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Edge-Gold Coated Silver Nanoprisms: Enhanced Stability and Applications in Organic Photovoltaics and Chemical Sensing

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ABSTRACT

We report a facile synthetic route for edge gold-coated silver nanoprisms (GSNPs) and their comprehensive optical and structural characterization. The GSNPs exhibit remarkably high stability towards chemical etching and excellent performance as both optical antennae for light-harvesting applications and refractive index sensors. We show that when embedded into a photovoltaic bulk heterojunction film of poly(3-hexylthiophene)/phenyl-C61-butyric acid methyl ester (P3HT/PCBM), plasmonic GSNPs act as optical antennae to substantially enhance light absorption in the active organic solar cell layer. We measure a ≈ 7 -fold enhancement in the polaron generation yield through photoinduced absorption spectroscopy. Owing to the high stability, large sensitivity factors and strong field enhancement effect, these GSNPs exhibit great potential as optical probes for sensing and photovoltaic applications. We also show that the refractive index sensing figure of merit (FoM) of GSNPs can reach 4.05 RIU^{-1} , and suggest based on finite-difference time-domain (FDTD) calculations that the FoM of GSNPs could reach even higher values with better control of particle dispersity.

Introduction

The unique optical properties of noble metal nanoparticles have attracted significant interest due to their potential applications as refractive index sensors and optical nanoantennas, anticipating their use in fields including biosensing and thin-film photovoltaics.¹ These optical properties are governed by the localized surface plasmon resonance (LSPR), i.e., the collective oscillation of the metal's conduction band electrons, induced by the electromagnetic field of incident light.²⁻⁴ The LSPR wavelength of a metal nanoparticle is controlled by the nanostructure's shape,⁵ size,⁶ electron density,⁷ surface chemistry,⁸ interparticle spacing,⁹ choice of metal¹⁰ and surrounding medium.¹¹ The high sensitivity of the metal particles' LSPR response to changes of these chemical and physical parameters has resulted in the extensive development of noble metal nanostructures for technologically relevant applications including molecular and cellular imaging,¹² glucose concentration sensing,^{13,14} chemical and biological sensing,^{15,16} DNA hybridization control,¹⁷ as well as for enhancing the performance of optoelectronic devices such as LEDs and solar cells.^{18,19}

It has been demonstrated that anisotropic nanostructures of silver and gold, such as nanoprisms,²⁰⁻²² nanocubes,²³ nanoshells,²⁴ and nanostars,²⁵ are capable of showing higher LSPR sensitivities and stronger field enhancement than the spherical counterpart due to the intense surface charge polarizability arising from large shape asperities.²⁶ However, a major problem with many polyhedral noble metal nanoparticles is that the vertices that enable large field enhancements are susceptible to chemical attack, being often related to the high-energy facets.²⁷ Furthermore, among all noble metal nanostructures, silver nanoparticles usually exhibit superior optical properties, but weaker stability because silver metal is more easily oxidized than gold.^{27,28} As such, anisotropic silver nanostructures often become truncated over time and tend to evolve

towards more stable morphologies with less particle shape asperity. This is usually apparent through a broadening and blue shift of the LSPR band, along with a loss of surface plasmon intensity.²⁹ Consequently, besides featuring high dielectric sensitivity, LSPR-based metal nanostructures need to be structurally robust and amenable to chemical functionalization without undergoing morphology changes when integrated into optoelectronic devices such as bio/chemical sensors^{30,31} and thin-film solar cells.^{32,33}

A small number of attempts have been reported so far that address the problems related to the morphological instability of metal nanoparticles. For example, by using atomic layer deposition (ALD) of a sub-1 nm thick alumina layer, both the LSPR sensitivity and the shelf life of a lithographically patterned silver nanostructure could be increased.³⁴ Protective silica and polymer shells have also been explored in the past,^{35,36} but in general the shell thickness is difficult to precisely control when it is below 5 nm, which is crucial when utilizing the LSPR enhancement from the metal cores. Recently, Desiredy et al. demonstrated ultra-stable thiolate-protected silver nanoclusters but the approach remains unexplored for larger nanoparticles.³⁷ Aherne et al., on the other hand, have reported that gold-coating represents an efficient way of protecting the facets on the edges of silver nanoprisms against chemical etching by chloride.²⁸ Importantly, the structural modification of metal nanoparticles also influences their refractive index sensitivity according to the studies by Mahmud et al.^{38,39} For that reason, the development of a controllable, scalable and cost-effective method for protecting metal nanostructures, and consequently, minimizing possible morphology variations while maintaining the LSPR sensitivity towards the dielectric environment would be highly desirable.

Herein, through a facile wet chemistry approach, we demonstrate chemically stable optical nanoantennas based on silver nanoprisms (SNPs) with strong electric field enhancement

and high LSPR sensitivity by exploring both aforementioned effects, epitaxial edge gold-coating (to increase stability) and plasmonic particle-cavity formation (to enhance the sensitivity). The edge gold-coated silver nanoprisms (GSNPs) are synthesized by using SNP precursors *via* site-selective gold nanoframe formation on the edges of a SNP. The epitaxial edge gold-coating allows for a well-retained triangular shape with morphological inertness towards chemical etching and superior refractive index sensitivity as compared with the bare SNP. The excellent chemical resistance is of great benefit when aiming at strong plasmon resonances (high extinction) and reduced plasmon damping, which is critical for stable LSPR-based sensing and absorption enhancement.

There are only a few synthetic protocols that allow preservation of the narrow LSPR response of a silver nanoprism while overcoating it with Au.²⁸ The modified approach we present here, using hydroxylamine as a reducing agent, allows for a small and controlled rate of gold deposition on the edges of the prisms. This is critical for preserving the triangular shape and sharp tips. Moreover, motivated by the observation of high extinction ratios, large field enhancement effects (compared with the case of spherical nanoparticles),^{40,41} and remarkably high stability of the prepared GSNPs, we explore their application for light harvesting in organic photovoltaic films based on polymer/fullerene blends.

Materials and Experimental Methods

Synthesis of Triangular Silver Nano-Prisms (SNPs): The SNP preparation was carried out by using a modified protocol based on previous reports.^{42,43} In a typical synthesis, ultrapure water (95 mL), AgNO₃ (0.6 mL, 30 mM), and sodium citrate (1 mL, 35 mM) were combined in a 250 mL three-neck flask. The flask was immersed in an ice bath, and the solution was bubbled with

nitrogen gas under vigorous stirring for one hour. Then 0.5 mL aqueous solution of NaBH_4 (70 mM, freshly prepared with ice-cold ultrapure water prior to injection) was rapidly injected into the solution. Over the next 20 min, 5-10 drops of NaBH_4 solution were added into the reaction solution at 2-min intervals. Then 0.5 mL solution of BSPP (5 mM) and 0.5 mL solution of NaBH_4 were simultaneously added dropwise to the solution over a 10-min period. The resulting colloid of Ag nanoparticles was gently stirred for 3 h in the ice bath and allowed to age at $\sim 4^\circ\text{C}$ for 24 hours in a dark place. For the photomediated growth of SNPs, typically, 30 mL colloid solution of the prepared silver nanoparticles was irradiated by a 150-W halogen lamp coupled with an optical bandpass filter centered at $460\pm 20\text{ nm}$, $500\pm 20\text{ nm}$ or $550\pm 20\text{ nm}$ for 2~5 hours.

Synthesis of edge gold-coated silver nanoprisms (GSNPs): The as-prepared silver nanoprism solution (15 mL) was added into 25 mL ultrapure water in a glass vial, which was maintained in an ice bath. The solution was stirred for 30 min followed by simultaneous infusion (at a rate of 0.5 ml/hour) of aqueous solutions of hydroxylamine (3 mM) and HAuCl_4 (0.37 mM) via two separate tubes on a mechanical syringe pump. During the infusion process the solution was vigorously stirred.

LSPR Sensitivity Analysis: Aqueous solutions of sucrose (780 μL) with concentrations varying from 10 to 50 wt% were used to attain different refractive indices of the solution medium. A drop of as-prepared GSNP solution (20 μL) was added into these sucrose solutions, and the extinction spectra of the resulting mixture solutions were measured to monitor the LSPR shift of GSNPs as a function of refractive index change.

Self-assembly of nanoprisms on glass substrates and polymer film processing: Glass slides (15x15 mm) were pretreated with Piranha solution (H_2O_2 : H_2SO_4 1:3, v/v) for 2 hours and then immersed in a 2-propanol solution of 1% 3-aminopropyltrimethoxysilane in the presence of

0.1% acetic acid for 2 h. (Caution, Piranha solution is a very strong oxidizing agent and extremely dangerous. It should be handled with great care.) The modified substrates were rinsed with ethanol three times, and then immersed in the nanoprism (G SNP or SNP) solutions for 12-24 hours. Afterwards, the glass slides coated with self-assembled nanoprisms were carefully rinsed three times with ethanol prior to measurements by UV-Vis spectroscopy. For polymer blend coating, these nanoprism-coated glass slides were transferred into a glove box (< 1 ppm O_2 and H_2O) and overcoated with a 35-nm film of the blend components P3HT (Rieke Metals) and PCBM (Nano-C) (1:1) (15 mg/mL in chlorobenzene, spin coated at 1800 RPM for 1 min). The P3HT:PCBM films were dried in a vacuum chamber overnight.

Photoinduced absorption spectroscopy (PIA). The apparatus for PIA spectroscopy was designed and assembled in our group. The setup and detection scheme involving standard lock-in techniques are described in detail elsewhere.⁴⁴ The sample is irradiated with a 200 Hz pump beam (typically 455 or 530 nm) while simultaneously probed with a monochromatic source that can be swept over a large spectral range. The change in transmission (dT) of the sample is detected through a lock-in amplifier, allowing the recording of both “in-phase” (X-channel, shorter-lived carriers) and “out-of-phase” (Y-channel, longer-lived carriers) components.

FDTD simulation procedure: FDTD calculations were performed with Lumerical software, version 8.6.⁴⁵ To calculate the absorption and scattering cross sections of the metal nanoprisms a 3D total-field scattered-field source (TFSF) was used around the particle to inject an electromagnetic plane wave. A power monitor placed inside the TFSF source analyzes the power absorbed by the particle while a second power monitor outside the TFSF source measures the power flow scattered from the particle. By evaluating the net power (the power flow through all

sides of the power box) and normalizing by the source intensity, the absorption and scattering cross section can be calculated.

For describing the silver metal and water (solvent), we used experimentally measured permittivity data by Palik.⁴⁶ The optical constants for gold were taken from Johnson and Christy.⁴⁷ Both can be accessed from the Lumerical software. For parametrization of the material data, a multi-coefficient model as provided by the Lumerical software was used (the material fits are shown in the Supporting Information, Figure S8). We implemented perfectly matched layer (PML) boundary conditions in x, y and z direction. A uniform mesh size of 1 nm was used to cover the TFSF region and the region of the power monitors.

Results and discussion

Bare silver nanoprisms with narrow size distribution and tailored LSPR wavelengths were prepared as the GSNP precursors through a plasmon-mediated photochemical route.⁴⁸ As illustrated in Figure 1, each individual silver nanoprism contains two main (111) facets on the triangular-shaped planes. The gold-coating process on the silver nanoprism edges was carried out by slowly and simultaneously adding chloroauric acid (HAuCl_4) and hydroxylamine (HyA) to the Ag nanoprism solution at an optimum pH and infusion rate according to our previously reported protocol with some modifications.⁴³ Because the relative surface energies of the different facets in face-centered cubic (FCC) silver are in the order of $\gamma_{111} < \gamma_{100} < \gamma_{110}$,⁵⁰ the gold atom deposition is initiated preferentially at the prism edges. The resulting edge-gold-coated structures exhibit much higher stability than bare SNPs because the prism tips and also edges are protected by an inert layer of gold, while the (111) planes are intrinsically stable.^{28,43} Note that for illustrating the gold deposition process we adopted a simplified model, in which the prism edges have flat rectangular surfaces. In reality, the morphology is more complicated and

the edge planes may be better represented by different combinations of (110), (100) and (111) facets.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations (Figure 2C and Figure S1) confirm that our epitaxial gold-coating approach creates GSNPs with a uniform gold frame coverage of the SNP edges in very high yield (>99%). The gold coating is evidenced by the darker contrast at the prism edges and energy-dispersive X-ray (EDX) line-scan profiles on a single GSNP (Figure S2).⁴³ The gold ridge thickness was determined by chemically etching away the silver portion of the GSNPs with H₂O₂ solution (50 mM). High-angle annular dark-field (HAADF) images of single GSNPs (Figure S2) acquired with a scanning transmission electron microscope (STEM) corroborate the uniformity and thickness of the gold ridge. By plotting the ridge thickness as a function of the gold-deposition time, we find that the gold-coating process can be fitted with an asymptotic exponential equation (Figure 2E), revealing a growth rate of $\approx 0.01 \text{ nm} \cdot \text{s}^{-1}$ towards a final gold ridge thickness of 7.8 nm. Experimentally, we find that the gold ridge thickness plateaus at ≈ 6 nm.

The resulting GSNPs exhibit significantly enhanced stability. In particular, the tips of the gold-coated nanoprisms show high resistance towards truncation and roundness, which is frequently observed in the case of the bare SNPs, even in the dark.²² The improvement in stability is demonstrated through a comparative etching experiment, in which GSNPs and SNPs were exposed to a 30 mM NaCl solution. Figure 3 shows that the extinction band of SNPs dramatically shifted and broadened within half an hour, while the LSPR signature of GSNPs remained almost unchanged throughout 48-hour exposure. This observation suggests that a thin layer of gold can protect the triangular shape and keep the nanoprism tips intact even in the presence of an aggressive chemical environment. The latter is an important prerequisite for

maintaining intense light concentration around the nanoprisms when integrated into a plasmonic sensor or optoelectronic device.

Structure variations induced by gold deposition and etching

The site-selective gold deposition protocol presented here led to two distinct metal nanostructures *via* control of the oxidizing power of the applied solutions of HyA and HAuCl_4 : edge gold-coated silver nanoprisms (G SNP) and gold nanoframes (AuNFs). Based upon the TEM analysis of samples taken during the gold deposition processes, four main morphological stages can be distinguished, as illustrated in Figure 1.

A) Initial growth of sub-nanometer Au clusters on the tips of the SNPs: This step occurs within the first 5 minutes at a very low concentration of HAuCl_4 . At this point, the amount of gold ions is not sufficient to form a complete frame-like structure on the nanoprism edges (stage A). The gold cluster growth starts as a heterogeneous nucleation at the three nanoprism tips first, followed by continuous Au deposition on the prism edges to form an ultrathin gold nanoframe. This is confirmed by STEM images combined with EDX mapping as shown in Figure 4.

B) Formation of thin gold ridges on the SNP edges: The deposition of gold extends from the prism tips towards the center of the prism edges, leading to a nanoframe of Au around the prism edges with gradually increasing thickness. The ridge thickness of this Au nanoframe can be tuned from 1.8 to 6 nm by controlling the edge-gold-coating time.⁵² At the end of this stage, G SNPs with a uniform gold frame are produced (stage B).

C) Pinhole formation on (111) facets: By continuously increasing the HAuCl_4 concentration after the gold nanoframe formation, the silver part of the G SNPs is slowly etched away. Typically, the etching starts from the center of the nanoprism and continues concentrically

towards the three prism edges. As shown in Figure S4, this process most likely leads to gold-framed nanoprisms with increasing pinhole sizes that can be controlled by adjusting the etching time and rate. The resulting structures in this stage are denoted as “etched GSNPs” (stage C).

D) Formation of gold nanoframes upon complete silver etching: After the addition of excess HAuCl_4 , the silver portion of the GSNPs is entirely etched away. As a result, gold nanoframes with well-retained triangular shape and slightly larger edge lengths are obtained (stage D). The reaction ends at this stage as there is no more silver to be consumed.

Note that stage C and D can be manipulated by introducing a more effective silver etchant such as H_2O_2 or $\text{NH}_4\text{OH}+\text{H}_2\text{O}_2$,⁵² which allows a better control of the particle shape dispersion. In this study, H_2O_2 was used in cases where controlled etching of GSNPs was required to clearly differentiate between the optical properties of structurally similar nanoprisms, e.g., etched GSNPs with different pinhole radii (see Table 1).

Optical Properties and Refractive Index Sensitivity of GSNPs

We monitored the LSPR evolution of SNPs during the gold-coating process in stage A and B and the etching process in stage C by using UV-Vis spectroscopy. An aliquot of the solution was taken at 5-min intervals for characterization purposes. The slow gold-coating and etching processes combined with the high LSPR sensitivity of the resulting nanoprisms allowed us to track the morphological transformations of the particles based upon the evolution of the extinction spectrum. As a result of the site-selective deposition of gold in stage A and B, the LSPR band exhibits a red-shift with a concomitant increase in intensity (Figure 5). The shift and change in intensity of the LSPR was observed for two batches of nanoprisms with different edge lengths (25 ± 5 nm and 34 ± 5 nm, Figure 5). An interpretation of this observation is provided

further below when discussing the electrodynamics simulation results. In stage C, with increasing void area (addition of more HAuCl_4) in the interior of etched GSNPs, the in-plane dipole plasmon peak continues red-shifting towards the near-infrared region while losing intensity at the same time.

Refractive index sensing measurements were performed by using aqueous solutions of sucrose at different concentrations (0 to 50 wt% sucrose) to adjust the refractive index of the surrounding medium. The bulk refractive index sensitivity of the particles in stage A to C is evaluated by following the method used by Sherry et al.,²³ which plots the observed energy shift in eV normalized by the full width at half maximum (FWHM) *versus* the refractive index change (Δn). The slope of the linear regression of this representation represents the figure of merit (FoM) of LSPR sensitivity. This refractive index sensing method accounts for the LSPR wavelength and its FWHM, enabling a comparison between particles of different size and shape.^{23,53} We also extracted the more common but less meaningful sensitivity simply based on wavelength shift per refractive index unit (RIU). The results are summarized in Table 1.

Figure 6A shows the normalized energy shift *versus* refractive index change for the particles in stage A to C. We did not observe differences in sensitivity for the nanoprisms immediately before and after tip-gold deposition in stage A due to very minor morphological differences. Importantly, transformation from stage A to B is accompanied by an increase in FoM. A FoM of $\sim 4.1 \text{ RIU}^{-1}$ at λ_{max} of 718 nm is achieved in stage B. This result suggests that the edge-gold-coating on SNPs can increase not only the particle stability but also FoM (refractive index sensitivity) at the same time. The sensitivity response of the nanoprisms is likely to be dominated by changes in particle shape and morphology. According to Figure 3, the gold coating, however, better retains the sharp tips which we propose contributes to the enhanced

sensitivity of the GSNP compared to SNP in real environments. Previously determined FoMs for SNPs were in the range of 2.3 – 3.3 RIU⁻¹.²⁰

For stage C, we distinguish between different sub-stages C_1 to C_n depending on the pinhole diameter in the triangular face (see also Figure S4). Although the creation of a pinhole in the GSNP results in increased refractive index sensitivity in terms of wavelength shift per refractive index unit, the overall FoM drops from 4.05 in stage B to 2.70 in stage C_1 . The refractive index sensitivity of stage C decreases further with increasing void area. Figure 6B summarizes the experimental FoM and sensitivity values for the GSNPs in stage A to C_n . In the case of stage D, the optical density of the gold nanoframes formed from GSNPs was too low to accurately determine the FoM.

Electrodynamics Simulations

In order to better understand the optical properties of the metal nanostructures at different stages of growth, we carried out electrodynamics simulations by using the finite-difference time-domain (FDTD) method. The particle dimensions used for the simulations (Figure S6A, inset) are based on the results of TEM and atomic force microscopy (AFM) measurements (Figure 1 and Figure S5) and correspond to the average particle dimensions. Figure 7A shows the wavelength dependent Mie extinction cross section (scattering + absorption) for the precursor SNP and the particles in stages A to D. In the case of the simulated spectrum of the SNP, the plasmon line width (0.12 eV) is similar to those reported for single silver nanoprisms.⁵⁴ Moreover, the simulated spectrum matches the LSPR position for the dipole and quadrupole resonances reported previously (Table 1 and Figure S7), suggesting a reliable description by the FDTD formalism.²⁶

The simulated spectra of the nanostructures shown in Figure 7A follow the same trend as the experimental spectra. When gold clusters start growing at the tips of the SNP, the in-plane dipole plasmon peak red shifts by only a few nanometers (stage A). A uniform gold-coating (3 nm) on the SNP edges (stage B) leads to an additional red-shift of the LSPR band with increased extinction cross section. This red-shift can be attributed to two effects. First, the complex dielectric constant of gold is larger than that of silver,⁵⁵ which means that gold particles have a lower localized surface plasmon resonance frequency than the equivalent silver particles. Second, adding an additional gold layer to the SNP edges leads to an increase of the overall edge-length, which enlarges the distance of charge oscillation and reduces the oscillation frequency, resulting in a red-shift of the LSPR wavelength. In addition, the extinction coefficient correlates with the particle volume, which explains the larger extinction cross section of the GSNP (stage B) as compared to the corresponding SNP precursor. Importantly, likely due to its larger volume,⁵⁶ the GSNP features a larger scattering to absorption ratio than SNP as shown in Figure S6B. This enhanced ratio could potentially magnify the particle's scattering behavior inside an OPV device, and consequently increase the probability for photon absorption by the active layer as opposed to the metal particle.

In the simulation result of stage C (Figure S4A), we observe that with increasing void radius, the LSPR peak continuously red shifts. This trend becomes more pronounced when the silver part of the GSNP is fully etched away (stage D). The experimentally observed and computed evolution of the LSPR with increasing silver etching is in agreement with previous experimental results and discrete-dipole-approximation (DDA) calculations for other shapes of hollow particles.^{24,57,58}

In addition, we calculated the bulk refractive index sensitivity of the particles in the stages A to D in terms of wavelength shift/refractive index unit and FoM (Figure 7B and Table 1). Qualitatively, the simulations capture the increase in FoM for a gold-framed SNP as compared to a bare SNP. The simulations also reproduce the broadening of the line width, and consequently, the decrease in FoM (though increase in wavelength shift/refractive index) for GSNPs with increasing void radius. The increase in wavelength shift/refractive index is due to the strong spectral red shift of the dipole resonance. Note that the simulated FoMs for the different stages are significantly larger than the experimental values. This is primarily because the simulations are run on a single particle level, leading to a significantly narrower (~ 0.12 eV) width (FWHM) of the dipole plasmon mode than in the experimental spectra. Table 1 summarizes and compares the experimental and theoretical FoMs and refractive index sensitivity values for the nanoprisms in stage A to D. We note that the theoretical FoM of the GSNP is among the highest FoMs so far reported for dipole resonances in metal nanoparticles,²³ suggesting that the GSNPs are well-suited for plasmonic sensor applications, especially if the size and shape dispersity that broadens the ensemble linewidth can be brought under synthetic control.

Plasmon-Enhanced Charge Carrier Generation in OPV^{59,60}

To demonstrate the potential of GSNPs as optical antennas for light trapping inside OPV cells with sub-100 nm active layers,^{44,61,62} we prepared four batches of GSNPs with LSPR signatures in the range 500 to 600 nm (Figure 8) and investigated their plasmonic effect on charge carrier generation in 35 nm P3HT:PCBM blend films by using photoinduced absorption (PIA) spectroscopy. PIA measures the concentration and lifetime of long-lived photoexcitations (here polarons with $\approx$ ms lifetimes).^{63,64} Performed in a pump-probe arrangement, the change in

transmission (dT) is measured using lock-in detection synchronized to a modulated pump beam. In the P3HT:PCBM system, positive charges are created on the P3HT backbone upon photoinduced electron transfer from P3HT (donor) to PCBM (acceptor). By comparing the change in transmission at the P3HT polaron peak with and without metal nanoprisms, we can quantify the occurrence of plasmon-enhanced charge carrier generation. This is possible because the change in transmission at the polaron peak is proportional to the number of P3HT polarons generated by the pump.⁶⁵

Figure 8a shows solutions of the four different batches of GSNPs (G1–G4) with LSPR wavelengths located between 490 to 580 nm. We specifically designed GSNPs with a LSPR band at ~500 nm in order to ensure considerable spectral overlap with the P3HT absorption since a larger spectral overlap is expected to cause stronger charge carrier enhancement. Note that bare gold nanoprisms were not considered for this work because the LSPR band of gold nanoprisms typically is found in the far red and NIR (> 700 nm) and has less favorable spectral overlap with the P3HT:PCBM absorption. The GSNP samples were prepared by using three batches of SNPs as precursors. We tested different methods for nanoprism immobilization on glass by using APTMS or Poly(2-vinylpyridine) (PVP) as the anchoring molecule (Figure S9 and S10). Typically, high optical density (OD) up to 0.4 can be achieved by using vapor phase (VPS) or solution phase silanization. However, in the case of VPS, high OD (>0.3) was typically accompanied by agglomeration, leading to broadened extinction peaks. Nanoprism films with less aggregation can be obtained by using either APTMS or PVP through a solution phase self-assembly process.^{66,67} Figure S11A shows representative UV-Vis spectra of GSNPs on glass. Overcoating of the GSNPs with the P3HT:PCBM blend typically leads to a ~150 nm red shift of the LSPR band, as indicated by Figure S11C.

By using PIA spectroscopy, we compared the P3HT polaron yields for samples of P3HT:PCBM films on glass and on top of GSNPs *versus* the bare SNPs. Figure 9A shows representative PIA spectra (X-channel) of P3HT:PCBM films on top of four different batches of GSNPs (G1 to G4). The signal at around 1.25 eV is attributed to the high-energy absorption of the P3HT polaron.⁶⁸ As is clearly discernible from Figure 9A, the presence of GSNPs greatly enhances the generation of photoinduced polarons inside the polymer blend.

We evaluated the amplitude of the polaron signal for more than 40 nanoprism/blend samples prepared by using different batches of SNPs or GSNPs. Figure 9B plots the relative polaron yield as a function of the relative extinction for GSNPs (black squares) and SNPs (red dots) at a pump wavelength of 630 nm. Both polaron yield and extinction values are normalized to those of the reference polymer film without nanoprisms. Importantly, the polaron yield correlates linearly with the extinction of the sample, suggesting an optical enhancement effect (i.e., a plasmonic effect). We observe that samples prepared from bare SNPs feature a larger dispersion of polaron yields than the samples with GSNPs, resulting in linear regressions R^2 of 0.15 and 0.75, respectively. The low R^2 in the case of SNP might be ascribed to the weak stability of SNPs when exposed to the polymer blend and chlorinated solvent during sample preparation. The GSNPs are chemically more stable and thus less susceptible to diminishment of their light concentration properties when embedded in the polymer blend film, contributing to the more reproducible (and hence larger average) enhancement in polaron yields compared to SNP. Note that when the polaron yield is plotted for a single batch of GSNPs (Figure S12), we observe a linear relationship as a function of the relative extinction with R^2 close to one.

In comparison, the GSNP batches G2 and G4 provide the best enhancement (Figure S12A and B) since their LSPR bands have a large spectral overlap with the P3HT absorption.

The maximum charge carrier enhancement achieved is 6.7 using the GSNP batch G4 (Figure S12B). Figure 14B also compares the polaron yields measured in the present work (black squares) with the previous result by Kulkarni et al.⁴⁴ obtained with bare silver nanoprisms (red squares). While the work by Kulkarni et al. demonstrated charge carrier enhancements of $\approx 3\times$ at relative high ODs, in this work we achieve enhancements of $\approx 7\times$ at more moderate ODs. We attribute the difference to the improved shape asperity of the particles prepared in the present work.

We further measured and compared the polaron lifetime for both types of nanoprisms to rule out its impact on the improved enhancement effect. As shown in Figure S13, we found that the polaron lifetimes are similar within a small discrepancy of 30% between the sample prepared with GSNP batch G4 (1.23 ms) and the sample using SNPs reported by Kulkarni et al. (1.61 ms). This similarity means that differences in polaron lifetime cannot be the major reason for the observed difference in polaron yield enhancement. Therefore, we propose that improved optical absorption is most likely responsible for the increases in charge carrier yields in the P3HT:PCBM blend reported in the present work.

We also performed PIA measurements by using a pump wavelength of 530 nm, closer to the absorption peak of P3HT. In this case, the polaron enhancement achieved was $3\times$ by using the GSNP batch G4 (Figure S14). This demonstrates that shape dispersed plasmonic GSNPs can contribute to high charge carrier enhancement throughout a broad range of excitation wavelengths, which is favorable for achieving large power conversion efficiency improvements in OPVs.

Conclusion

We studied the formation, properties, and applications of plasmonic edge-gold-coated silver nanoprisms (GSNPs) as well as the evolution of their structure variations during the gold-coating process. We have shown that controlled gold nanoframe formation can be explored as an effective means for preventing morphological changes and disruptions of optical properties with the additional benefit of improved LSPR sensitivity. These observations allow gold-framed silver nanoprisms to be employed as optical antennas in chemically adverse environments while maintaining a high local electromagnetic field concentration at the particle shape asperities (tips). As one possible application, we demonstrated enhanced charge carrier generation yields ($\approx \times 7$) in organic bulk-heterojunction films. This work demonstrates the technological viability of large-area plasmonic devices based on anisotropic metal nanoparticles with highly sensitive and tunable optical properties.

Figure 1. Schematic illustrations and TEM/STEM images of synthesized triangular metal nanostructures at different stages during the gold coating process, including tip-gold-coated SNP (stage A), edge-gold-coated SNP (GSNP, stage B), etched GSNP (stage C), and triangular gold nanoframe (stage D).

Figure 2. (A) TEM image of SNPs; (B) TEM image of GSNPs; The inset at the top left corner shows an enlarged view of GSNPs with a scale bar of 10 nm. The gold ridges on the prism edges are clearly discernible; The inset at the bottom right corner shows a schematic representation of the GSNP structure; (C) SEM image of self-assembled GSNPs on a glass slide; (D) Plot of the deposited gold-ridge thickness as a function of the gold-coating time. The line is a fit to the experimental data based upon the function $f(x) = a \times (1 - \exp(-K \times (x - c_0)))$ with $a=7.8$ nm, $K=0.009 \text{ min}^{-1}$ and $c_0= 9.5$ min.

Figure 3. Comparative etching experiment showing the spectral evolution of a mixture of 1 mL NaCl solution (30 mM) with 1 mL solution of (A) GSNPs and (B) SNPs.

Figure 4. (A) HAADF-STEM image and (B-D) STEM-EDX mapping images of an individual tip-gold-coated Ag nanoprism at stage A. Note that (B) and (C) show the EDX signal for silver and gold, respectively, while (D) displays the signal for gold and silver at the same time.

Figure 5. Spectral evolution of wavelength and optical density of the extinction peak during edge-gold-coating of silver nanoprisms with an average edge length of (A) 25 ± 5 nm and (B) 34 ± 5 nm. (C) and (D) show photographs of the nanoprism solutions during the gold-coating process for (A) and (B), respectively.

Figure 6. (A) Energy shift normalized by the FWHM of the plasmon band as a function of the refractive index change for the nanoprisms in stage A, B, C₁ and C₂; (B) The refractive index sensitivity (wavelength/refractive index unit) and FoM of the prism structures at different stages.

Table 1. Summary of experimentally measured and calculated LSPR peaks at different stages and the corresponding refractive index sensitivities.

Stage Name	Calculation			Experimental			
	LSPR nm (eV)	FoM (RIU ⁻¹)	Sensitivity (nm.RIU ⁻¹)	LSPR nm (eV)	FoM (RIU ⁻¹)	Sensitivity (nm.RIU ⁻¹)	FWHM (eV)
SNP	700 (1.77)	9.55	441	687(1.80)	3.87	402	0.28
A	715 (1.73)	9.32	451	692(1.79)	3.87	402	0.28
B	744 (1.67)	10.09	456	718 (1.72)	4.05	427	0.26
C ₁	753 (1.65)*	--	--	746 (1.66)	2.70	495	0.38
C ₂	790 (1.57)*	9.75	496	816.5 (1.51)	2.56	461	0.34
C ₃	1046 (1.19)*	7.35	707	--	--	--	--
D	1600 (0.78)	5.85	1133	--	--	--	--

(*) The diameter of the pinhole used in the FDTD simulations is 6, 13, 34 nm for C₁, C₂ and C₃, respectively. The LSPR wavelength refers to the plasmon resonance in water.

Figure 7. (A) FDTD calculated extinction spectra and (B) corresponding normalized relative energy shifts vs. refractive index change for the nanoprisms at different stages. The structures at different stages are illustrated in the inset of (A). The lines in (B) are linear regression fits. The fitting results and the plasmon resonances are summarized in Table 1. The particle dimensions used for the FDTD calculations were 55 nm edge length, 7 nm height and 3 nm thickness of gold coating.

Figure 8. (A) Photographs of the colloidal particle solutions of SNPs and GSNPs used for self-assembly on glass; (B) Extinction spectra of three SNP batches (with LSPR peaks at 477, 526 and 557 nm) and the resulting four different batches of GSNPs (with LSPR peaks between 490 and 580 nm) in solution; (C) Schematic illustration of self-assembled GSNPs on a glass slide covered by P3HT:PCBM blend, which was used for studying the plasmonic enhancement in a bulk-heterojunction blend.

Figure 9. (A) Representative photoinduced absorption spectra of the GSNP batches G1 to G4; (B) Relative polaron yields (derived from the X-channel PIA signal at the polaron peak) as a function of the relative thin film extinction (absorption and scattering, $A + S = 1 - T$) at the pump wavelength of 630 nm. The PIA signal at ≈ 1.25 eV originates from the formation of P3HT polarons inside the polymer blend. Note that negative dT/T values represent an increase in absorption while positive dT/T values represent an increase in transmission (bleach). The polaron yields in (B) include the results from the nanoprism/blend samples prepared by using SNPs or GNSPs of different batches. For comparison, (B) includes the previous result by Kulkarni et al using bare SNPs (hollow squares).⁴⁴ The lines are linear fits to the data. The fit parameters are (i) $y = 1.98x - 1.49$ ($R^2 = 0.75$) (this work) and $y = 0.24x + 0.67$ ($R^2 = 0.91$) (Kulkarni et al.). All values in (B) are normalized to the results for the bare polymer blend.

Supporting Information. FDTD simulation results and spectroscopic data for a wider range of particles; additional electron microscopy images, and Energy-dispersive X-ray spectroscopy results. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Author Contributions

M.M.S. designed, synthesized and characterized the SNP and GSNP nanoparticles. C.X. interpreted all the nanoparticle related characterization data. M.S. carried out the PIA experiments and the FDTD simulations and wrote the sections of the manuscript dealing with PIA and FDTD, and helped interpret the FOM data. DSG helped interpret the PIA and FDTD data. All authors revised the manuscript and have given approval to the final version of the manuscript.

§These authors contributed equally.

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Table of content

A facile route for synthesis of edge gold-coated silver nanoprisms (GSNPs) is presented with systematic studies on their structural evolution and optical properties during the reaction. GSNPs exhibit high stability against chemical etching and excellent performance as both refractive index sensors and optical antennae for light-harvesting applications.