Optical and electrical properties of Au nanoparticles in two-dimensional networks: an effective cluster model

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Abstract: We report a study of the optical and electric properties of Au nanoparticle networks grown on the porous alumina membrane by dry atom sputtering deposition approach. An effective cluster model was developed to evaluate the dielectric function and the electrical conductivities of the nanoparticle networks by taking into account the effects of the Au particle size, the Au volume fraction, and the particle-particle interaction. The calculated transmission spectra from the model were in good agreement with the experimental data. The percolation threshold of the as-fabricated structure was predicted to occur at Au volume fraction of 0.18, consistent with the dc electric resistance measurement.

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References and links
I Introduction

The interaction of light with metal nanoparticles has been of great interest for both fundamental research and technological applications. The optical spectra of noble-metal particles and metal-insulator nano-composites are dominated by the resonant coupling of the incident field with the collective oscillations of conducting electrons, known as the surface-plasmon resonance (SPR). In recent years, a wide variety of plasmonic nano-structures have been fabricated [1–4] and studied extensively on their fascinating optical properties and potential applications in X-ray optics, nonlinear optics, microelectronics, biological labeling and diagnostic, and nano-photonics.

The resonant coupling of a surface plasmon and a photon is called a surface plasmon polariton (SPP). For metallic particles or voids of various topologies, the excitation of electron surface plasmas is confined to the curved geometries, resulting in the so-called localized surface plasmon resonance (LSPR). For particles with diameter \( d << \lambda \), the conducting electrons inside a particle move all in phase, generating a dipolar field outside the particle. For particles of larger size, the spectral response may be complicated by the excitation of higher-order modes and the retardation effects [7]. In general, the spectral position of the LSPR depends on the dielectric properties, the size and the shape of the metal particles [5,6], as well as on the dielectric function of the host matrix due to the screening of the Coulomb attraction between the oscillating electrons [2].

The optical responses of metal-dielectric nano-composites change drastically with the structural geometry of individual particles and the aggregate topology [7]. The geometric and aggregational complexity in such systems makes the precise modeling somewhat formidable. Instead, these systems can be treated as an optically quasi-homogeneous effective-medium material, with a proper macroscopic dielectric function that describes the linear response to the external electromagnetic field. Among all the theoretical models to interpret the optical
properties of inhomogeneous media, one of the earliest and also the best known is Maxwell-Garnett (MG) equation [8] in the form:

\[ \varepsilon_{\text{MG}} = \varepsilon_h + 3\varepsilon_i f \frac{\Lambda}{1 - f \Lambda}, \text{ with } \Lambda = \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h} = \frac{\alpha}{3\varepsilon_h V} \]  \hspace{1cm} (1)

where \( \varepsilon_i \) and \( \varepsilon_h \) are the dielectric constants of the host matrix and the embedded particles respectively, \( \alpha \) is the polarizability of a spherical particle with respect to the environment, \( V \) is the volume of the particle, and \( f \) is the total particle volume fraction in the system. The original model was subsequently modified by many researchers to take into account the effects of particle size and shape, as well as the role of coating layers of particles ([7] and references there in). However, MG theory was derived under the assumption that the separations between the particles are sufficiently large so that the independent scattering occurs and the Lorentz local-field correction applies. It becomes inapplicable to systems with high particle volume fractions where a particle is subject to a non-uniform field due to both the surrounding material and the nearby particles. Although in the metal-rich limit, the film can be modeled as dielectric particles embedded in a continuous metallic medium, the MG theory fails in situations where particles are aggregated and the particle-particle interactions become important.

Another self-consistent effective medium theory was originally put forward by Bruggeman [9]. For a two-component mixture with dielectric constant \( \varepsilon_i \) and \( \varepsilon_j \), the effective medium (EM) permeability \( \varepsilon_{\text{BR}} \) is given by

\[ V_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} + V_j \frac{\varepsilon_j - \varepsilon_m}{\varepsilon_j + 2\varepsilon_m} = 0, \]  \hspace{1cm} (2)

where \( V_i \) and \( V_j \) are the volume fractions of dielectric \( \varepsilon_i \) and \( \varepsilon_j \), and \( V_i + V_j = 1 \). In the case of metal-dielectric composite medium, Bruggeman model does predict a percolation threshold for electrical conductivity but fails in describing correctly the optical dielectric anomaly predicted by the MG theory. Such dielectric anomaly is due to the short-range interaction between the nearest metal-dielectric interface at a microstructural level, while the Bruggeman model considers only the metal-EM and dielectric-EM interfaces [10].

In this paper, we propose a theoretical model incorporating the advantages of both MG and Bruggeman model, and apply it to the Au nanoparticle networks as-fabricated in our experiments. Two MG-types of structural units are considered, the non-interacting metal particles as Phase-I and the clusters of touching metal particles as Phase-II. The as-fabricated nanoparticle networks are then modeled as a mixture of the two phases to which the Bruggeman equation is applied. This model, which we refer to as “the effective cluster model”, properly accounts for the observed optical and electric responses by including the effects of particle size, particle shape, and the dipole-dipole interaction between neighboring particles. Of particular importance is that the volume fractions of the two phases are not parameters out of the fitting in the calculation. Instead, they are evaluated from the samples’ scanning electron microscopic (SEM) images. Therefore, the theoretical prediction of the proposed model can be compared directly with the experimental data. The layout of this article is as follows: In section II, we describe the experimental details regarding the preparation of the Au nanoparticle networks and the characterization by SEM, optical transmission and reflection measurements; Our proposed “effective cluster model” is then outlined in section III, where we considered the roles of particle size, particle shape, and dipole-dipole coupling among neighboring particles. In section IV, we calculate the transmission and reflection spectra with the effective dielectric function obtained in section III. Using this effective cluster model, the normalized conductivities of the as-fabricated...
samples are also calculated as a function of the Au filling factor $f$. The main conclusions are summarized in section V.

II Sample fabrication and characterization

The commercial Anodisc® porous alumina membrane (PAM) were used as the templates for the fabrication of the Au nanoparticle networks [11]. Dry atom sputtering deposition approach was employed to deposit Au nanoparticles on the branched side of Anodisc® PAM which contains densely packed pores with diameters of 100nm and 200nm, respectively [11]. The size and the density of the deposited particles were controlled by applying different deposition time, and accurately measured by scanning electron microscope (SEM). The average thicknesses of the networks were estimated from the total amount of Au deposited on a substrate with pre-fixed area. Au nanoparticle networks with an average “film thickness” of 10nm to 60nm were fabricated. All the as-fabricated samples exhibited a narrow dispersivity in particle size. SEM was employed to characterize the size, the shape, the aggregation topology of the Au particles as well as the Au volume fractions in each sample [11]. Optical reflectance measurements in the range of near-infrared (NIR) to mid-IR were performed on the as-fabricated samples by FTIR (Fourier Transform Infra-Red) system (FTS 6000, Bio-Rad). Reflection spectra in the visible region were measured with homemade optical setup on all the as-fabricated samples while the transmission spectra were measured on the samples with PAM substrates removed and supported on quartz plate. Four-point probe method was applied to measure the dc resistances of all the samples.

III The effective cluster model

In this section, we outline our effective cluster model and some of our considerations when applying the effective medium theory to calculate the optical properties of the Au nanoparticles networks fabricated in our experiments.

A. Size effect

The change in the LSPR bandwidth and the shift in the resonance peak position are called the “size effect”, including both the intrinsic size effect and the extrinsic size effect.

When the sizes of metal clusters become comparable to or smaller than the electron mean-free-path, about 50nm for bulky Au in a Drude-Sommerfeld model [7], the effective mean-free-path is then smaller than that in the bulk material. In the classical picture the electrons are scattered by the surface, strongly affecting their response to the incident electromagnetic field. The intrinsic size effect reflects the change of atomic structure of the cluster and the influence of the cluster surface, which can be expressed in the form of a size-dependent dielectric function. As a result, the damping constant in the Drude dielectric function is replaced by [12-13]:

$$\Gamma = \Gamma_{\text{int}} + A\nu_f/R,$$

where $A$ is the particle shape parameter and is taken as 1 for a perfect spherical particle, $R$ is the “average” size parameter and is simply the radius for a spherical particle, $\nu_f$ is the Fermi velocity. Thus the size-dependence of the dielectric function is [7]:

$$\varepsilon(\omega) = \varepsilon_{\text{bulk}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\Gamma_{\text{int}}\omega} - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega},$$

where $\varepsilon_{\text{bulk}}(\omega)$ represents the contribution of the interband and core electrons to the dielectric function of the bulk Au, $\omega_p$ describes the unscreened plasma frequency for the conduction electrons. For our calculation, we have adopted the following values: $\omega_p = 13.8 \times 10^5$ s$^{-1}$. 

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The difference between the bulk metal dielectric function and the particle dielectric function only become significant on the imaginary part of \( \varepsilon(\omega) \) in the long wavelength region, which increases the bandwidth of plasmon resonance with the decrease of particle size.

For larger particles, the multipole modes start to contribute to the extinction and scattering spectra, originated from the size-dependent interference of the retarded electromagnetic wave. Our calculation based on the discrete dipole approximation (DDA) method shows that such extrinsic size effect is less important for the geometric and topological structures observed in our samples where the radii of individual particles are always smaller than 60nm [11].

**B. Electrodynamic correction by the modified long wavelength approximation (MLWA)**

When a small metallic particle is irradiated by light, in the case that the particle size is much smaller than the wavelength of light, the electric field of the light can be taken as constant, and hence the interaction of light with the particle can be analyzed in the quasi-static approximation (QSA) with the neglect of electrodynamics. In order to extend the electrostatic treatment to larger particles in which the electrostatic approximation gradually fails, the modified long-wavelength approximation (MLWA) is employed in our calculation to include the perturbative correction to the electrostatic approximation.

In the quasistatic treatment, the induced polarization \( \mathbf{P} \) in a small particle of size \( R \) with an externally applied electric field \( \mathbf{E} \) is \( \mathbf{P} = \alpha \mathbf{E} \), where \( \alpha \) is the particle polarizability. The electrodynamic correction of MLWA involves rewriting the above equation as [14]

\[
\mathbf{P} = \alpha \left( \mathbf{E} + \mathbf{E}_{\text{rad}} \right),
\]

where the radiative correction field \( \mathbf{E}_{\text{rad}} \) is

\[
\mathbf{E}_{\text{rad}} = \frac{2}{3} i k^3 \mathbf{P} + \frac{k^2}{R} \mathbf{P}.
\]

The first term in this expression describes the radiation-damping arising from the spontaneous emission by the induced dipole which results in broadening and strongly decreased magnitude of the resonance enhancement for large particle volumes. The second term is the dynamic depolarization of the radiation across the particle surface due to the finite ratio of particle size to wavelength [13]. The particle polarizability, after the MLWA, is given by \( \tilde{\alpha} = F \alpha \), with

\[
F = \left( 1 - \frac{2}{3} i k^3 \alpha - \frac{k^2}{R} \alpha \right)^{-1}.
\]

Using this model, the QSA can be extended to describe particles with the radius comparable to 10% of the incident wavelength [15].

**C. Aggregation effect**

For an ensemble of metal nanoparticles in sufficiently low concentration, the optical properties can be described well by the Mie theory. For the as-fabricated nanoparticle networks, the filling factor is not low enough where the dipole-dipole interaction between particles can be neglected. To determine the optical response of cluster aggregates, the Generalized Mie Theory (GMT) was formulated analytically by summing up the electromagnetic scattering fields onto a given cluster from its neighbors and solving the linear equations in a self-consistent manner [7,16,17]. Here we use an alternative solution in which we classified the densely packed aggregates into two or several typical topologies and treated the as-fabricated nanoparticle network as a multi-component system with the general effective medium theory. From the SEM images of the as-fabricated Au nanoparticles networks in our experiment, it can be observed clearly that, depending on the filling factors, the nanoparticles exist either as the isolated particles or as well-patterned aggregates in which nano-particles are...
in contact with its neighbors to form short chains and/or enclosed rings. The as-fabricated network sample as a whole is a mixture of these two types of Au clusters.

We now employ the theory of Yamaguchi [18, 19], where the dipole-dipole interactions between nearest particles were accounted for by introducing a set of effective depolarization factors $L_i$ in the expression of polarizability [20–22]

$$\alpha_i = \frac{\varepsilon_0 - \varepsilon_i}{\varepsilon_0 + L_i (\varepsilon_0 - \varepsilon_i)} V, \ i = x, y, z$$

(5)

Here the depolarization factors $L_i$ were reinterpreted as the quantities that describe the anisotropic deformation of the interaction fields instead of the particle shape. For the sake of convenience, we adopt the value of $L$ calculated by Granqvist and Hunderi [21,22] from the theory of Clippe et al. [23] for certain symmetry cluster arrays.

Our as-fabricated nanoparticle networks were then treated as a mixture of two phases with the geometric configurations observed in the SEM micrographs, one phase with isolated non-interacting particles and the other with clusters in a ring aggregation topology. Given the region volume fractions occupied by these two phases are $V_{\text{single}}$ and $V_{\text{cluster}}$, respectively, one obtains the Bruggeman’s effective medium expression as

$$V_{\text{single}} \frac{\varepsilon_{\text{single}} - \varepsilon_{BR}}{\varepsilon_{\text{single}} + 2 \varepsilon_{BR}} + V_{\text{cluster}} \frac{\varepsilon_{\text{cluster}} - \varepsilon_{BR}}{\varepsilon_{\text{cluster}} + 2 \varepsilon_{BR}} = 0,$$

(6)

with $V_{\text{single}} + V_{\text{cluster}} = 1$, and

$$\varepsilon_{\text{single}} = \varepsilon_{\text{air}} \left(1 + \frac{2}{3} p_s \Lambda_s \right), \quad \Lambda_s = \frac{\varepsilon_{\text{metal}} - \varepsilon_{\text{air}}}{\varepsilon_{\text{metal}} + 2 \varepsilon_{\text{air}}}$$

(7)

$$\varepsilon_{\text{cluster}} = \varepsilon_{\text{air}} \left(1 + \frac{2}{3} p_c \Lambda_c \right), \quad \Lambda_c = \frac{1}{3} \sum_{i=1}^{3} A_i \frac{\varepsilon_{\text{metal}} - \varepsilon_{\text{air}}}{\varepsilon_{\text{air}} + L_i (\varepsilon_{\text{metal}} - \varepsilon_{\text{air}})}$$

(8)

with $p_s$ and $p_c$ are the gold filling factors for the isolated non-interacting spheres and the ring aggregates, respectively, $\Lambda_i$ is the normalized polarizability, and $L_i = 0.186$, $L_c = 0.413$, corresponding to the two aggregate modes having a finite net dipole moment in the plane of the networks that can be excited by the incident light (the 12-sphere ring geometry in [21]) and $A_i$ is the oscillator strength of each mode. Given the total metal volume fraction $f$, we have $V_{\text{single}} p_s + V_{\text{cluster}} p_c = f$.

Thus the region volume fractions $V_{\text{single}}$ and $V_{\text{cluster}}$ are

$$V_{\text{single}} = \left(p_s - f\right)/\left(p_c - p_s\right), \ V_{\text{cluster}} = 1 - V_{\text{single}}$$

(9)

In Eq. (6)-(9), the structure parameters $f$, $p_s$, and $p_c$ are estimated from the samples’ SEM micrographs. As mentioned in Section I, two types of templates were used in the fabrication of the nanoparticles networks to allow the variation of the relative values of $p_s$ and $p_c$. Hence the effect of cluster topology can be studied both experimentally and numerically.

The effective conductivity $\sigma_e$ of the network can then be determined:
\[ V_{\text{single}} \left( \frac{\sigma_{\text{cluster}} - \sigma_{\text{e}}}{\sigma_{\text{single}} + 2\sigma_{\text{e}}} \right) + V_{\text{cluster}} \left( \frac{\sigma_{\text{cluster}} - \sigma_{\text{e}}}{\sigma_{\text{cluster}} + 2\sigma_{\text{e}}} \right) = 0. \quad (10) \]

In our effective cluster model, the Au nanoparticles are only connected and extending an electrical transport path throughout the sample in the aggregated cluster phase. Hence Eq. (10) can be simplified in a special case that

\[ \sigma_{\text{e}} = 0 \quad V_{\text{cluster}} < V_c \]
\[ \sigma_{\text{e}} = \frac{2}{3} \sigma_{\text{cluster}} \left( V_{\text{cluster}} - V_c \right) \quad V_{\text{cluster}} > V_c \]

where \( V_c = \frac{1}{3} \) is the connectivity threshold predicted by EMA [24].

Finally, the transmission spectra were calculated using electromagnetic wave formulism [25], with the effective dielectric function of the films evaluated from Eq. (6). A 3-layer model was employed in the calculation of transmittance: a layer of Au nanoparticle network with the experimentally determined average film thickness supported on a layer of Al₂O₃ of 20 nm thick which in turn is placed on a quartz substrate.

IV Results and discussion

The SEM micrograph of a typical Au nanoparticle network with Au filling factor of 21% is shown in the inset of Fig. 1. The bright spots are the Au particles and the light-grey ‘wall’ beneath the particles is the PAM membrane. Following the narrow wall boundaries between the pores in the membrane, a large portion of gold nanoparticles forms ring-like topology with 2 nearest neighbors.

![SEM micrograph of Au nanoparticle network](image)

**Fig. 1.** (Color online) (a) Measured reflectance of the nanoparticle network with Au filling factor of 21% on the PAM substrate. (b) Resistance of nanoparticle networks versus the Au filling factor using four-point probe method. Inset: the SEM micrograph of the sample in (a).

Optical reflectance in the wavelength range from 350nm to 3µm were measured at small incident angle \( (<10^\circ) \) for all the samples fabricated. In Fig. 1(a), the solid line shows the measured reflection spectra versus wavelength for a typical Au nanoparticle network on the PAM substrate with Au filling factor of 21%. It is interesting that although the Au volume fraction in the network is lower than the percolation threshold predicted by the Bruggman equation [9] for metal-insulator composites, the optical response of the sample shows the typical bulky metal-like characters. Its reflectance in the infrared region increases monotonically with wavelength. Moreover, the reflection spectrum exhibits only a reflection
dip instead of a scattering maximum near the LSPR anticipated for non-interacting nanoparticles. All the as-fabricated samples with various Au volume fractions \((0.18 \leq f \leq 0.68)\) show the same kind of reflection behavior with the dip position varying with \(f\). The dc electrical resistance measurement is consistent with such bulky metal-like behavior. Figure 1 (b) displays the resistance of the Au nanoparticle networks measured at \(300^\circ\text{K}\) using the four-point probe method. There was no apparent insulator-metal transition being observed in the whole range of the \(f\) values studied. The as-fabricated nanoparticle networks are conductive even at the low \(f\) values (<0.33). Individual nanoparticles separated by large distances normally display resonant peaks in the far-field scattering spectra arising from the well-known dielectric anomalies peculiar to the metal-dielectric composite. These single-particle modes split into various coupling modes for small cluster aggregates, originated from the anisotropy of the interaction field and sensitive to the aggregate topology. However, as shown in Fig. 1(a), no such resonance peaks were observed in the reflection spectrum from the visible to near-infrared region. Both the bulky metal-like behavior in the low \(f\) values and the non-single-particle-type reflectance suggest that the complex aggregate effects dominate the optical responses of the as-fabricated nanoparticle networks and that the characteristic features of single metal-dielectric nano-composite were smeared out. As a consequence, the traditional MG theory and EMT model become inappropriate in describing the optical responses of our samples.

With the effective cluster model proposed in Section III, the Au nanoparticle networks are regarded as a mixture of two phases, with Phase-I consisting of isolated non-interacting particles and Phase-II consisting of the aggregated clusters packed in a ring-like topology. The effective dielectric function of the nanoparticle networks was then described by Bruggeman’s EMT expression (Eq. (6) as a 2-phase composite.

Figure 2 displays the calculated transmission spectra for pure Phase-I (Fig. 2a), pure Phase-II (Fig. 2b) and a mixture of the two phases in our effective cluster model for nanoparticle networks of \(f = 21\%\), \(R = 15\text{nm}\) (solid line in Fig. 2c). As a comparison, the experimental transmission spectrum is also plotted in Fig. 2 (c) (open circles). For the non-interacting Au nanoparticles of 15nm in radius, the transmission shows a well-defined dip centered at about 520nm, originated from the excitation of LSPR on the Au particles. For the aggregated clusters in a closely packed ring topology, the transmission behaves similar to that of a medium with dielectric inclusions embedded in Au matrix and exhibits an enhanced transmission peak with respect to a bulky Au metal material. This extraordinary transmission is the signature of a nano-porous metallic medium. Figure 2(c) shows the calculated and observed transmission spectra for a mixture of two phases with the region fractions \(V_{\text{nap}}\) and \(V_{\text{clus}}\) evaluated from the SEM micrographs. As can be seen, the observed spectrum is very well reproduced by the calculation from our effective cluster model where the two chosen structural units were introduced in an experimentally determined proportion.
Fig. 2. (Color online) Optical transmission spectra of nanoparticle film with Au filling factor of 21% calculated for non-interacting Au spheres (a), Au clusters of particles arranged in a 12-membered ring geometry (b), and our cluster model (c). The calculation is based on the dielectric function of bulk Au from [26]. The experimental data measured with a Tungsten lamp are also plotted in (c) (open circles).

Figure 3 shows the experimental and calculated transmission spectra for samples with various Au filling factors. These 5 samples are grown on the PAM membranes with the average pore size of 100nm in diameter. The average radii of the Au nanoparticles in the 5 samples are 15nm, 18nm, 24nm, 28nm, and 32nm, respectively [11]. Using our effective cluster model, the calculated spectra are in good agreement with the experimental data in terms of both the peak positions and the band profiles for all the \( f \) values examined. The marginal deviations of the peak positions are caused understandably by the simplification in our model that contains only two phases of particular structures. The noticeable discrepancy between the calculated and the observed optical spectra is the magnitude of transmission. The calculated transmittances are about 20% larger than the measured ones in the spectral range of \( 300 \leq \lambda \leq 800 \) nm. It comes presumably from the under-estimated oscillator strength for the aggregated clusters and the higher order multiple scattering processes both of which were not included in our model.
Fig. 3. (Color online) Optical transmission spectra of a series of Au nanoparticle networks. The open blue circles are the experimental data (associated with the left Y axis) measured with a Tungsten lamp and the solid red curves are the calculated data using our effective cluster model. The theoretical curves are normalized with respect to the experimental values by multiplying a factor of 0.7 to 0.85. With the effective cluster model, the region fraction of Phase-I \( V_{\text{Phase-I}} \) in the above samples are calculated to be: (from top to bottom) 66%, 48%, 37%, 34%, and 32%, respectively.

In the nanoparticle networks described in this work, there is no propagating mode supported by the structure since the voids between the Au particles are smaller than half the wavelength of the transmitted light. Considering the effect of the ring aggregates, we assigned the transmission band around 500nm to the LSP–assisted evanescent tunneling which coupled the incoming light to LSP dipole excitation and produced evanescent waves tunneling through the voids. Both the wavelengths at which the enhanced transmission occur and the magnitude of the enhancement are determined by the corrugation geometry of the metal-dielectric interface. In Fig. 3, the enhancement factors, i.e. the ratio of transmission at the peak to those at the side, are more pronounced with larger Au volume fraction. Because the resonance energy is localized in the region of highest curvature or in the voids enclosed by the closely spaced nanoparticles, the higher enhancement is expected to occur with increased particle packing density or decreased void size. The peak position in the transmission spectra is determined by two factors, the LSPR of individual metal particles from Phase-I and the void resonance in the rings enclosed by the Au particles from Phase-II. With the increase of Au filling factor, the overall influence on the transmission peak position from the above two factors may compensate each other since the former resonance shifts the peak position to the
red as the particles size increases and the inter-particle distance decreases [7], while the latter shifts the peak position to blue when the void size decreases and film thickness increases [27–29]. The relative weights of the two factors for a given sample may be estimated semi-quantitatively from the region fractions of the two phases. According to the effective cluster model for our samples, the non-interacting particle mode from Phase-I would have a larger weight at small $f$ while the void mode (from the Phase-II) is expected to play a dominant role when $f > 32\%$. This was indeed what have been observed in the transmission spectra with different $f$ values. As shown in Fig. 3, the transmission peak first red-shifted with the increase of particle size and particle density at low $f$ values. Further increase of $f$ results in the formation of more aggregated clusters and a significant decrease of the voids size. As a consequence, the contribution of void resonance outweights that of the single particle modes and the transmission peak shift to the blue.

We thus suggest that the observed strong enhancement of the transmission comes from the contributions of energy tunneling through voids. Another independent evidence for the strongly coupled metal clusters in the as-fabricated nanoparticle networks is the observation of strong surface-enhanced Raman scattering (SERS) form a monolayer of non-resonant molecules, 4-mercaptobenzoic acid, self-assembled on the surface of the sample [11] upon excitation at 632.8nm. This observation is consistent with the notion that the inter-particle coupling plays a dominant role in the optical response of our samples [30, 31].

The effective conductivities of the nanoparticle networks are calculated as a function of the Au volume fraction using Eq. (11). The solid line in Fig. 4 shows the normalized conductivity calculated from the general Bruggeman’s equation without considering the aggregation effect. It predicted the well-known percolation threshold at $f = 1/3$. With our effective cluster model (the red dashed line), the percolation threshold in our sample is calculated to occur at $f = 0.18$, assuming that only the metal in the aggregated clusters phase (Phase-II) contributes to the percolation conductivity. It is in good agreement with the dc electrical resistance measurement, shown as the scattered dots.

![Fig. 4. (Color online) Normalized conductivity $\sigma/\sigma_0$ as a function of the Au filling factor. The green solid line is calculated from the Bruggeman’s equation in the general effective medium theory. The red dashed line is calculated from our effective cluster model (Eq. (10–11)). The blue scatters are the experimental data measured by the four-point probe method.](#)
V Conclusions

We studied the electrical and optical properties of Au nanoparticles in two-dimensional networks grown on the nano-porous alumina membranes. The dc electrical resistance measurement shows that the nanoparticle networks are conductive even at small metal volume fraction, suggesting that the percolation threshold in the as-fabricated samples is much lower than that predicted by the Bruggeman’s equation in the general effective medium theory. Due to the aggregation effect, the optical transmission spectra exhibited an enhanced transmission band around 500nm arising from the energy tunneling through LSP dipole excitation. An effective cluster model was proposed to obtain the effective dielectric function of the nanoparticle networks. The model treats the networks as a two-component mixture composed of non-interacting particles (Phase-I) and clusters in a ring-like arrangement (Phase-II). Thus, the effects of particle size, shape, metal volume fraction, and the particle-particle interaction are all included in the model. The calculated transmission spectra from our model were in good agreement with the experimental data. With the same effective cluster model, the percolation threshold of the as fabricated nanoparticle networks was predicted to occur at $f = 0.18$, which agrees with the resistivity measurement.

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Author contributions: YSL and XYL conceived the idea of the sample fabrication, developed and optimized the sample fabrication conditions, fabricated all the samples in this study, and conducted the SEM and SERS study. HMS and KSW conducted the optical and conductivity measurements and devised the effective cluster model. HMS and KSW drafted the paper. All authors participated in the revision of the paper to its final version.