

Visible-Light-Driven Green Assembly of Anisotropic Silver Nanocrystals via Ligand-to-Metal Charge Transfer Chemistry

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Research Article

Keywords: anisotropic silver nanoparticles, ligand-to-metal charge transfer, photoinduced self-assembly, reactive oxygen species, colorimetric sensing

Posted Date: July 30th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10193364/v1>

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Additional Declarations: No competing interests reported.

Abstract

The controllable growth and photochemical formation mechanisms of anisotropic noble-metal nanocrystals represent a crucial frontier in the development of sustainable plasmonic materials. Herein, we construct an entirely green, visible-light-driven photochemical system comprising dextran, trisodium citrate (TSC), and AgNO_3 to achieve the highly controlled self-assembly of spiky silver nanocrystals. Capitalizing on the interfacial electron separation process induced by ligand-to-metal charge transfer (LMCT), this system drives the directional growth of silver nanostructures without requiring exogenous reducing agents or surfactants. In situ monitoring reveals a sequential morphological evolution spanning spherical, rod-like, and platelet intermediates, culminating in hierarchical spiky architectures that manifest pronounced plasmonic enhancement effects. Through a combination of in situ electron paramagnetic resonance (EPR), chemical quenching kinetics, and time-resolved NMR analyses, we unveil for the first time a triple-parallel photocatalytic reduction network. This network is driven synergistically by direct LMCT photoreduction, superoxide anion radical ($\cdot\text{O}_2^-$)-mediated cascade reduction, and singlet oxygen ($^1\text{O}_2$)-mediated secondary reduction, while simultaneously clarifying the dual role of dextran in sacrificial electron donation and interfacial stabilization. Density functional theory (DFT) calculations corroborate that TSC exhibits a thermodynamic preference for adsorption on the $\text{Ag}\{111\}$ facet, elucidating the facet-directed mechanism underlying the anisotropic growth of the spiky architecture. This work establishes a comprehensive mechanistic framework for LMCT-driven green photochemical nano-assembly and offers a sustainable strategy for the rational architectural design of advanced anisotropic noble-metal nanomaterials.

1. Introduction

The rational design and synthesis of anisotropic noble-metal nanomaterials with tailored morphologies and distinctive optoelectronic properties have emerged as critical research frontiers in microelectronics, interfacial catalysis, and advanced sensing[1]. Among the diverse library of metallic nanostructures, silver nanocrystals have attracted particular attention owing to their exceptionally high molar extinction coefficients in the visible spectrum and outstanding localized surface plasmon resonance (LSPR) characteristics[2]. Crucially, the geometric morphology of a nanocrystal functions as the primary control variable governing its electromagnetic response—a relationship that underpins the structure–property paradigm at the nanoscale[3]. Compared with optically isotropic spherical particles exhibiting a single dipolar plasmon mode, anisotropic nanocrystals with high surface curvature and hierarchically branched architectures—including nanorods, nanoplates, and nanostars—sustain complex multipolar plasmon resonances[4]. These structures spontaneously concentrate and dramatically amplify the local electromagnetic field at their tips and nanogaps, generating high-density plasmonic ‘hotspots’[5]. Even subtle dielectric perturbations in the surrounding medium, or specific molecular adsorption at the nanocrystal–solution interface, can induce pronounced broadband spectral shifts and morphological reconstruction, establishing a robust physicochemical foundation for the development of high-sensitivity, instrument-free colorimetric sensing platforms[6].

Despite their immense promise, conventional synthetic paradigms for high-performance anisotropic silver nanocrystals have long confronted severe challenges in terms of ecological compliance and manufacturing sustainability. Prevailing thermochemical routes rely critically on either high-energy-density, highly toxic reducing agents (e.g., sodium borohydride) or structure-directing surfactants (e.g., cetyltrimethylammonium bromide, CTAB) that impose preferential crystal facet coverage[7]. These exogenous species not only passivate surface active sites and suppress the intrinsic plasmonic response, but also raise serious toxicological concerns in direct-contact applications such as biomedical devices and active food packaging, where stringent regulatory compliance is mandatory[8]. There is therefore a compelling and urgent scientific imperative to develop photochemical strategies capable of achieving precision synthesis of anisotropic noble-metal nanocrystals under mild, aqueous, and environmentally benign conditions.

Among emerging green, light-driven fabrication strategies, photochemical routes exploiting ligand-to-metal charge transfer (LMCT) mechanisms have recently emerged as ideal platforms for the synthesis of contamination-free, high-purity nanomaterials[9]. In LMCT-active systems, transition metal ions coordinate with specific organic ligands to form complexes in which, upon photoexcitation at a characteristic wavelength, electrons are directly injected from the ligand's occupied molecular orbitals into the unoccupied orbitals of the metal ion[10]. This process achieves precise metal ion reduction without requiring an auxiliary semiconductor photocatalyst or high-energy UV irradiation, embodying exceptional atomic economy through its 'coordinate-to-sensitize, in situ-to-activate' intrinsic mechanism[11]. As a prototypical bifunctional polycarboxylate ligand, trisodium citrate (TSC) coordinates in situ with Ag^+ to form highly photoactive $[\text{TSC}-\text{Ag}^+]$ chromophores and exhibits thermodynamically selective adsorption affinity toward specific low-index crystal facets—a feature critical for anisotropic morphology control[12]. However, the excited-state charge-separation dynamics triggered by LMCT are inherently transient and are frequently accompanied by rapid non-radiative relaxation and energy dissipation[13]. More importantly, the cascade oxidation–reduction dynamics mediated by dissolved oxygen species in solution—including the in situ generation, transformation, and consumption of reactive oxygen species (ROS)—and their coupling with the nucleation–growth kinetics of the nanocrystal over its full lifetime have remained largely opaque, owing to the absence of rigorous, time-resolved spectroscopic evidence. This fundamental gap has severely constrained the rational design of anisotropic morphologies via LMCT-directed photochemistry[14].

A second key scientific challenge concerns how natural macromolecules can synergize with photochemical reduction systems to achieve high-yield, high-stability controlled synthesis. Dextran, a water-soluble polysaccharide with a densely hydroxylated backbone, has traditionally been regarded solely as a passive steric stabilizer that prevents colloidal aggregation[15]. However, in a dynamically evolving multicomponent photocatalytic interface, a deeper and mechanistically unresolved question arises: can the rich polyhydroxyl microenvironment of the flexible polymer chain accelerate the transient LMCT excited-state charge separation through interfacial electronic coupling? Can dextran serve as a sacrificial electron-transfer conduit driving catalytic regeneration of the ligand? These intimate interfacial

synergy mechanisms have yet to be revealed through the concerted application of quantum chemical computation and multidimensional modern spectroscopy.

Addressing these intertwined challenges, the present work constructs a fully biocompatible, visible-light-LED-responsive ternary LMCT photocatalytic self-assembly system comprising flexible biomass-derived dextran, bifunctional ligand TSC, and silver nitrate. We systematically deconstruct the photoinduced morphological evolution and growth mechanism of anisotropic silver nanocrystals, and demonstrate their integration into device architectures for intelligent health monitoring in complex matrices. By combining in situ EPR spectroscopy, spatiotemporally resolved NMR, and systematic quenching kinetics experiments, we present, for the first time, a complete cartography of a triple-parallel photocatalytic reduction network—encompassing direct LMCT photoreduction, $\bullet\text{O}_2^-$ cascade reduction, and $^1\text{O}_2$ -mediated secondary reduction—and quantitatively establish the interfacial synergy mechanism by which dextran amplifies the overall photocatalytic yield approximately 2.1-fold through regeneration of TSC via elimination of the TSC radical cation ($\text{TSC}^{\bullet+}$). DFT calculations quantify the thermodynamic preference of TSC for Ag{111} facets, providing an atomic-scale mechanistic basis for the directional anisotropic growth. We further identify a critical methodological pitfall associated with the use of NaN_3 as a spin quencher in LMCT-type photocatalytic systems. Finally, leveraging the dense plasmonic hotspots of the resulting spiky nanocrystals for ultra-sensitive colorimetric detection of sulfur-containing VOCs released during meat spoilage, we construct flexible photonic hydrogel sensing labels that enable real-time, zero-energy, naked-eye qualitative and quantitative monitoring of the total volatile basic nitrogen (TVB-N) index across the entire supply chain. This work not only establishes a systematic mechanistic paradigm for LMCT-driven green photochemical precision synthesis, but also provides a universally applicable scientific strategy for the design of low-carbon, environmentally sustainable intelligent active packaging materials.

2. Materials and Methods

2.1 Reagents and Materials

Dextran (MW 40,000), trisodium citrate (TSC, $\geq 99\%$), silver nitrate (AgNO_3 , $\geq 99.8\%$), sodium sulfide (Na_2S , $\geq 98\%$), disodium ethylenediaminetetraacetate (EDTA-2Na), sodium azide (NaN_3), methanol (MeOH, analytical grade), tert-butanol (TBA, $\geq 99\%$), isopropanol (IPA, $\geq 99\%$), p-benzoquinone (PBQ, $\geq 98\%$), and triethanolamine (TEOA, $\geq 99\%$) were all purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Superoxide dismutase (SOD, ≥ 3000 U/mg) was obtained from Sigma-Aldrich (St. Louis, MO, USA). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetramethylpiperidine (TEMP), and 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) were purchased from TCI Chemicals (Tokyo, Japan) for EPR radical detection. All aqueous solutions were prepared with ultrapure water (resistivity ≥ 18.2 M Ω ·cm). Fresh chicken wings, pork, and lobster were sourced from a local market immediately prior to use, with the same batch of samples used for both colorimetric detection and TVB-N parallel determination.

2.2 Photocatalytic Synthesis of Anisotropic Silver Nanoparticles

Anisotropic silver nanoparticles (AgNPs) were synthesized via a ternary LMCT photocatalytic system under visible-light LED irradiation. Under standard conditions, dextran (1 mg/mL) and TSC (10 mM) were dissolved in ultrapure water, followed by the addition of AgNO_3 to a final concentration of 0.01 μM under magnetic stirring. The mixture was transferred to a quartz reaction cell and irradiated with a visible-light LED source (wavelength range: 400–700 nm; irradiance: $\sim 50 \text{ mW/cm}^2$) for predetermined intervals (10, 20, 30, 40, and 60 min). The reaction temperature was maintained at $25 \pm 0.5^\circ\text{C}$ throughout using a thermostated recirculating water bath. To systematically investigate the influence of synthetic parameters, irradiation time (10–60 min), reaction temperature ($25\text{--}75^\circ\text{C}$), dextran concentration (1–4 mg/mL), TSC concentration (2–10 mM), and AgNO_3 concentration (0.01–0.13 μM) were each independently varied while all other parameters were held at their standard values. All experiments were conducted in independent triplicate ($n = 3$).

2.3 Nanoparticle Characterization

UV–visible (UV–Vis) absorption spectra were acquired using a SpectraMax M3 microplate reader (Molecular Devices, Sunnyvale, CA, USA) over 200–1000 nm, with ultrapure water as the blank reference, to monitor the evolution of the LSPR absorption features during photocatalytic synthesis. Fourier-transform infrared (FTIR) spectra were collected on an Antaris II FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) in attenuated total reflectance (ATR) liquid mode ($500\text{--}4000 \text{ cm}^{-1}$; 32 scans; resolution 32 cm^{-1} ; 25°C) to probe functional group changes and ligand–metal interactions. Raman spectra were recorded on a HORIBA LabRAM HR Evolution confocal Raman microscope (HORIBA Scientific, France) with a 50 $\times$ objective lens and 532 nm laser excitation (scan range $400\text{--}4000 \text{ cm}^{-1}$; integration time 20 s; 2 accumulations; spectral resolution 2 cm^{-1}), with each sample measured in triplicate. ^1H and ^{13}C NMR spectra were acquired on a 600 MHz superconducting NMR spectrometer (D_2O solvent; TMS internal standard, $\delta = 0 \text{ ppm}$) to track structural transformations and oxidation events involving dextran and TSC during photocatalysis. Dynamic light scattering (DLS) and zeta potential measurements were performed to quantify hydrodynamic diameter and surface charge dynamics, respectively. X-ray photoelectron spectroscopy (XPS) was conducted with monochromatic Al K α radiation, with binding energy calibration referenced to the adventitious C 1s peak at 284.8 eV; high-resolution spectra were deconvoluted using a mixed Gaussian–Lorentzian function to quantify elemental valence states and surface ligand coordination.

2.4 Density Functional Theory (DFT) Calculations

All the DFT calculations were conducted based on the Vienna Ab initio Simulation Package (VASP). The exchange-correlation potential was described by the Perdew–Burke–Ernzerhof (PBE) generalized gradient approach (GGA). The electron-ion interactions were accounted by the projector augmented wave (PAW). All DFT calculations were performed with a cut-off energy of 400 eV, and the $3\times 3\times 1$ Monkhorst-Pack grid k-points were selected to sample the Brillouin zone integration. The energy and

force convergence criteria of the self-consistent iteration were set to 10^{-4} eV and -0.02 eV $\text{\AA}^{-1}$, respectively. DFT-D3 method is adopted to describe the van der Waals interaction.

The adsorption energy (E_{ads}) of adsorbate A was defined as

$$E_{\text{ads}} = E_{\text{*A}} - E_{\text{A}} - E_{\text{sub}}$$

where $E_{\text{*A}}$ represent the energy of A adsorbed on the surface. E_{sub} is the energy of clean surface, E_{A} represent the energies of A

2.5 Identification of Reactive Oxygen Species and Quenching Experiments

In situ EPR measurements were performed at room temperature using the following spin-trapping probes: DMPO (100 mmol/L) in aqueous and methanolic phases for the detection of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, respectively; TEMP (100 mmol/L) for $^1\text{O}_2$ trapping; and TEMPO (100 mmol/L) for detection of the photo-oxidative intermediate ($\text{h}^+/\text{TSC}\cdot^+$). EPR spectra were recorded under dark conditions and after 1, 5, and 10 min of visible-light irradiation. Control experiments under N_2 atmosphere were performed in hermetically sealed systems following 30 min of N_2 purging. Radical quenching agents were employed as follows: MeOH (1% v/v), TBA (10 mM), and IPA (10 mM) as $\cdot\text{OH}$ scavengers; SOD (50 U/mL) as a $\cdot\text{O}_2^-$ -specific quencher; NaN_3 (10 mM) as a putative $^1\text{O}_2$ quencher; EDTA-2Na (5 mM) as a photo-oxidative species ($\text{TSC}\cdot^+$) quencher; PBQ (1 mM) as a chemical $\cdot\text{O}_2^-$ quencher; TEOA (5 mM) as a photogenerated hole quencher; and additional AgNO_3 (1 mM) as a photogenerated electron quencher. All quenching experiments were conducted under standard synthesis conditions with 60 min irradiation, and silver nanocrystal yield was quantified by absorbance at 420 nm (A_{420} ; $n = 3$). A supplementary $\text{N}_2 + \text{NaN}_3$ combined experiment was conducted in a hermetically sealed, N_2 -purged system to disambiguate the quenching mechanism of NaN_3 .

2.6 Colorimetric Detection of Sulfur-Containing Compounds

Anisotropic AgNPs synthesized at three representative AgNO_3 concentrations (0.01, 0.03, and 0.13 μM) under standard conditions (60 min irradiation) were used as colorimetric probes. Aliquots (1 mL) of each nanoparticle suspension were treated with Na_2S solutions at concentrations ranging from 0 to 100 μM , mixed, and allowed to react for 15 min at room temperature before recording UV–Vis absorption spectra. The absorbance change at 420 nm (ΔA_{420}) was used as the quantitative readout, and a linear calibration curve was constructed ($n = 3$). Selectivity was evaluated by separately adding 50 μM of common meat-spoilage volatiles—including Na_2S , methanethiol, acetic acid, butyric acid, trimethylamine, cadaverine, and putrescine—to AgNP suspensions (0.01 μM AgNO_3 -derived) and recording the corresponding ΔA_{420} responses. Post-reaction nanoparticle morphology and elemental composition were characterized by TEM combined with HAADF-STEM and energy-dispersive X-ray (EDX) elemental mapping.

2.7 Real-Time Colorimetric Monitoring of Meat Freshness

Colorimetric sensing labels were fabricated by mixing equal volumes of each AgNP suspension (0.01, 0.03, or 0.13 μM AgNO_3 -derived) with pre-heated 2% (w/v) agarose solution (100°C), rapidly casting the mixture into cylindrical molds (diameter 1 cm), and allowing gelation at room temperature to yield optically transparent composite hydrogel discs. Fresh chicken wings (~ 80 g), pork (~ 100 g), and lobster (~ 70 g) were placed in separate 10 cm-diameter Petri dishes; the sensing labels were affixed to the inner surface of each dish lid, positioned above but not in direct contact with the meat, to sample volatile headspace gases. Samples were stored at 4°C (refrigeration) or 25°C (ambient temperature) and photographed at defined time intervals under a standardized light source. TVB-N content was determined according to the Chinese National Standard GB 5009.228–2016 using an automatic Kjeldahl apparatus: 10 g of minced chicken breast was combined with 100 mL of ultrapure water, shaken for 30 min, filtered, and a 10 mL aliquot of the filtrate was distilled with 1 g of MgO; results are expressed as mg TVB-N per 100 g of meat. Freshness thresholds were defined as: fresh (< 15 mg/100 g), sub-fresh (15–25 mg/100 g), and spoiled (> 25 mg/100 g), consistent with Chinese food safety standards (n = 3).

3. Results and Discussion

3.1 Photocatalytic Evolution of the Dextran/TSC/Ag⁺ Ternary System: From LMCT Activation to Anisotropic Nanocrystal Assembly

Under visible-light irradiation, the ternary dextran/TSC/Ag⁺ system drives the photoreduction of Ag⁺ through LMCT-mediated interfacial charge separation, simultaneously inducing directed self-assembly and anisotropic growth of silver nanocrystals. Figure 1a schematically illustrates the overall mechanism underlying the visible-light-driven LMCT-induced nanocrystal assembly process. Under standard LED irradiation (dextran 1 mg/mL, TSC 10 mM, AgNO_3 0.01 μM), the formation of silver nanocrystals exhibits pronounced time-dependent optical evolution (Fig. 1b). As irradiation time increases from 10 to 60 min, the solution color progressively transitions from pale yellow to orange, then to purple and finally to green, while the UV–Vis absorption spectrum evolves from an initially broadened single band into a characteristic dual-peak structure whose intensity continuously amplifies—hallmarks of the progressive development of anisotropic plasmonic architecture[16]. The emergence of this dual-peak LSPR fingerprint constitutes direct optical evidence for the excitation of multipolar plasmon modes characteristic of the spiky nanocrystal geometry.

Corroborating the UV–Vis spectral evolution, time-dependent surface charge measurements (Figure S1) provide independent electrochemical evidence for the photoinduced self-assembly process. Zeta potential measurements reveal a monotonic positive drift from 26.43 ± 0.68 mV at 10 min to 50.05 ± 1.08 mV at 60 min, synchronized with the dual-peak intensity enhancement. This trend reflects the progressive accumulation of TSC and dextran molecules at the nanocrystal surface as nucleation and

growth proceed, forming an increasingly thick electrical double layer. The subsequent dynamic ligand reorganization at the surface—transitioning from TSC-dominant early-stage adsorption to dextran-dominant coverage at later stages, as quantitatively established by XPS analysis presented below—further reinforces the electrostatic repulsion between nanoparticles, steadily improving colloidal stability over the course of irradiation[17].

Component control experiments (Figure S2) definitively establish the identity of the photoactive species responsible for nanocrystal formation. Under identical visible-light conditions, both the pure Ag^+ solution and the binary dextran/ Ag^+ system yield A_{420} values indistinguishable from zero, demonstrating no detectable LSPR response. In contrast, the binary TSC/ Ag^+ system produces a clear silver nanocrystal absorption signal ($A_{420} = 0.1763 \pm 0.0084$), conclusively identifying the $[\text{TSC}-\text{Ag}^+]$ coordination complex as the sole visible-light photosensitizer. Importantly, the yield obtained with the TSC/ Ag^+ binary system ($A_{420} = 0.1763$) is substantially lower than that of the complete ternary system ($A_{420} = 0.372$; Fig. 1b), with the ~ 2.1 -fold yield enhancement attributable to the synergistic contribution of dextran, the mechanistic origin of which is elaborated in Section 3.4.

To resolve the chemical structural evolution of individual components during nanocrystal formation, FTIR spectroscopy was performed on samples collected at successive irradiation times (Fig. 1c). Prolonged irradiation is accompanied by a progressive increase in the C–O–C stretching vibration at 1172.95 cm^{-1} , attributable to surface-enhanced adsorption of dextran glycosidic linkages onto the growing nanocrystal surface[18]. Concurrently, the asymmetric carboxylate ($-\text{COO}^-$) stretching band at 1644.66 cm^{-1} continuously diminishes, directly reflecting the consumption of TSC carboxylate groups as LMCT-active coordination sites[19]. The intensity increases observed for the C = O stretching band at 1748.12 cm^{-1} and the C–H stretching bands at 2855.27 and 2926.21 cm^{-1} are consistent with a time-dependent increase in organic molecule adsorption at the silver surface.

Raman spectroscopy (Fig. 1d) independently corroborates the nanocrystal formation process. Prior to irradiation (0 min), the characteristic Ag–Ag vibrational mode at 227.56 cm^{-1} is absent; upon illumination, this feature progressively intensifies in a manner that tracks irradiation time, providing direct evidence for the photogeneration and continuous accumulation of Ag^0 nuclei[20]. The time-dependent intensification of the Ag–Ag vibrational peak is strictly synchronized with the dual-peak UV–Vis evolution, together constituting a mutually corroborating spectroscopic record of nanocrystal growth.

^1H NMR spectroscopy (Fig. 1e) discloses the structural transformation of TSC during photocatalysis. As irradiation proceeds, three emerging olefinic proton resonances at 5.91, 6.08, and 6.15 ppm grow progressively in intensity. These signals are assigned to cis/trans- α,β -unsaturated carboxylate intermediates (e.g., aconitate/itaconate) generated by photo-oxidative dehydrogenation of TSC[21]. This result directly validates the hypothesis that TSC functions as a photosensitizing electron donor that is progressively consumed via oxidative dehydrogenation—a conclusion that is fully consistent with the time-dependent attenuation of the $-\text{COO}^-$ band at 1644.66 cm^{-1} in the FTIR spectra. ^{13}C NMR spectra (Figure S3) confirm that the carbon backbone of both dextran (40–110 ppm) and TSC remains intact

throughout the reaction, with no new peaks or main-chain fragmentation signals, ruling out deep mineralization or backbone degradation and confirming the overall structural integrity of all components.

TEM imaging (Fig. 1f) reveals a striking, well-defined morphological evolution trajectory during nanocrystal growth. At 10 min, the system is dominated by discrete small nanoplates and short nanorods constituting the primary nanocrystal seeds. By 20 min, these primary crystallites coalesce through oriented attachment or facet-selective overgrowth into irregular flower-like microplate assemblies. Between 30 and 50 min, selective growth on specific crystal facets drives the progressive outgrowth of elongated, needle-like protrusions from the plate cores, yielding the characteristic anisotropic spiky architecture. By 60 min, the central plate scaffold is largely consumed, leaving a compact anchoring core from which increasingly elongated, thickened spikes extend radially, completing the transformation from randomly aggregated platelets to highly directional, complex multi-spike superstructures. This sequential evolution discloses a stepwise photoinduced assembly mechanism: rapid isotropic Ag^0 nucleation in the early stage is followed by $[\text{TSC}-\text{Ag}^+]$ -directed passivation of $\text{Ag}\{111\}$ facets, which progressively channels anisotropic growth along non- $\text{Ag}\{111\}$ directions, ultimately yielding the high-aspect-ratio spiky topology (the thermodynamic basis of this facet-selective passivation— $E_{\text{ads}} = -2.827$ eV on $\text{Ag}\{111\}$ —is quantitatively confirmed by DFT calculations in Section 3.3).

XPS analysis provides quantitative time-resolved insight into the evolution of surface composition during nanocrystal formation (Figs. 1g–j). Survey spectra (Fig. 1g) show a monotonic increase in Ag 3d atomic percentage from 0.29% (10 min) to 0.33% (30 min) and 1.04% (60 min), in quantitative agreement with the time-dependent intensification of the Ag–Ag Raman band and the dual-peak UV–Vis response[22]. High-resolution Ag 3d spectra (Fig. 1h) display Ag $3d_{5/2}$ and Ag $3d_{3/2}$ binding energies of ~ 367.8 and ~ 373.8 eV, respectively, with a spin–orbit splitting of ~ 6.0 eV, consistent with metallic Ag^0 at all irradiation times; no residual Ag^+ signal (~ 368.3 eV) is detected, confirming quantitative photoreduction of Ag^+ driven by $[\text{TSC}-\text{Ag}^+]$ LMCT excitation.

Quantitative C 1s deconvolution (Fig. 1i) reveals the dynamic restructuring of the surface ligand shell: at 10 min, TSC's C–C-rich backbone dominates the surface (C–C: 52.11%; C–O: 33.78%), reflecting the preferential early-stage adsorption of TSC on freshly nucleated silver seeds. With increasing irradiation, C–C contributions decline continuously (52.11% $\rightarrow$ 45.75% $\rightarrow$ 39.89%) while C–O contributions rise in parallel (33.78% $\rightarrow$ 39.71% $\rightarrow$ 45.09%), manifesting a progressive ligand reorganization in which TSC is consumed and dextran increasingly dominates as the principal surface-stabilizing species[23]. This dynamic is directly corroborated by the FTIR data—the time-dependent attenuation of the $-\text{COO}^-$ signal and enhancement of the dextran C–O–C vibration—and is fully consistent with the positive zeta potential drift described above[24]. O 1s spectra (Fig. 1j) further reinforce this picture: the C = O component (assigned to TSC carboxylate) decreases from 23.56% at 10 min to 16.80% at 60 min, mirroring the ^1H NMR evidence for progressive TSC oxidative dehydrogenation, while the C–O component (dextran hydroxyl) rises from 71.68% to 79.28% in synchrony with the C 1s trend. A persistent Na KLL Auger

feature throughout the O 1s spectra confirms sustained TSC coordination at the nanocrystal surface across all irradiation stages[25].

Taken together, the complementary UV–Vis, zeta potential, FTIR, Raman, NMR, TEM, and XPS datasets construct a self-consistent, time-resolved kinetic picture of photoinduced nanocrystal assembly: [TSC–Ag⁺] LMCT excitation initiates Ag⁰ nucleation in the early stage; anisotropic growth then proceeds under the cooperative direction of TSC (crystal facet selection) and dextran (colloidal stabilization), progressively converging toward a stable spiky architecture as TSC surface coverage gives way to dextran dominance.

3.2 Parametric Control of Photoinduced Anisotropic Assembly and the TSC Facet-Directing Mechanism

Building on the multidimensional kinetic picture established in Section 3.1, we systematically investigated the influence of reaction temperature, dextran concentration, TSC concentration, and AgNO₃ concentration on the optical properties and morphology of the resulting silver nanocrystals, thereby elucidating the structure–function relationships of each component in LMCT-driven anisotropic assembly (Fig. 2).

Temperature dependence (Figs. 2a–b): Elevating the reaction temperature from 25 to 75°C progressively sharpens and intensifies the characteristic UV–Vis dual-peak response. TEM imaging at 75°C reveals more elaborate spiky architectures with greater numbers of protrusions and higher aspect ratios. The underlying physicochemical rationale is multifold: higher temperatures simultaneously accelerate the LMCT photoreduction rate and Ag⁰ nucleation flux, enhance the diffusional deposition rate of Ag⁺ onto non-Ag{111} facets, and thermodynamically reinforce TSC adsorption coverage on Ag{111} facets—a confluence of effects that collectively amplifies the kinetic driving force for anisotropic growth.

Dextran concentration dependence (Figs. 2c–d): Varying dextran concentration from 1 to 4 mg/mL induces negligible changes in peak position, peak shape, and nanocrystal yield, and TEM images at high dextran concentrations are indistinguishable from those at the standard condition. This insensitivity indicates that, within the experimental concentration window, dextran does not function as a crystal facet-directing morphology agent; rather, as established by the XPS analysis in Section 3.1, its primary role is to provide steric stabilization through the conformational flexibility of the polysaccharide backbone, independent of its concentration over this range.

TSC concentration dependence (Figs. 2e–f): Reducing TSC concentration to 2 mM causes the UV–Vis absorption to revert from a dual-peak to a weaker single-peak profile, and TEM imaging reveals exclusively isotropic spherical nanoparticles—the anisotropic character is entirely abolished. This observation constitutes unambiguous evidence for the critical facet-directing function of TSC: the tricarboxylate geometry of TSC, with two carboxylate groups separated by two carbon atoms, is geometrically commensurate with the threefold symmetry of the Ag{111} surface, enabling multipoint

Ag–O coordination that selectively blocks and caps this facet, thereby forcing Ag⁺ deposition to proceed preferentially along non-Ag{111} directions and driving anisotropic growth. This facet-selective passivation mechanism is quantitatively confirmed by DFT calculations in Section 3.3 (E_{ads} : Ag{111} = -2.827 eV vs. Ag{111} = -2.132 eV and Ag{111} = -1.553 eV). When TSC is insufficient (≤ 2 mM), incomplete Ag{111} passivation allows thermodynamically driven isotropic growth to dominate, yielding spherical nanoparticles.

AgNO₃ concentration dependence (Figs. 2g–i): Ag⁺ concentration exerts the most dramatic influence on nanocrystal morphology and optical properties. As AgNO₃ concentration increases from 0.01 to 0.13 μM , the solution color shifts progressively from green through purple, orange, deep yellow, and yellow to pale yellow, while the UV–Vis profile transitions from a well-resolved dual-peak to a single peak that blue-shifts from ~ 600 to ~ 440 nm; TEM images simultaneously reveal the progressive disappearance of the spiky architecture and its replacement by spherical nanoparticles. The mechanistic rationale is straightforward: at low Ag⁺ concentrations, the relative abundance of TSC per [TSC–Ag⁺] chromophore ensures high Ag{111} facet coverage, favoring anisotropic growth. As Ag⁺ concentration rises, the rate of bulk Ag⁰ deposition outpaces the kinetics of facet-selective TSC adsorption, and isotropic rapid growth becomes dominant. Significantly, the Ag⁺ concentration-dependent tunability of the LSPR absorption maximum across a broad spectral window (440–650 nm) provides a versatile suite of optical probes for multi-channel colorimetric sensing applications, as exploited in Section 3.5.

3.3 DFT Elucidation of the TSC/Dextran Interfacial Electronic Synergy, Facet-Selective Adsorption, and O₂ Activation Mechanism

To quantitatively elucidate the synergistic electronic roles of TSC and dextran during AgNP photocatalytic formation, and to provide quantum-chemical underpinning for the morphological trends observed in Section 3.2, systematic DFT calculations were performed (Fig. 3).

Differential charge density analysis (Fig. 3a; optimized geometries in Figure S5) reveals that both TSC and dextran adsorb stably at the Ag surface, forming well-defined interfacial contact structures that provide the structural basis for electronic coupling. Upon TSC adsorption, pronounced interfacial charge redistribution occurs, with electrons migrating primarily from the TSC carboxylate moieties toward the Ag surface, generating a substantial electron-accumulation region at the interface with a net charge transfer of 0.473 e. This strong electronic coupling quantitatively corroborates the LMCT photoactivity of the [TSC–Ag⁺] chromophore, in complete accord with the component control experimental data in Section 3.1[26]. The further introduction of dextran elevates the total interfacial charge transfer to 0.882 e, demonstrating that dextran not only acts as a steric stabilizer and sacrificial electron donor but also substantially enhances interfacial electron delocalization and migration, promoting LMCT-driven charge separation efficiency—a theoretical prediction that quantitatively accounts for the experimentally observed ~ 2.1 -fold yield amplification by dextran[27].

d-Band center analysis (Fig. 3b) reveals that the Ag d-band center shifts from -3.807 eV in bare Ag to -2.514 eV upon TSC adsorption and further to -2.192 eV upon co-adsorption of dextran. According to d-band theory, the upward shift of the d-band center toward the Fermi level enhances the coupling of the metal surface with adsorbate antibonding orbitals, indicating that TSC and dextran jointly elevate the electronic reactivity of the Ag surface—providing a critical electronic structural basis for O_2 activation and subsequent ROS generation (Section 3.4)[28]. Work function analysis (Figs. 3c–e) further substantiates this trend: successive introduction of TSC and dextran reduces the Ag work function from 4.225 eV to 4.188 eV and 4.159 eV, respectively, consistent with enhanced electron transfer propensity and facilitated LMCT charge extraction[29].

To quantitatively rationalize the TSC-concentration-dependent morphological control observed in Section 3.2, the adsorption of TSC on the three principal Ag crystal facets was evaluated by DFT (Fig. 3f; relaxed adsorption geometries in Figure S6). TSC adsorption energies on Ag{111}, Ag{100}, and Ag{110} are -2.827 , -2.132 , and -1.553 eV, respectively. The markedly more negative adsorption energy on Ag{111} demonstrates clear thermodynamic preference for this facet, providing a high deposition energy barrier that redirects subsequent Ag^+ reduction and deposition to non-Ag{111} crystal directions, driving the progressive transition from isotropic to high-aspect-ratio spiky morphology[30].

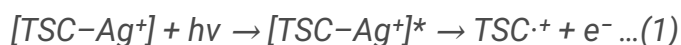
The O_2 activation behavior in the different surface environments was further probed theoretically (Figs. 3g–i). O_2 adsorption energies on bare Ag, Ag-TSC, and Ag-TSC-dextran surfaces are -0.312 , -0.845 , and -1.236 eV, respectively, demonstrating that TSC and dextran synergistically enhance O_2 binding. The adsorbed O–O bond length elongates progressively from 1.298 Å (Ag- O_2) to 1.334 Å (Ag-TSC- O_2) and 1.382 Å (Ag-TSC-dextran- O_2) (Fig. 3h), reflecting progressive electron injection into the O_2 π^* antibonding orbital and commensurate O–O bond weakening—a hallmark of catalytic O_2 activation[31]. Differential charge density maps (Fig. 3i) confirm that interfacial electron transfer toward adsorbed O_2 increases substantially from 0.216 e (bare Ag) to 0.427 e (Ag-TSC) and 0.852 e (Ag-TSC-dextran). Density of states (DOS) analysis (Figure S8) shows a marked increase in electronic states near the Fermi level upon TSC and dextran introduction, consistent with the d-band center upshift and work function reduction[32]. Collectively, these DFT results establish that the interfacial electronic coupling environment created by TSC and dextran effectively promotes electron transfer from the Ag surface to O_2 , providing crucial theoretical support for the photocatalytic generation of $\cdot O_2^-$ (Pathway B, Section 3.4).

3.4 Reactive Oxygen Species Identification and Mechanistic Elucidation of the Triple-Parallel Photocatalytic Reduction Network

Grounded in the interfacial electronic activation framework established by DFT in Section 3.3, we now construct a comprehensive mechanistic evidence base through systematic in situ EPR measurements and multi-reagent quenching experiments (Fig. 4).

In situ EPR spectroscopy provides direct molecular-level evidence for the full spectrum of reactive oxygen species generated by the ternary dextran/TSC/Ag⁺ system under irradiation. Spin-trapping probes were employed with specificity for distinct reactive intermediates: DMPO in aqueous and methanolic phases for ·OH and ·O₂⁻ detection, respectively; TEMP for ¹O₂ trapping; and TEMPO for monitoring the photogenerated oxidative intermediate (h⁺/TSC·⁺)[33]. Figures 4a–c demonstrate that under dark conditions, all three radical adduct signals are absent; upon visible-light irradiation, well-resolved characteristic EPR multiplets for ·OH, ·O₂⁻, and ¹O₂ emerge and intensify progressively—unambiguously confirming the in situ generation of all three ROS under photocatalytic conditions. Conversely, Fig. 4d shows that the TEMPO EPR signal, initially strong in the dark, undergoes time-dependent attenuation upon irradiation, consistent with TEMPO oxidation to EPR-silent TEMPO⁺ by the photogenerated TSC·⁺. The strictly photon-dependent nature of all four responses—dark-state signal absence, quantitative signal gain (·OH/·O₂⁻/¹O₂) or signal loss (TEMPO) upon illumination—systematically maps the ROS generation profile of the ternary system under visible-light drive[34].

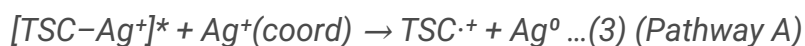
Mechanistically, visible-light excitation of the [TSC–Ag⁺] coordination complex initiates charge separation to generate a photoreductant electron (e⁻) and the TSC radical cation (TSC·⁺):



Quenching experiments and reduction pathway analysis (Fig. 4e): Treatment with the three ·OH scavengers MeOH (1% v/v), TBA (10 mM), and IPA (10 mM) leaves the silver nanocrystal yield statistically unchanged relative to the untreated control ($A_{420} \approx 0.37$ vs. 0.372; $p > 0.05$, Figure S4), collectively establishing that ·OH makes no substantive contribution to the Ag⁺ reduction process[35]. The minor ·OH detected in EPR originates from a decoupled secondary pathway: nascent Ag⁰ nanoparticles catalyze Fenton-like decomposition of H₂O₂ (itself produced by ·O₂⁻ disproportionation, vide infra) rather than from direct participation in Ag⁺ reduction:

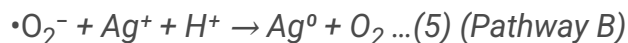


N₂ purging to remove dissolved O₂ reduces the silver yield from $A_{420} = 0.372$ to 0.290 (~ 78% retention), confirming that [TSC–Ag⁺]* can transfer its photogenerated electrons directly to the coordinated Ag⁺ center through intramolecular charge transfer in an O₂-independent direct photoreduction pathway (Pathway A):

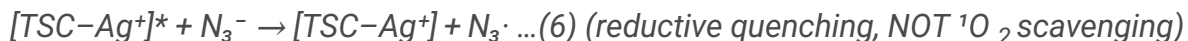


Addition of SOD—which exclusively disproportionates ·O₂⁻—precipitates a dramatic yield collapse to $A_{420} = 0.013$ (96.5% inhibition), establishing ·O₂⁻ as the overwhelmingly dominant reductant in this system. The far greater suppression by SOD compared with N₂ purging (only ~ 22% yield loss) reveals O₂'s true mechanistic role[36]: under aerobic conditions, dissolved O₂ outcompetes coordinated Ag⁺ for photogenerated electrons by virtue of its superior electron affinity, diverting the dominant reductive flux

from Pathway A to Pathway B, in which O_2 is reduced to $\bullet O_2^-$, which in turn reduces Ag^+ , fully consistent with the DFT-predicted O_2 activation behavior:

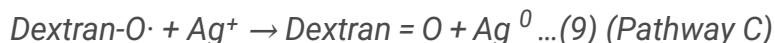
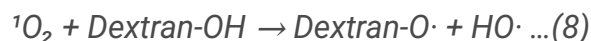
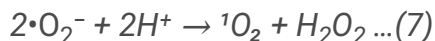


NaN_3 addition reduces the yield to $A_{420} = 0.0086$ (97.7% inhibition), a magnitude comparable to SOD. However, attributing this extreme suppression solely to $^1O_2$ quenching constitutes a serious methodological error. The decisive evidence comes from a supplementary $N_2 + NaN_3$ experiment (Fig. 4e): under N_2 atmosphere, where O_2 —and hence $^1O_2$ substrate—is largely absent, Pathway A alone still yields $A_{420} = 0.290$ (~ 78%); the subsequent introduction of NaN_3 under these conditions abolishes the yield entirely[37]. This unequivocally demonstrates that the extreme inhibition by NaN_3 is caused by N_3^- acting as a potent electron donor that reductively quenches $[TSC-Ag^+]^*$, severing the shared photocatalytic driving force of all three pathways at their common source:



This mechanistic insight carries significant methodological implications: in LMCT-driven photocatalytic systems, the use of NaN_3 as a selective $^1O_2$ quencher is fundamentally unreliable and risks systematic misinterpretation of the photocatalytic driving force[38]. EDTA-2Na addition reduces yield to $A_{420} = 0.275$ (~ 26% inhibition)—a moderate suppression arising from two concurrent mechanisms: competitive chelation of Ag^+ as photocatalytically inert $[EDTA-Ag^+]$ complexes, reducing the effective Ag^+ concentration; and consumption of $TSC\cdot^+$ by EDTA as a sacrificial electron donor, weakening the LMCT oxidative half-cycle[39]. The much smaller yield reduction relative to SOD and NaN_3 (> 96%) confirms that the photo-oxidative intermediate ($TSC\cdot^+$) pathway contributes modestly but non-dominantly to the overall photocatalytic efficiency.

$\bullet O_2^-$ generated in abundance via Pathway B undergoes self-disproportionation to yield $^1O_2$ and H_2O_2 . The $^1O_2$ so generated then oxidizes dextran hydroxyl groups to produce reducing carbon-centered radicals (Dextran-O $\cdot$)[40], which can further reduce Ag^+ , constituting a $^1O_2$ -mediated indirect secondary reduction pathway (Pathway C):



Dextran amplifies the photocatalytic efficiency of the ternary system through two mechanistically distinct and mutually reinforcing contributions—collectively explaining the ~ 2.1-fold yield enhancement relative to the binary TSC/ Ag^+ system: (i) Catalytic TSC regeneration: the $TSC\cdot^+$ radical cation generated

upon LMCT excitation is continuously reduced back to TSC by the sacrificial electrons provided by dextran hydroxyl groups, sustaining forward cycling of the LMCT catalytic loop (Eq. 10); (ii) Colloidal stabilization: the flexible polysaccharide backbone sterically encapsulates nascent Ag^0 nuclei, maintaining long-term colloidal dispersibility and enabling continuous accumulation of nanocrystalline product.



To establish the generality of these dextran-mediated mechanisms, 24 structurally diverse carbohydrate molecules—encompassing monosaccharides, disaccharides, sugar alcohols, and polysaccharides—were examined as dextran replacements under identical reaction conditions (sugar 1 mg/mL; TSC 10 mM; AgNO_3 0.05 mM). All 24 sugar systems produced characteristic dual-LSPR-peak UV–Vis profiles indicative of anisotropic AgNP formation (Figure S9), with differences confined to peak position, peak intensity, and long-wavelength absorption breadth; the fundamental anisotropic character was universally preserved. This sugar-structure-independent universality confirms that the mechanistic role of hydroxyl-bearing carbohydrates in this LMCT system—hydroxyl-driven $\text{TSC}\cdot^+$ scavenging for photocatalytic cycle regeneration and interfacial steric stabilization—is intrinsic to the polyhydroxyl functionality rather than specific to dextran.

The complete photocatalytic mechanism is summarized in Fig. 4f: visible-light LMCT excitation of $[\text{TSC}-\text{Ag}^+]$ generates $[\text{TSC}-\text{Ag}^+]^*$, which in parallel drives three Ag^+ reduction pathways; dextran sustains the photocatalytic cycle through $\text{TSC}\cdot^+$ reduction and stabilizes the growing nanocrystals via steric encapsulation; $\cdot\text{OH}$ is generated exclusively through the secondary Ag^0 -catalyzed Fenton-like decomposition of H_2O_2 (itself derived from $\cdot\text{O}_2^-$ disproportionation), decoupled from the primary Ag^+ reduction routes; and NaN_3 suppresses all pathways indiscriminately through reductive quenching of the shared excited-state precursor, rather than through selective $^1\text{O}_2$ scavenging.

3.5 Colorimetric Sensing Mechanism and Nanoscale Structural Evolution upon Sulfide Exposure

Exploiting the precise structure–property relationships established in Sections 3.1–3.2 and the LMCT-driven synthesis platform described in Section 3.4, we systematically evaluated the colorimetric sensing performance of three morphologically distinct AgNP probes—synthesized at AgNO_3 concentrations of 0.01, 0.03, and 0.13 μM , representing the spiky, mixed, and near-spherical morphological extremes, respectively—toward sulfide as a representative sulfur-containing analyte (Fig. 5a–c).

The spiky nanocrystals (0.01 μM AgNO_3) exhibit the most dramatic dose-dependent spectral evolution (Fig. 5a): across a Na_2S concentration range of 0–100 μM , the characteristic dual-peak absorption collapses progressively, accompanied by pronounced band broadening and a red-shift, while the solution color transitions in a visually unambiguous manner from pale green through pale yellow to colorless (Fig. 5a, inset). The ΔA_{420} response is linearly correlated with Na_2S concentration (Figure S10; $R^2 =$

0.99768). The mixed-morphology system (0.03 μM ; Fig. 5b, Figure S11; $R^2 = 0.99545$) and near-spherical system (0.13 μM ; Fig. 5c, Figure S12; $R^2 = 0.99519$) display progressively diminished spectral response amplitude and reduced naked-eye color discrimination; notably, the spherical nanoparticle system exhibits an inverse response mode in which Na_2S induces intensity enhancement rather than suppression—attributable to S^{2-} -driven particle assembly rather than spike dissolution. These comparative results confirm the sensing sensitivity advantage conferred by the anisotropic spiky morphology: the high-curvature spike tips concentrate extraordinarily intense local electromagnetic fields, and the coordinatively unsaturated surface atoms at these high-curvature sites provide abundant, thermodynamically preferred binding sites for S^{2-} .

The thermodynamic driving force for the colorimetric response is rooted in the strong soft–soft affinity between Ag and S. According to Pearson’s Hard and Soft Acids and Bases (HSAB) theory[41], Ag^+ is a prototypical soft acid and S^{2-} is a strong soft base; the exceptionally low solubility product of Ag_2S renders Ag–S bond formation thermodynamically spontaneous and irreversible under ambient conditions. The S^{2-} ions displace the organic surface ligands (TSC/dextran) with overwhelming thermodynamic advantage, rapidly constructing a surface Ag–S coordination shell and nucleating an Ag_2S passivation layer. Selectivity validation experiments (Figure S13) demonstrate negligible ΔA_{420} responses (< 0.02) toward common non-sulfur meat spoilage volatiles (acetic acid, butyric acid, trimethylamine, cadaverine, putrescine, each at 50 μM), reflecting the vastly superior affinity of Ag for soft S donors relative to hard/borderline N and O species.

TEM combined with HAADF-STEM and EDX elemental mapping was employed to trace the dose-dependent nanoscale morphological and compositional evolution of spiky nanocrystals upon sulfide treatment (Figs. 5d–h). At low Na_2S concentration (10 μM), mild geometric blunting of spike tips is observed while the multi-spike skeleton is largely retained (Fig. 5d). As Na_2S concentration increases (20–40 μM), spike number and length decrease sharply and nanoparticle outlines become progressively smoother (Figs. 5e–f). At high concentrations (80–100 μM), the high-curvature spiky features are completely etched, and nanoparticles collapse to near-spherical morphologies (Fig. 5g). The thermodynamic priority of tip etching is governed by the Gibbs–Thomson effect: the chemical potential of surface atoms at high-curvature spike tips is substantially elevated above that of flat crystal facets, rendering them kinetically and thermodynamically preferred sites for S^{2-} -induced coordination dissolution and Ag_2S re-precipitation. HAADF-STEM images and EDX elemental maps directly visualize this inside-out sulfidation dynamics: low-contrast heterogeneous shell regions at the nanoparticle periphery correspond to in situ-formed Ag_2S , with sulfur uniformly distributed across the nanoparticle surface and progressively penetrating inward.

This nanoscale morphological reconstruction mechanistically explains the macroscopic colorimetric signal transduction: the thermodynamically prioritized erosion of high-energy anisotropic spike tips by S^{2-} , concurrent with the growth of a low-dielectric Ag_2S passivation layer, simultaneously modulates the plasmonic response through geometric deconstruction (dismantling the field-enhancement hotspots at spike tips) and dielectric reconstruction (modifying the local dielectric environment and reshaping the

collective electron oscillation landscape). The concerted action of these two mechanisms yields a sensitive, dose-dependent, spectrally abrupt colorimetric readout that is directly and quantitatively linked to sulfide concentration.

3.6 Real-Time Colorimetric Monitoring of Meat Freshness

Leveraging the high sensitivity (ΔA_{420} linear range 0–100 μM , $R^2 > 0.995$) and high selectivity (Ag–S soft–soft affinity) of the anisotropic AgNPs toward sulfur-containing volatile analytes established in Section 3.5, all three morphological variants were immobilized within agarose hydrogel supports to fabricate colorimetric sensing labels for real-time, naked-eye freshness monitoring of chicken wings, pork, and lobster under refrigerated (4°C) and ambient (25°C) storage conditions (Fig. 6).

The colorimetric responses of all three sensing labels correlated robustly with the spoilage progression of all three meat types, and the temporal dynamics of color change maintained strict correspondence with the measured TVB-N concentration trajectories. At 25°C, chicken wings elicited a visible colorimetric response within 12 h, coinciding with TVB-N levels reaching the sub-fresh threshold (15 mg/100 g); by 24 h, a pronounced color transition was evident alongside TVB-N values exceeding the spoilage threshold (25 mg/100 g). Under refrigeration (4°C), colorimetric transitions were significantly delayed (36–48 h to reach discernible color change), consistent with the expected retardation of microbial growth and proteolytic activity at low temperature and in precise agreement with the slow TVB-N accumulation kinetics. Lobster samples, owing to the high protein content and intrinsic autolytic enzyme activity characteristic of crustaceans, exhibited the most rapid spoilage trajectory at 25°C, with the color transition sequence and TVB-N growth curves in close mutual agreement.

The core practical advantages of this colorimetric strategy are fourfold: (1) entirely instrument-free operation—freshness grade is directly readable by the naked eye; (2) one-step fabrication via direct visible-light LMCT photocatalysis followed by agarose gelation; (3) cost-effective, non-toxic, and fully biocompatible materials (dextran, TSC, agarose)—a substantial advantage over CTAB- or NaBH_4 -based conventional silver nanoparticle routes; and (4) real-time, continuous monitoring capability covering the full cold-chain logistics-to-consumer scenario. These attributes collectively overcome the inherent limitations of conventional TVB-N titrimetry (time-consuming, requiring trained operators) and GC-MS (expensive instrumentation), establishing a compelling case for practical deployment in food supply chains and consumer-facing applications.

4. Conclusions

In conclusion, we have developed an entirely green, visible-light-driven photochemical framework consisting of dextran, trisodium citrate (TSC), and AgNO_3 to achieve the highly controlled self-assembly of anisotropic spiky silver nanocrystals under exceptionally mild conditions. Operating via an LMCT-mediated interfacial charge separation process, the silver nanostructures undergo a sequential structural evolution—spanning spherical, rod-like, and platelet intermediates—before culminating in

hierarchical spiky architectures that manifest powerful plasmonic resonance features. Spectroscopic and surface analyses reveal a dynamic ligand exchange process where TSC steers early facet-directed growth, while dextran provides long-term interfacial stability to preserve the branched architecture. DFT calculations confirm that the thermodynamic affinity of TSC for Ag{111} facets serves as the primary driver directing anisotropic growth. By integrating in situ EPR, chemical quenching matrices, and time-resolved NMR, we have mapped out a triple-parallel photocatalytic network driven by direct LMCT reduction, $\bullet\text{O}_2^-$ cascade reduction, and $^1\text{O}_2$ -mediated secondary reduction loops, while highlighting the dual role of dextran in driving ligand regeneration and providing steric stabilization. Furthermore, this study unmaskes a method error where NaN_3 induces direct excited-state quenching within LMCT systems, offering a valuable reference for future mechanistic studies of light-driven nano-assemblies. Benefiting from their highly branched branches, the resulting spiky nanocrystals deliver outstanding plasmonic hotspots and excellent sensitivity toward volatile sulfur effluents, demonstrating great potential for smart optical materials and advanced interfacial sensing. This work establishes a rigorous mechanistic model for LMCT-driven green chemistry and provides fresh architectural design concepts for the sustainable fabrication of advanced anisotropic nanomaterials.

Declarations

Conflict of Interest

The authors declare no conflict of interest.

Author Contribution

J.Y. conceived and designed the study, performed the core experiments, analyzed the data, and wrote the main manuscript text. Y.O. and X.B. assisted with the experimental procedures and collected the data. Y.H. and Y.L. prepared the figures and conducted the literature review. J.Y. supervised the project and handled the correspondence. All authors reviewed and approved the final manuscript.

Acknowledgements

This work was supported by the Scientific Research Startup Foundation of Chuzhou University (2024qd40), the Natural Science Research Project of the Anhui Provincial Department of Education (2025AHGXZK30523), the Open Research Project of the Anhui Engineering Research Center for Chujun (Chrysanthemum) Cultivation and Deep Processing (2025CJZX05), and the National College Student Innovation and Entrepreneurship Training Program (202510377046, 202510377048).

References

1. Nobeyama T (2026) Size-controlled growth of anisotropic gold nanoparticles. *Nat Reviews Phys* 8(4). <https://doi.org/10.1038/s42254-026-00928-7>
2. Hu F, Yang G, Zheng L-M, Liang G-J, Wang Q-M (2025) Deciphering icosahedra structural evolution with atomically precise silver nanoclusters, *Science* 389, no. 6763 <https://doi.org/10.1126/science.adx6639>
3. Hae DW, Lee H, Kook HJ et al (2026) Growth-Directing Nanostructured Interfaces via Block Copolymer-Templated Au Nanoseed Arrays for Stabilized Zinc Anodes in Lean-Zinc Batteries. *Nano-Micro Lett* 18(1). <https://doi.org/10.1007/s40820-026-02167-y>
4. Shelke Y, Nair S, Vutukuri A (2026) Shape anisotropy governs organization of active rods: Swarming, turbulence, flocking, and jamming. *Science* 392:6794. <https://doi.org/10.1126/science.ady7618>
5. Zhang J, Song C, He X, Liu J, Chao J, Wang L (2025) DNA-mediated precise regulation of SERS hotspots for biosensing and bioimaging. *Chem Soc Rev* 54(12). <https://doi.org/10.1039/D5CS00124B>
6. Jo Y-M, Jeon M, Kim D-H, Kim J, Dincă M (2026) Methanol-Ethanol Discrimination and Selective Sensing Enabled by Molecular Sieving in Conductive MOFs, *Advanced Materials* n/a, no. <https://doi.org/https://doi.org/10.1002/adma.73406>. n/a
7. Xia Q, Jia Y, Bi C et al (2025) Nanoporous Ag Microparticles with Tailorable and Noncontaminated Nanopores for SERS Sensing Applications. *Adv Mater* 37:13. <https://doi.org/https://doi.org/10.1002/adma.202414962>
8. Gao D, Zhang M, Liang H et al (2026) Bio-based polymeric nanocarriers: From design of stimuli-responsive nanocarriers to targeted agrochemical delivery. *Prog Polym Sci* 177. <https://doi.org/https://doi.org/10.1016/j.progpolymsci.2026.102120>
9. Chen Y, Yang X, Li K et al (2024) Phenolic Ligand–Metal Charge Transfer Induced Copper Nanozyme with Reactive Oxygen Species-Scavenging Ability for Chronic Wound Healing. *ACS Nano* 18(9). <https://doi.org/10.1021/acsnano.3c10376>
10. Huang K-Y, Yang Z-Q, Yang M-R et al (2024) Unraveling a Concerted Proton-Coupled Electron Transfer Pathway in Atomically Precise Gold Nanoclusters. *J Am Chem Soc* 146(12). <https://doi.org/10.1021/jacs.4c01180>
11. Wang Z, Hao M, Li C et al (2026) Electron-Rich Nanorelay Enhances Ligand-to-Metal Charge Transfer in Lanthanide Metal–Organic Frameworks during Photocatalytic CO₂ Conversion. *Adv Mater* 38(7). <https://doi.org/https://doi.org/10.1002/adma.202512763>
12. Zhang J, Wu K, Gao X et al Achiral and chiral ligands synergistically harness chiral self-assembly of inorganics. *Sci Adv* 10, no. 42, <https://doi.org/10.1126/sciadv.ado5948>
13. Pan S-Q, Luo P, Huang Q et al (2025) Spontaneous Catalytic Reaction of a Surfactant in the Interfacial Microenvironment of Colloidal Gold Nanoparticles. *J Am Chem Soc* 147(2). <https://doi.org/10.1021/jacs.4c16796>
14. Saad AM, Mady AH, Sayed MS, Kim G, Kim M, Kim WK (2025) Boosting water oxidation kinetics of BiVO₄ through a metal-organic co-catalyst enriched with phosphate groups (Co,Fe-NTMP): Insights

- from LMCT mechanism and DFT study. *Appl Catal B: Environ Energy* 370.
<https://doi.org/https://doi.org/10.1016/j.apcatb.2025.125163>
15. Gimenis GHB, Spadeto JPM, Colombari FM et al (2026) Conformational gating mechanism for processive catalysis of $\beta(1,3)$ -glucans. *Nat Commun* 17(1). <https://doi.org/10.1038/s41467-026-71224-2>
 16. Ke S, Li W, Guo G et al (2026) Homogeneous Template-Directed Synthesis of Hollow Porous Nitrogen-Rich Conjugated Polymers with Adjustable Mesopore to Macropore, *Advanced Functional Materials* n/a, no. <https://doi.org/https://doi.org/10.1002/adfm.75403>. n/a
 17. Park J, Ha J, Kim D et al (2026) Ligand-Mediated Surface Carrier Modulation in Perovskite Nanocrystals for Charge-Symmetric LEDs. *Adv Mater* 38.
<https://doi.org/https://doi.org/10.1002/adma.202520499>
 18. Yu J, Huang M, Tian H, Xu X (2023) UV-light-driven synthesis of Ag-Zn nanoparticles encased in hydrogels for H₂S sensing. *Food Packaging Shelf Life* 39.
<https://doi.org/https://doi.org/10.1016/j.fpsl.2023.101151>
 19. Xie A, Brunner JS, Chakraborty S et al (2026) Citrate clearance is a major function of aconitase 2 in the canonical TCA cycle, *Cell* 189, no. 9 <https://doi.org/https://doi.org/10.1016/j.cell.2026.01.028>
 20. Guo X, Wang X, Wen S et al (2025) Silver Nanoparticle-Grafted Amidoxime Covalent Organic Framework: A Highly Sensitive and Selective SERS Substrate for Uranium Detection in Natural Water Systems. *Adv Funct Mater* 35:38. <https://doi.org/https://doi.org/10.1002/adfm.202500901>
 21. Suri J, Jordan C, Teschers CS et al (2026) Fluorinated Glycan Frameshifts: Automated Synthesis Expedites the Study of Glycan-Protein Interactions by ¹⁹F-BioNMR. *Angew Chem Int Ed* 65(12).
<https://doi.org/https://doi.org/10.1002/anie.8014647>
 22. Yang Z, Gong X, Hu Y, Yue P, Lü B, Peng F (2024) Green synthesis of lichenan-decorated silver nanoparticles for catalytic hydrogenation of organic dyes and bacterial disinfection. *Chem Eng J* 487. <https://doi.org/https://doi.org/10.1016/j.cej.2024.150516>
 23. Shaban SM, Kim S, Basiony NME et al (2025) Ecofriendly Sunlight-Mediated Nontoxic Bimetallic Nanoparticles: Synthesis, Reusable Catalytic Membrane, and Biosensor Applications, *Advanced Science* 12, no. 27 <https://doi.org/https://doi.org/10.1002/advs.202503120>
 24. Li Y, Wang L, Zhang F, Zhang W, Shao G, Zhang P (2023) Detecting and Quantifying Wavelength-Dependent Electrons Transfer in Heterostructure Catalyst via In Situ Irradiation XPS, *Advanced Science* 10, no. 4 <https://doi.org/https://doi.org/10.1002/advs.202205020>
 25. Zhang X, Guo X, Jiao H et al (2025) Orbital-Tailored Pt Sites via Atomic-Level Carrier Pre-Design for Enhanced Photocatalytic Hydrogen Evolution. *ACS Nano* 19:45.
<https://doi.org/10.1021/acsnano.5c16095>
 26. Xue F, Zhang C, Cheng C et al (2024) Selective light-driven methane oxidation to ethanol. *Nat Commun* 15(1). <https://doi.org/10.1038/s41467-024-54835-5>
 27. He C, Yang R, Zhong C et al (2026) Light-driven restructuring generates nanoisland NiIr alloy for efficient methane dry reforming. *Nat Commun* 17(1). <https://doi.org/10.1038/s41467-026-68429-w>

28. Li W-Q, Chen Y, Lu X et al (2026) Photoinduced nitrogen spillover enables ammonia synthesis on iron–aluminium dual-site catalysts. *Nat Synthesis*. <https://doi.org/10.1038/s44160-026-01013-8>
29. Luo D, Xiao H, Yang Y et al (2025) Photo-Self-Fenton Reaction Mediated by Silver Single Atom and Cluster Photocatalysts for Highly Selective Generation of Singlet Oxygen Toward Efficient Organic Wastewater Treatment. *Angew Chem Int Ed* 64(23). <https://doi.org/10.1002/anie.202504028>
30. Zhang J, Yu G, Yang C et al (2025) Reinforced ROS Generation and Anti-Photocorrosion for Boosted Photooxidation Disinfection by IEF-Enhanced Type II Charge Carrier Dynamics, *SusMat* 5, no. 2 <https://doi.org/10.1002/sus2.70002>
31. Liu X, Ma Y, Wang Y et al (2026) Dual-Gas Activation Nanodomains Enable Solar-Powered Selective Methane Conversion. *Adv Mater* 38. <https://doi.org/10.1002/adma.202521696>
32. Wang C, Liu Z, Peng Q et al (2025) Bimetallic Cu₁₁Ag₃ Nanotips for Ultrahigh Yield Rate of Nitrate-to-Ammonium. *Angew Chem Int Ed* 64(3). <https://doi.org/10.1002/anie.202415259>
33. Jiang L, Xie S, Chen H et al (2025) Visible-light-promoted peroxymonosulfate activation for ACE degradation: Overlooked role of photogenerated hole. *Appl Catal B: Environ Energy* 365. <https://doi.org/10.1016/j.apcatb.2024.124881>
34. Xu Z, Yu S, Xie X et al (2023) Target-triggered Fe₃O₄@NPC-UCNPs assembly for photoactivatable biosensing of Aflatoxin B₁. *Chem Eng J* 470. <https://doi.org/10.1016/j.cej.2023.144028>
35. Si Q, Feng X, Teng Y et al (2025) Constructing effective and low-toxic removal of combined contaminants by intimately coupled Z-scheme heterojunction photocatalysis and biodegradation system. *Appl Catal B: Environ Energy* 365. <https://doi.org/10.1016/j.apcatb.2024.124909>
36. Guo Y, Ma W, Chong M et al (2024) Generation of holes from intra-valence band for enhanced oxidation potentials under visible light, *Chem* 10, no. 4 <https://doi.org/10.1016/j.chempr.2024.01.022>
37. Nong S, Wang M, Wang X et al (2024) A multifunctional guanosine-based carbon dots for dead microbial imaging and synergistic broad-spectrum antimicrobial therapy. *Chem Eng J* 485. <https://doi.org/10.1016/j.cej.2024.150123>
38. Wang Y-X, Zhang J, Su H-F et al (2023) Photochemical Synthesis of Atomically Precise Ag Nanoclusters. *ACS Nano* 17(12). <https://doi.org/10.1021/acsnano.3c02005>
39. Liu Y, He X, Liu X, Li B, Ma J-G, Cheng P (2025) Light-induced Enhancement of Energetic Charge Carrier Extraction and Modulation of Local Charge Density to Impact Selectivity in Plasmonic Nanometals. *Angew Chem Int Ed* 64:14. <https://doi.org/10.1002/anie.202422034>
40. Li G, Wang M, Yang D et al (2025) Single bond regulated ¹O₂ and [•]O₂ – selective generation of heptazine-based conjugated polymers for high-selectivity photocatalysis. *Adv Powder Mater* 4(4). <https://doi.org/10.1016/j.apmate.2025.100299>

41. Qi X, Xie Y-L, Niu J-Y et al (2025) Application of Hard and Soft Acid-base Theory to Construct Heterometallic Materials with Metal-oxo Clusters. Angew Chem Int Ed 64(1).
<https://doi.org/https://doi.org/10.1002/anie.202417548>

Figures

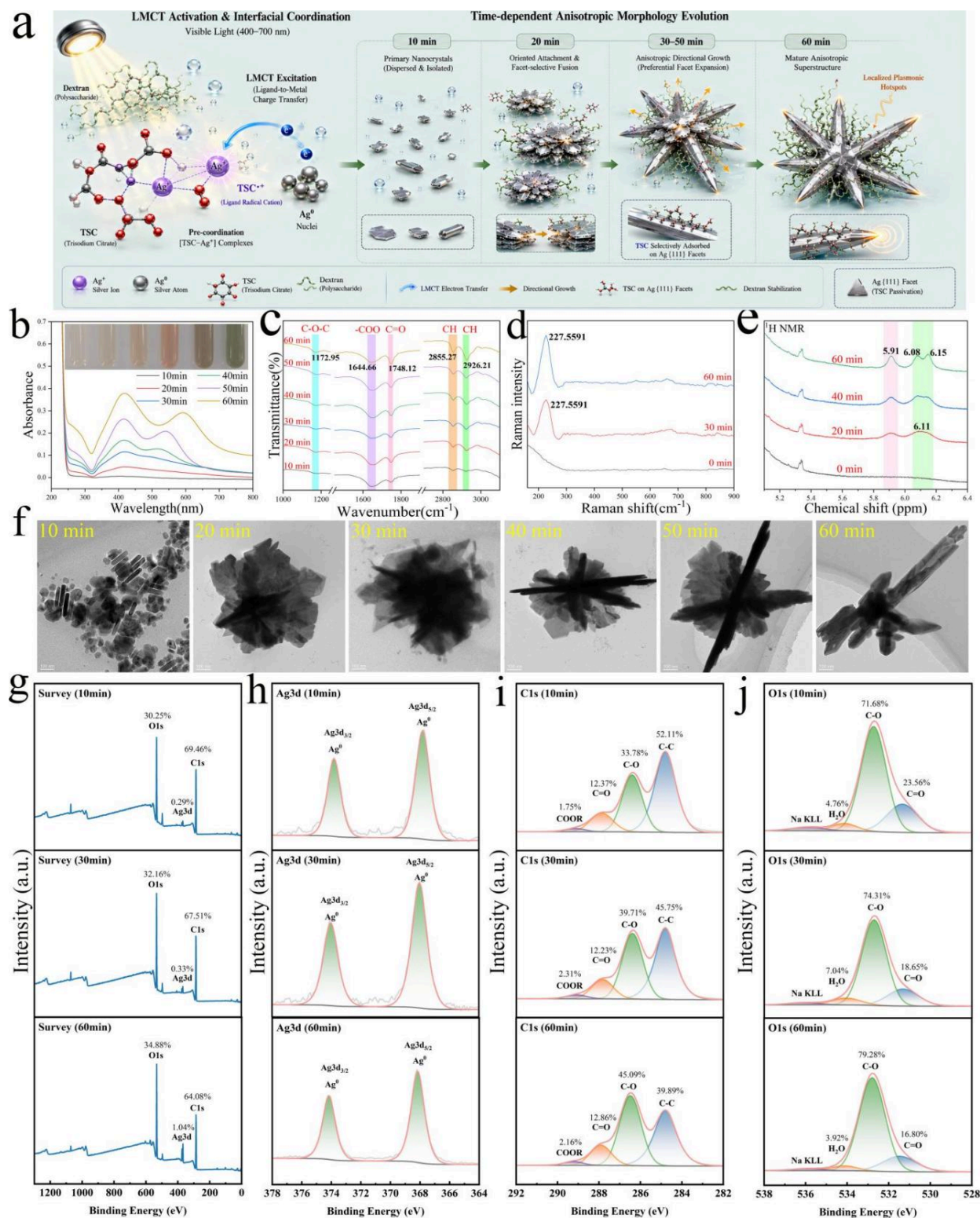


Figure 1

Multi-dimensional structure and characterization of anisotropic silver nanoparticles photocatalytically synthesized via the dextran/TSC/Ag⁺ ternary system. (a) Schematic illustration of the mechanism for visible-light-driven LMCT-induced photocatalytic synthesis and anisotropic self-assembly growth of silver nanoparticles. (b) UV-Vis absorption spectra of the system under different illumination times and the corresponding color changes of the solutions (inset). (c) FTIR spectra, (d) Raman spectra, and (e) ¹H NMR spectra of the samples at different illumination times, showing the time-dependent evolution of main functional groups and chemical bonds. (f) TEM images of the samples at different illumination times and the pure dextran control (scale bar: 100 nm). (g) Quantitative changes in the atomic percentage of Ag 3d in the survey XPS scans, alongside high-resolution (h) Ag 3d, (i) C 1s, and (j) O 1s XPS spectra of the samples, revealing the dynamic evolution of surface ligands from TSC to dextran.

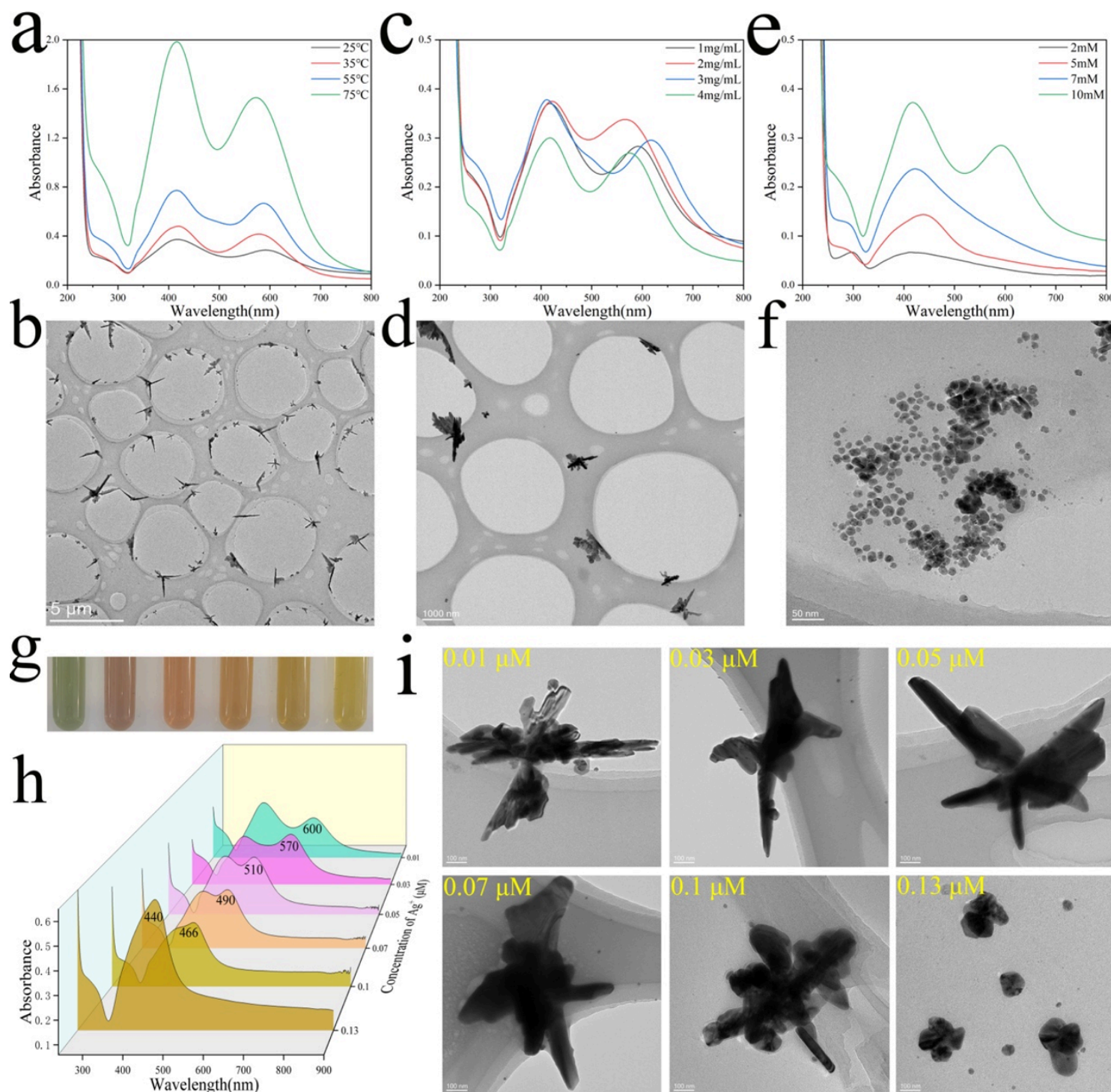


Figure 2

Influence of synthesis parameters on the optical properties and morphology of anisotropic silver nanoparticles. (a) UV-Vis absorption spectra of silver nanoparticles at different reaction temperatures and (b) TEM image of the sample synthesized at 75 °C. (c) UV-Vis absorption spectra at different dextran concentrations and (d) TEM image at a concentration of 4 mg/mL. (e) UV-Vis absorption spectra at different TSC concentrations and (f) TEM image of the sample (spherical particles) at a concentration of 2 mM. Sample photographs (g), corresponding UV-Vis absorption spectra (h), and TEM images (i) under different AgNO_3 concentrations (0.01, 0.03, 0.05, 0.07, 0.10, 0.13 μM). All TEM scale bars are 100 nm.

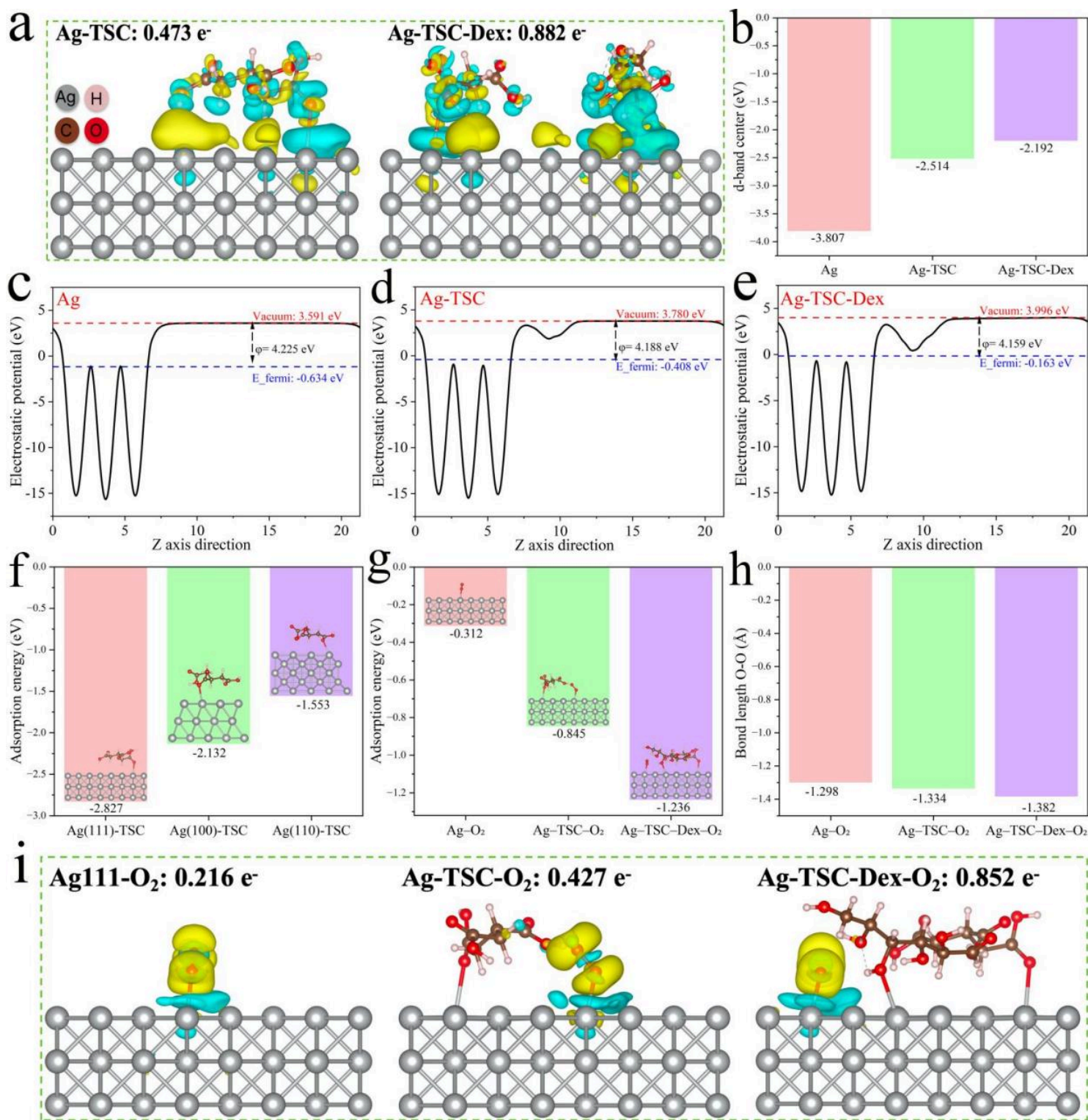


Figure 3

DFT theoretical calculations revealing the mechanism of TSC/dextran synergistic electronic regulation, facet-selective adsorption, and O₂ activation. (a) Differential charge density maps of the Ag-TSC and Ag-TSC-Dex systems (interfacial charge transfer amounts are labeled). (b) Comparison of d-band centers among Ag, Ag-TSC, and Ag-TSC-Dex systems. (c–e) Electrostatic potential distributions along the z-axis and the corresponding work function variations for the three systems. (f) Comparison of adsorption

energies of TSC on Ag(111), Ag(100), and Ag(110) crystal facets. (g) Evolution of O₂ adsorption energies on different system surfaces, (h) variations in the O-O bond length of adsorbed states, and (i) the corresponding differential charge density maps. See Figures S5–S8 for geometrically optimized structures and total density of states analysis.

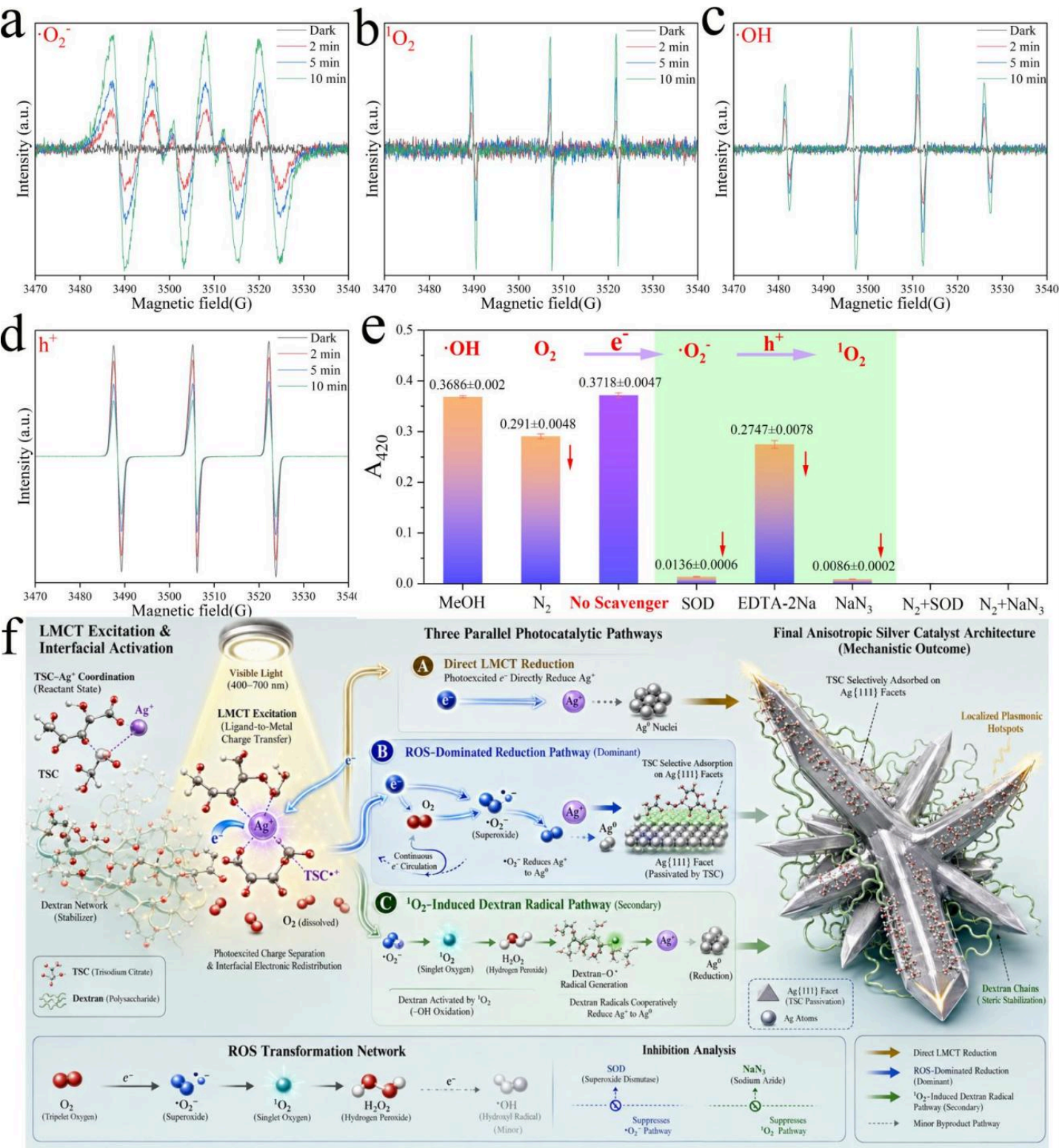


Figure 4

Identification of reactive oxygen species (ROS) and the complete LMCT photocatalytic mechanism. EPR signal evolution of (a) $\cdot\text{O}_2^-$, (b) $^1\text{O}_2$, (c) $\cdot\text{OH}$, and (d) h^+ . (e) Comparison of silver nanoparticle yields under different radical scavengers and component controls. (f) Schematic diagram of the three-pathway parallel mechanism for the visible-light-driven photocatalytic synthesis of anisotropic silver nanoparticles.

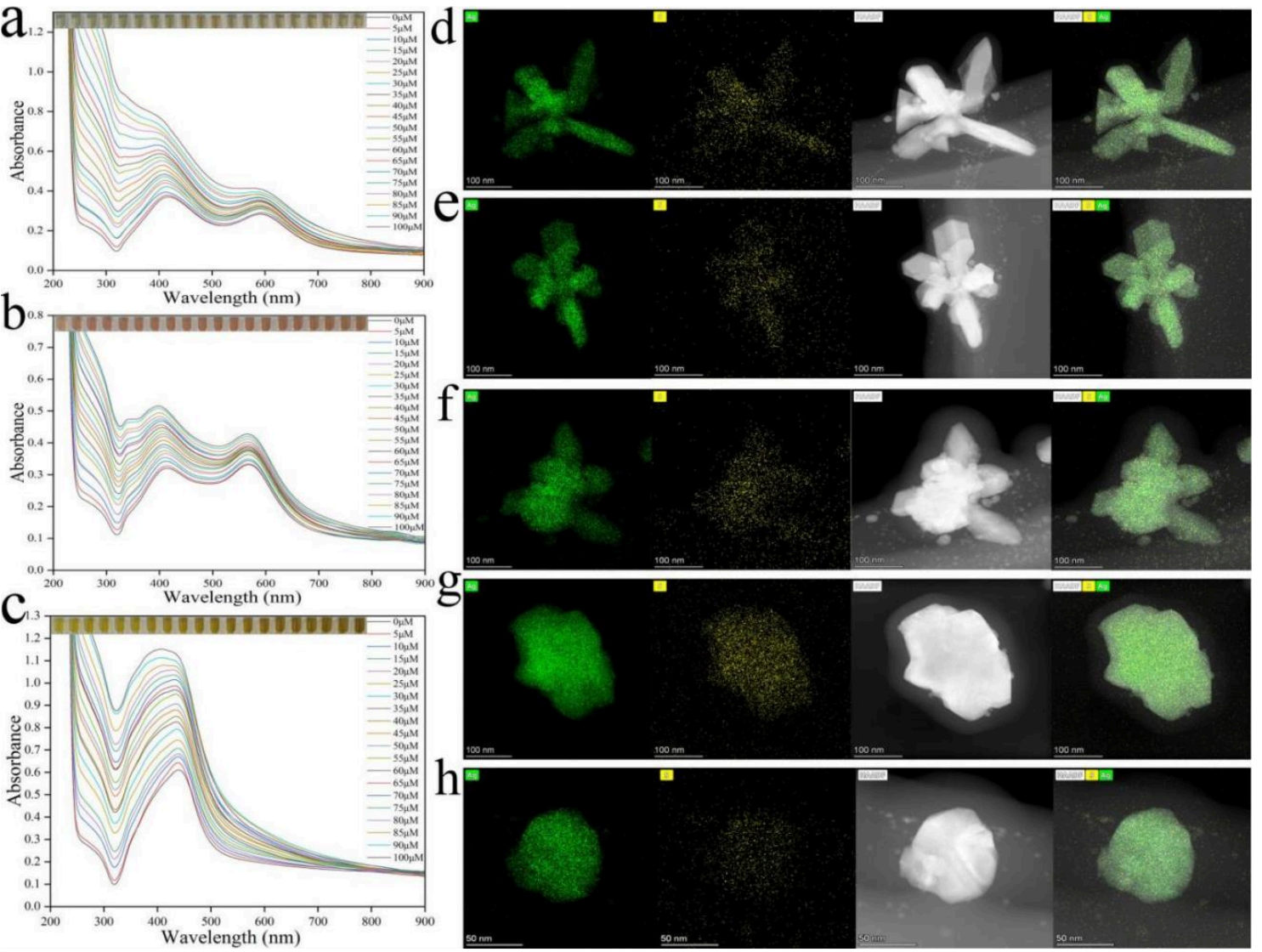


Figure 5

Colorimetric response performance, morphological evolution, and interfacial elemental distribution of anisotropic silver nanoparticles toward Na_2S . (a–c) UV-Vis absorption spectra of silver nanoparticles prepared with $0.01\ \mu\text{M}$ (spiky), $0.03\ \mu\text{M}$ (mixed phase), and $0.13\ \mu\text{M}$ (near-spherical) AgNO_3 , respectively, after reacting with various concentrations of Na_2S (insets show the corresponding colorimetric charts). (d–h) HAADF-STEM images and corresponding EDX elemental mapping images (scale bar: 100 nm) of spiky silver nanoparticles after reacting with different concentrations of Na_2S , demonstrating the interfacial evolution trajectory from spike dissolution to spherical restructuring.

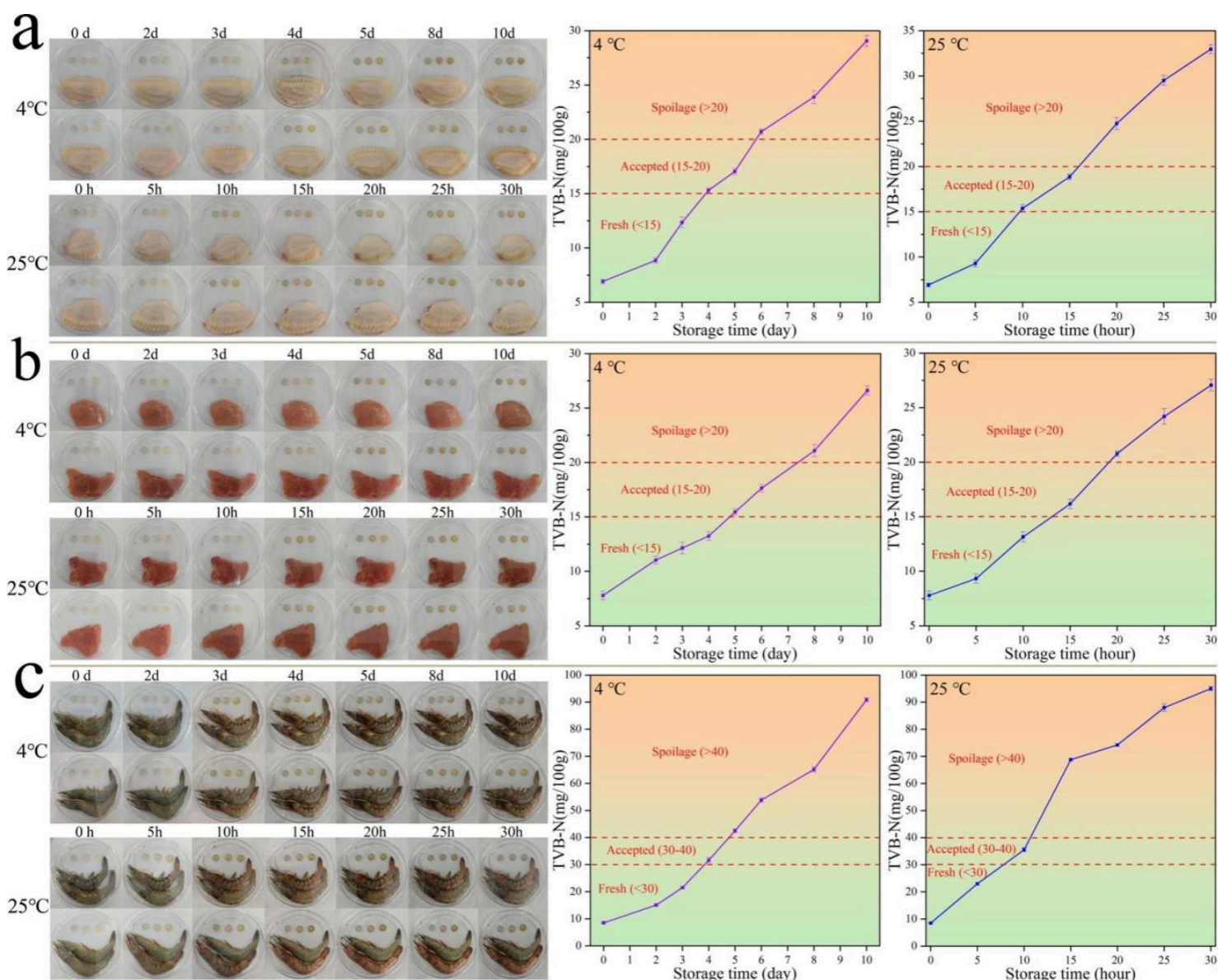


Figure 6

Real-time visual monitoring of freshness in three meat products using anisotropic silver nanoparticle colorimetric sensing labels. Real-time color response photographs of agarose-based colorimetric sensing labels for (a) chicken wings, (b) pork, and (c) lobster under storage conditions of 4 °C and 25 °C, along with the corresponding dynamic curves of TVB-N content.

Supplementary Files

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