm)	Aspect Ratio	^[b] LSPR (nm)
A1	25	7.42	54.80±3.41	33.44±2.39	1.31±0.32	597
A2	35	8.09	77.17±4.73	41.94±3.64	1.85±0.18	644
A3	40	8.58	92.67±3.45	47.21±2.28	1.97±0.11	680
A4	45	8.83	108.01±2.98	48.51±2.83	2.23±0.14	717
A5	50	8.99	120.63±3.65	52.28±3.20	2.31±0.14	750
A6	60	9.26	138.40±5.58	52.37±4.74	2.66±0.24	815
A7	70	9.42	150.23±3.36	53.92±3.70	2.80±0.18	845
A8	300	10.57	166.85±3.81	54.90±3.31	3.05±0.19	896

concentration of Na₂CO₃ solution is 0.2 mol·L⁻¹.

[b] The peak wavelength of the longitudinal LSPR band.

[a]
The

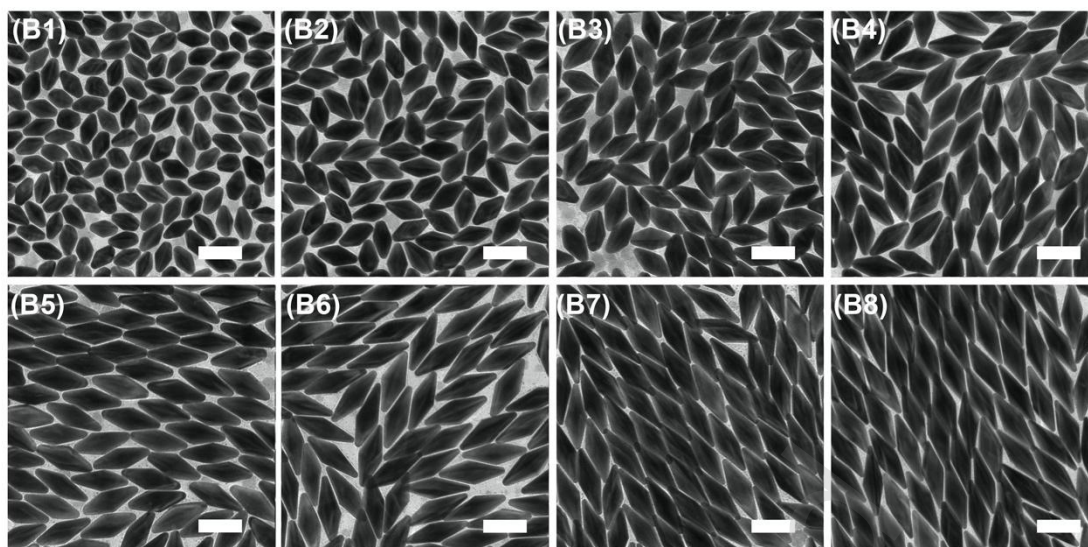


Figure S3. The TEM images of Au NBPs prepared from phenol at different pH values (6.88, 7.34, 8.03, 8.48, 8.72, 8.93, 9.07, and 9.19). Scale bar: 100 nm.

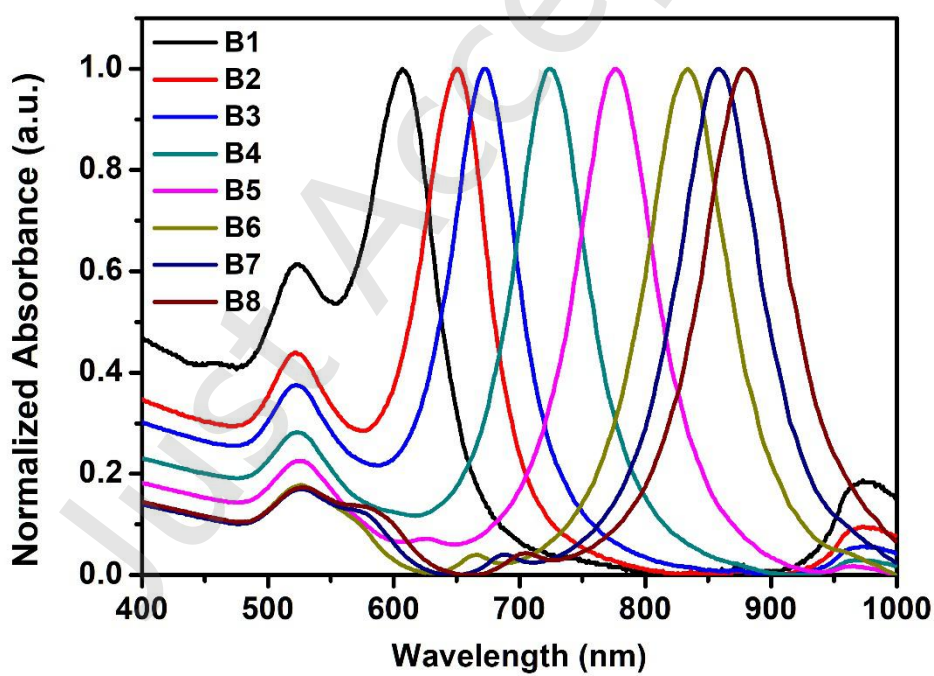


Figure S4. The normalized UV-Vis spectra of Au NBPs prepared from phenol at different pH values (6.88, 7.34, 8.03, 8.48, 8.72, 8.93, 9.07, and 9.19).

Table S2. Dimensions, aspect ratios, and LSPR of the Au NBPs prepared from phenol at different pH values.

Sample	^[a] Na ₂ CO ₃ (μL)	pH (initial)	Length (nm)	Width (nm)	Aspect Ratio	^[b] LSPR (nm)
B1	35	6.88	75.13±4.31	42.76±3.41	1.77±0.14	607
B2	40	7.34	95.91±3.51	49.21±3.09	1.96±0.13	650
B3	50	8.03	104.02±5.40	51.65±3.51	2.02±0.16	674
B4	60	8.48	123.25±5.26	54.36±3.81	2.27±0.16	725
B5	70	8.72	139.95±4.21	56.03±3.59	2.51±0.18	776
B6	80	8.93	150.68±5.08	57.07±4.67	2.66±0.22	834
B7	90	9.07	160.04±4.76	59.01±4.42	2.73±0.23	859
B8	100	9.19	167.24±5.37	60.13±3.97	2.79±0.21	880

[a] The concentration of Na₂CO₃ solution is 0.1 mol·L⁻¹.

[b] The peak wavelength of the longitudinal LSPR band.

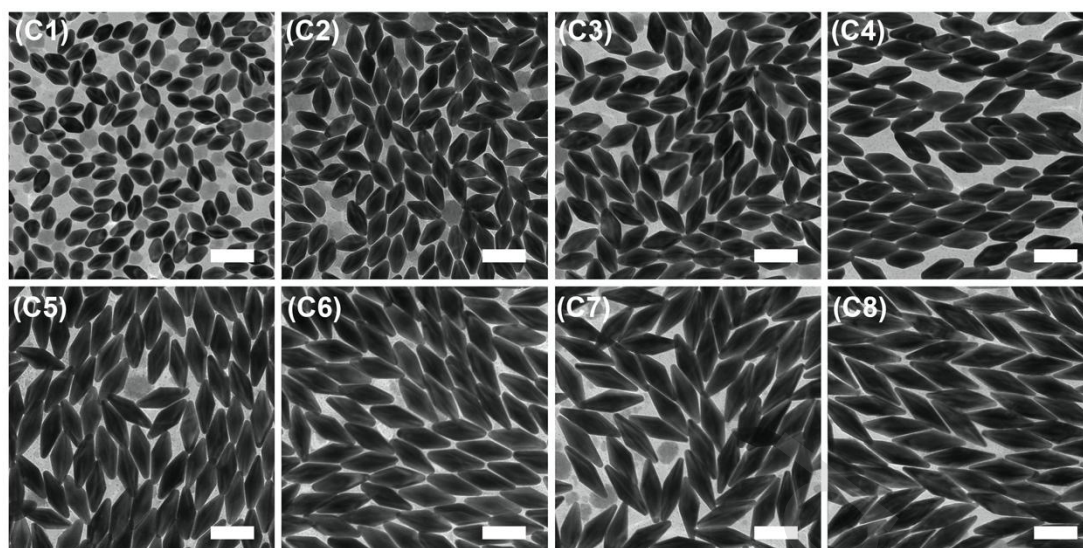


Figure S5. The TEM images of Au NBPs prepared from 4-methylphenol at different pH values (6.22, 6.38, 6.51, 6.63, 6.81, 6.94, 7.14, and 7.44). Scale bar: 100 nm.

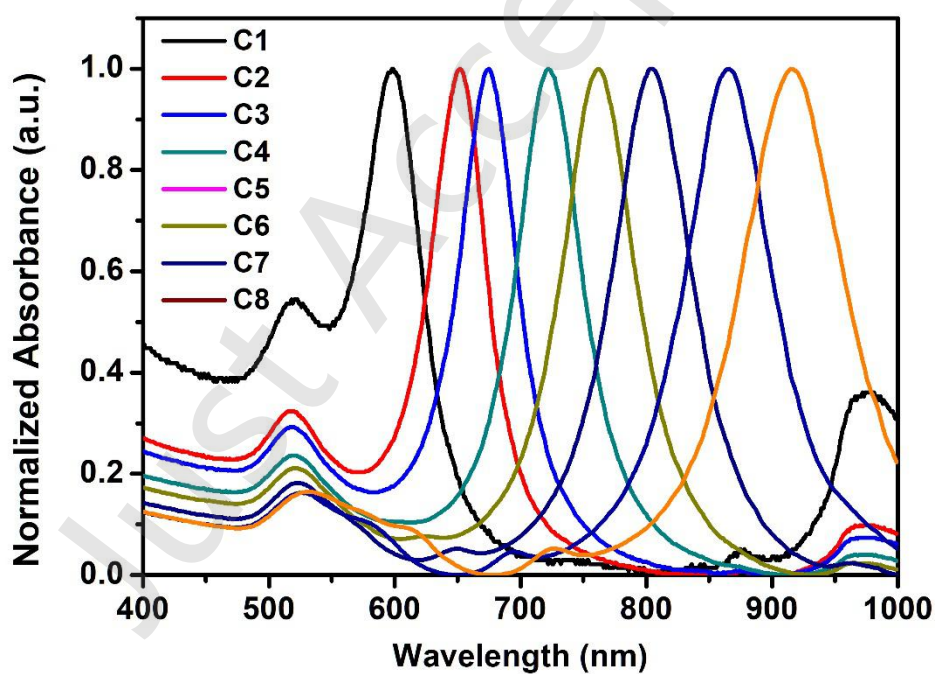


Figure S6. The normalized UV-Vis spectra of Au NBPs prepared from 4-methylphenol at different pH values (6.22, 6.38, 6.51, 6.63, 6.81, 6.94, 7.14, and 7.44).

Table S3. Dimensions, aspect ratios, and LSPR of the Au NBPs prepared from 4-methylphenol at different pH values.

Sample	^[a] NaHCO ₃ (μL)	pH (initial)	Length (nm)	Width (nm)	Aspect Ratio	^[b] LSPR (nm)
C1	50	6.22	62.12±4.35	35.88±2.65	1.74±0.16	599
C2	55	6.38	84.91±4.50	42.60±3.01	2.00±0.13	652
C3	60	6.51	92.69±4.44	45.25±3.14	2.06±0.17	675
C4	65	6.63	113.50±5.47	49.81±3.36	2.28±0.13	722
C5	75	6.81	130.84±4.95	51.00±3.30	2.58±0.18	761
C6	80	6.94	144.78±4.27	53.69±3.05	2.70±0.16	806
C7	100	7.14	156.63±5.75	54.68±3.97	2.88±0.22	865
C8	150	7.44	175.62±7.04	55.69±4.21	3.17±0.29	918

[a] The concentration of NaHCO₃ solution is 0.1 mol·L⁻¹.

[b] The peak wavelength of the longitudinal LSPR band.

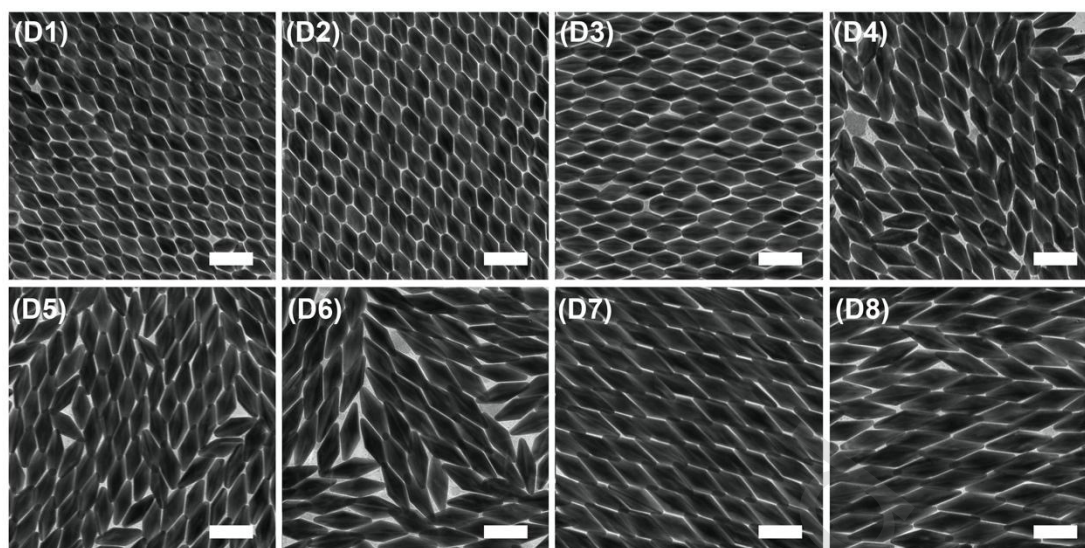


Figure S7. The TEM images of Au NBPs prepared from 4-methoxyphenol at different pH values (4.81, 5.25, 5.57, 5.67, 5.71, 5.86, 6.04, and 6.14). Scale bar: 100 nm.

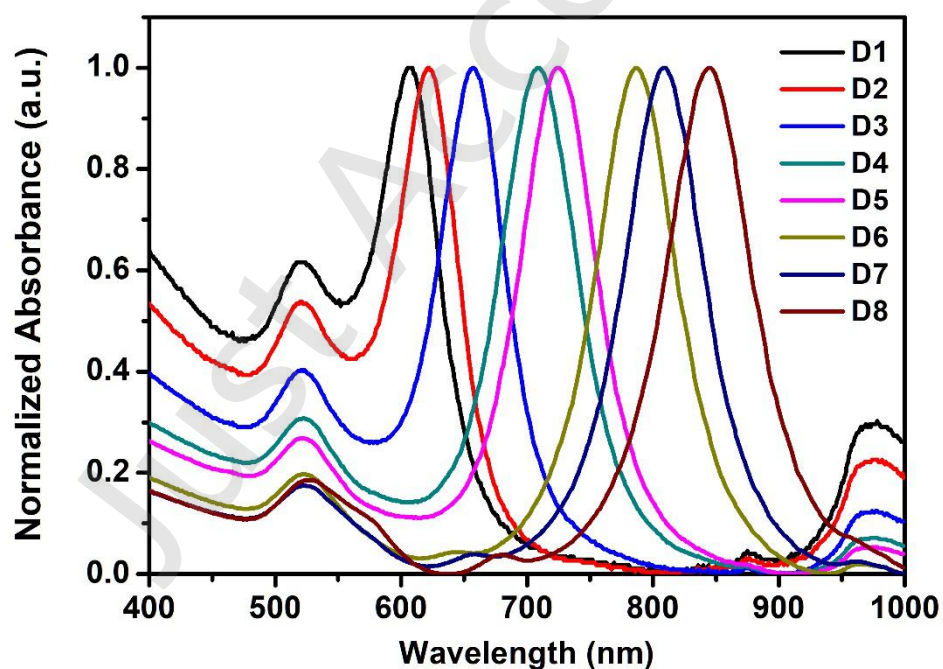


Figure S8. The normalized UV-Vis spectra of Au NBPs prepared from 4-methoxyphenol at different pH values (4.81, 5.25, 5.57, 5.67, 5.71, 5.86, 6.04, and 6.14).

Table S4. Dimensions, aspect ratios, and LSPR of the Au NBPs prepared from 4-methoxyphenol at different pH values.

Sample	^[a] NaHCO ₃ (μL)	pH (initial)	Length (nm)	Width (nm)	Aspect Ratio	^[b] LSPR (nm)
D1	52.5	4.81	62.37±3.49	36.11±2.22	1.73±0.12	607
D2	55	5.25	69.41±3.29	38.10±1.63	1.82±0.10	622
D3	58.5	5.57	87.38±5.27	41.78±2.53	2.10±0.16	658
D4	59.5	5.67	106.46±6.85	43.48±3.52	2.46±0.24	708
D5	60	5.71	113.04±5.29	44.44±3.13	2.55±0.18	725
D6	62.5	5.86	137.39±5.7	49.97±3.54	2.76±0.24	786
D7	65	6.04	142.45±4.13	50.58±3.61	2.83±0.2	809
D8	66	6.14	156.35±6.15	51.67±3.19	3.04±0.21	845

[a] The concentration of NaHCO₃ solution is 0.1 mol·L⁻¹.

[b] The peak wavelength of the longitudinal LSPR band.