Plasmon Excitation of Atomic Clusters and Their Assembly by Electrons and Photons

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Abstract The structures and properties of the atomic clusters are neither like those of the corresponding atoms and molecules nor bulk solid. It is quite natural that the materials composed of those clusters exhibit some new properties. Moreover, cluster assemblies have shown even large variety of optical, electric and magnetic responses due to localized coupling between the clusters, leading to the enhancement of certain unusual properties. In this review we present some examples such as the enhanced Raman scattering of ordered lattice of metal clusters, multi-phase plasmon excitation of silver cluster dimer and cluster chains by electrons and photons. We demonstrate that the novel properties of these cluster assemblies could have potential applications in manufacturing new-type nanomaterials and quantum devices, such as plasmonics and nano-optical devices.

1. Introduction
Atomic clusters (clusters for abbreviation) can be considered to special kinds of molecules and/or super-atoms, which are composed of several to tens of thousands atoms or molecules and have many extraordinary structures and properties related to their size and dimensions. Its research spans many subjects in physics, chemistry, astronomy, etc. particularly new growing point of material science.[1]

Clusters research began from 1970s. In 1976, France held the first meeting of International Symposium of small particles and inorganic clusters (ISSPIC), which already held 16 meetings by 2012. In 1980s, the research had breakthrough progress. The representative works are, in 1984, W. D. Knight and his collaborators in Berkeley observed sodium clusters have characteristic of magic numbers resembling electronic shell structures;[2] H. W. Kroto in Britain and R. E. Smalley in America and their coworkers found C_{60} when using plused laser evaporation molecular beam system to study carbon clusters [3], and won Nobel Prize in Chemistry in 1996. Afterwards, the novel
properties of electromagnetic, optics and the characteristic of chemistry reaction for a variety of different clusters have been found in succession. This have caught common concern of researchers in condensed matter physics, atomic and molecular physics, material science, chemistry and even nuclear physics. Entering the 21st century, clusters science has been developing in depth and breadth, crossing and merging together with other subjects like mesoscopic physics, material science and technology, and other new emerging science. Especially, as structural units, the manufacturing, observation, controlling, decoration and assembling of clusters would provide physics basis and technical support for people to produce nanostructures and nanodevices with quantum properties from zero dimension to three dimensions. This pushes forward current high-tech development of nanoscience and nanotechnology. In this talk we present our recent work, focusing on localized coupling effect of nanostructures formed by clusters, such as enhanced Raman scattering of ordered lattice of metal clusters, plasmon excitation of silver clusters by electrons and photons.

2. **Enhanced Raman Scattering of Ordered Cluster Arrays**

Localized surface plasmons (LSPs) are collective oscillations of free electron localized on metal nanoparticles (nanoclusters) or the surface of nanostructures. The frequency of surface plasmon absorption peak is the characteristic properties of the material especially for Au, Ag, Pd etc. The resonance frequency of surface plasmon mainly depends on: (1) the size and shape of nanoclusters[4-6], (2) the dielectric function of the substrate and the ambient environment[7-9], and (3) the space between clusters. Localized surface plasmons (LSPs), generates an enhanced local electric magnetic field on the surface of metal nanostructures, resulting in the surface enhanced Raman scattering (SERS) effect. At sametime SERS uses the greatly enhanced localized field of metal nanostructures to magnify the Raman scattering signal of adsorbed molecules. Because the SERS enhancement factor is very sensitive to the surface structure, it is very important to rationally design reproducible substrates of SERS. Densely packed ordered metal nanoparticle array as a kind of SERS substrate can not only contribute to the understanding of SERS mechanism through the combination with theoretical simulation but also acquire bigger field enhancement factor through the interaction of near field coupling. In addition the densely packed ordered lattice has spatial uniformity in high field region, so we can acquire stable, well-distributed signal of SERS.

We use densely packed silver nanoparticle lattice fabricated by cluster beam deposition system as SERS substrates respectively on the surface of quartz glass sheet and the surface of ribbon pattern SBS segmented copolymer orderly pattern template. We utilize self-designed and manufactured cluster beam deposition apparatus [10] and deposit Ag nanoparticles on amorphous carbon film and SBS orderly pattern template, respectively, and control the Ag nanocluster coverage rate of two samples at about 15%, as shown in Figure 1.
Figure 1(a) is random densely packed Ag nanoclusters, the particles are randomly distributed on the surface of the substrate. The average diameter of the particle is about 10.0nm, the standard deviation of the size distribution is about 3.0nm. But the Ag nanocluster chain array is different (as shown in Figure 1(b)), the space between chain is the same, about 38nm, corresponding to PS phase domain period of SBS segmented copolymer film. The average diameter of particles in Ag nanoparticle chain array is 10.5nm with standard deviation of statistical distribution is 2.0nm. The most probable space between clusters inside a chain is about 6.5nm. In lattice, the density of Ag nanoclusters reaches up to $2 \times 10^3$ per square micrometer.

We measure extinction spectra to study the local surface plasmon resonance (LSPR) of metal nanoclusters. The peaks of extinction spectra are corresponding to LSPR peak of metal nanoclusters. Figure 2 is the ultraviolet-visible light extinction spectra of Ag nanocluster-assembled film. The extinction spectra of Ag nanocluster chain lattice on the surface of orderly SBS copolymer pattern is obviously different from the extinction spectra of randomly distributed Ag nanocluster film on quartz where the peak of extinction spectra is at 385nm, while the former peak is sharp and narrow and located at 424nm, showing a red-shift of about 39nm. [11]

According to Mie theory and the simulation of discrete dipole approximation (DDA) [6] it is pointed out that the shifts of the LSPR absorption peak is very small for metal nanoparticles with the sizes below 30nm. Therefore, in the present case of densely packed Ag nanoparticle lattice with ~10nm particle diameter, no matter ordered or disordered, it will not lead to apparent red shift of LSPR peak as long as the particles have not aggregated. On the other hand, we haven’t found distinctly difference by comparing the SPR peak of disordered Ag nanoclusters embedded in SBS film.
with that of Ag nanoclusters deposited on quartz glass films, although the LSPR peak position of Ag nanoparticles is related to the ambient dielectric environment. This means the dielectric environment of SBS copolymer film and quartz glass film have little impact on the SPR peak of Ag nanoclusters. In fact, the refractive index of SBS copolymer film and quartz glass film are basically the same of ~1.5.

![Figure 2](image)

**Figure 2** The extinction spectrum of Ag nanocluster assembling film. (A) Random distributed Ag nanoclusters deposited on quartz glass film; (B) Ag nanocluster chain lattice on SBS copolymer film; (C) Random distributed Ag nanoclusters embedded in SBS film. [11]

It is known that the plasmon resonance peak of noble metal nanocluster will be red-shifted along with the decreasing of inter particle spacing. [12] We hold that the red shift of SPR peak between the ordered Ag nanoclusters lattice on SBS surface and the disorder distribution of Ag nanoparticles is caused by the difference of near field couplings between the former and latter.

In order to get quantitative results we put approximately 10 µL BPE methanol solution of $2 \times 10^{-6}$ M concentration on the surface of Ag nanoparticle assembled film, and make the solution quickly evaporated, and then BPE molecules cover the film surface. Thus we obtain the molecule surface density of about $2 \times 10^{-13}$ mol/mm$^2$, and about $1.2 \times 10^4$ BPE molecules in the laser spot, with the coverage rate of 4%, far below the thickness of one molecule monolayer. The curves A and B in Figure 3 give the SERS spectrum of BPE molecule absorbed on the surface of one dimensional Ag nanocluster chain lattice and the surface of disordered densely Ag nanocluster lattice. Spectra A, B have distinct Raman peaks at 1010, 1200, 1610, 1640 cm$^{-1}$. But the curve C is the Raman spectrum of the same concentration BPE solution dropped on the quartz glass film, and any Raman peaks of BPE molecule is hardly seen. It is indicated that the cross section of Raman scattering will be greatly enhanced when BPE molecules are attached on the surface of Ag nanoclusters.
Figure 3 Raman spectra of several kinds of BPE molecules on the surface: (A) BPE molecules absorbed on Ag nanocluster lattice on SBS template surface; (B) BPE molecules on disorderly Ag nanocluster lattice on the surface of quartz glass film; (C) BPE molecules on the surface of glass film. We use BPE methanol solution of concentration of $2 \times 10^{-6}$ M, the intensity of laser is 100 $\mu$W for (A, B, C), and (D) the Raman spectrum of BPE methanol solution of $4 \times 10^{-2}$ M and the laser intensity of 1mW where the spectral line is magnified by 150 times. Curve D is ordinary Raman spectrum of BPE molecules, used for calibrating. [11]

Figure 3 shows that the SERS intensity of BPE molecules attached on the Ag nanocluster lattice is stronger than that of BPE molecules attached on the disordered Ag nanocluster surface. The average SERS enhanced factor of ordered Ag nanocluster lattice is about $2.6 \times 10^6$, 5 times greater than disordered Ag nanoclusters. The reason may be as follows: (1) The ordered Ag nanocluster array on SBS template have high density of hot junctions, which enhance SERS factor; (2) The red shift of SPR peak of Ag nanocluster lattice makes it more closer to the laser wavelength, thus it is easier to achieve the enhancement of localized surface plasmon.

Moreover, the SERS intensity of the BPE molecules attached on disorderly distributed Ag nanocluster assembling film varies a lot with different locations on the surface of the substrate, where the statistical standard deviation is bigger than 35%. But the SERS intensity of BPE molecules attached on the surface of one dimensional Ag nanocluster chain lattice basement is quite homogeneous at different position, where the statistical standard deviation is less than 18%. This is because the hot junctions of the ordered nanocluster lattice have relatively uniform space distribution. Hence, the SERS measurements based on the ordered nanocluster lattice substrate are more reproducible and consistency.

We have further investigated the influence of orderly and disorderly Ag nanocluster assembling films by means of different molecular concentration measurements of SERS. We dissolve BPE
molecules in methanol to form a series of dilute solution with the concentrations of $2 \times 10^{-4} \text{M}$, $7 \times 10^{-5} \text{M}$, $2 \times 10^{-5} \text{M}$, $8 \times 10^{-6} \text{M}$, $3 \times 10^{-6} \text{M}$, $2 \times 10^{-6} \text{M}$, $1 \times 10^{-6} \text{M}$, $5 \times 10^{-7} \text{M}$ and $1 \times 10^{-7} \text{M}$ respectively. Then we drop $10 \mu\text{L}$ BPE methanol solution on $1 \text{ cm}^2$ substrate and let it vapor to dry quickly during SERS measurement. In such way, we can get a series of BPE molecule surface density, from $2 \times 10^{-11} \text{ mol/mm}^2$ to $1 \times 10^{-14} \text{ mol/mm}^2$, corresponding to the above-mentioned solution density respectively. We can then get a series of typical SERS spectra from BPE molecule attached on the surface of orderly Ag nanocluster chain lattice, as shown in Figure 4.

![Figure 4](image)

**Figure 4 (A)** Representative SERS spectra of different concentration of BPE molecules attached on the surface of Ag nanocluster chain lattice. The BPE molecule surface density corresponds to different spectrum from top to bottom are: $2 \times 10^{-11} \text{ mol/mm}^2$, $7 \times 10^{-12} \text{ mol/mm}^2$, $2 \times 10^{-12} \text{ mol/mm}^2$, $8 \times 10^{-13} \text{ mol/mm}^2$, $3 \times 10^{-13} \text{ mol/mm}^2$, $2 \times 10^{-13} \text{ mol/mm}^2$, $1 \times 10^{-13} \text{ mol/mm}^2$, $5 \times 10^{-14} \text{ mol/mm}^2$, and $1 \times 10^{-14} \text{ mol/mm}^2$, respectively. For clarity, adjacent spectra are displaced vertically. (B) The relationship between SERS intensity and BPE molecule surface density.

For most kinds of concentration of BPE molecule, we can clearly observe BPE main Raman peak from SERS spectrum. At the lowest concentration of BPE molecule ($1 \times 10^{-7} \text{M}$, the corresponding BPE molecule surface density is $1 \times 10^{-14} \text{ mol/mm}^2$), the signal peak nearly submerges into the background noise. For this concentration, it contains about $6 \times 10^2$ molecules in the detection zone of confocal Raman spectrometer (diameter approximately 350nm). Suppose the effective area of one BPE molecule is $30 \text{ Å}^2$ [13], we estimate the area coverage rate is only 0.2 % in this concentration of BPE molecule. The repeatability of SERS signal is very well when the concentration of BPE molecule is higher. We evaluate the enhanced Raman scattering performance of Ag nanocluster chain lattice by selecting 1610 and 1640 cm$^{-1}$ Raman peak of BPE molecules. Figure 4B shows average intensity areas of 1610 and 1640 cm$^{-1}$ Raman spectrum peaks with different concentrations of BPE molecules, it is obtained by statistical average the sum of the measured peak area of 20 different substrate locations. We can then identify that the relation between SERS intensity and BPE molecule surface density divides two regions. When the BPE molecule surface density is high, i.e., from $3 \times 10^{-13} \text{ mol/mm}^2$ to $2 \times 10^{-11} \text{ mol/mm}^2$, SERS intensity basically remains the same. On the other hand, when the BPE molecule surface density is reduced to $3 \times 10^{-13} \text{ mol/mm}^2$, the SERS intensity quickly declines along with deceasing BPE molecule surface density, and shows the linear relationship in log-log coordinate.
The relation can be fitted by the following formula:

$$\log(I_{SERS}) = 1.25 \log C_m + 11.53$$  

(3.2)

$I_{SERS}$ is the signal intensity of SERS, $C_m$ is the molecule density.

3. **Plasmon excitation and coupling effect among Ag clusters**

Surface Plasmon Resonance (SPR) takes place when the frequency of the incident light coincide with the frequency of valence electrons collective oscillations on noble metal nanoparticles. There are some difficulties by using optical probe to study the fine feature of plasmon coupling between nanoparticles, primarily because: (1) In the optical wavelength, the size and spacing of nanoparticles must be uniform, thus, the requirement of making a sample is very strict; (2) Many nanoparticles stay in the region of optical wavelength when the resonance happens, leading to some nonphysical influence on the coupling between the particles, and making more difficulty in data analysis. In 2007, Nalayah and his collaborators in France use Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS) to study the surface plasmon image of single Ag nanotriangle. [14]

![Figure 5](image_url)

**Figure 5** STEM-EELS of the plasmon characteristic of single Ag nanocluster: A) EELS spectrum image of single Ag nanocluster, (energy window: 3.3-3.6eV, the inset is the image); B) the energy curves corresponding to two points in A), where the upper curve corresponds to the marginal point whereas the lower curve corresponds to the central point (Black arrow points to the spherical mode of 3.4eV and the bulk phase mode of 3.8eV); C) Peak position changes with the diameter of cluster.
Similar to optical probe, the electric field induced by electron beam on the transmission location contains many different frequencies[15], this kind of electric field couples with the intrinsic plasmon oscillation mode of nanoparticles, and generates plasmon excitation response spectrum, having certain correspondence with optical absorption spectrum.[16,17] We use STEM-EELS to study the plasmon resonance feature of single Ag cluster, cluster pair in the cluster beam deposition.

![Figure 6](image)

**Figure 6** The plasmon coupling characteristic of two body system composed of two clusters. (A) EELS spectrum obtained from the locations shown in (B), STEM of two clusters. (C), (D), (E) are EELS spectra which have energy window 2.6-2.9eV, 3.2-3.5eV, 3.5-3.8eV respectively. The brightest point means the EELS intensity of this energy window is the greatest.

Figure 5A shows EELS spectrum image of single Ag nanocluster (inset is the STEM image of this cluster), EELS spectrum image is the result of intensity integral to energy window of EEL spectrum of image points. The brightness of a point represents the probability of plasmon excitation at the electron beam sampling point. The maximum intensity lies in the edge of the cluster, and its thickness is only 2nm, which means the cluster surface plasmon is local. [18] Figure 5B presents the EELS spectra of middle and edge positions of the cluster, the maximum position of edge spectrum lies at 3.4eV, it is the spherical mode of the Ag nanoparticle[14,17,19,20], corresponding to the peak at 365nm in optical absorption spectrum. When the electron beam is located at the center of the cluster, there is another peak of 3.8eV, belonging to the bulk phase excitation mode of Ag clusters, caused by interband transition.[17,21] Figure 5C shows the energy peak of spherical mode changes with the cluster size, showing distinct red shift. When the diameter of the cluster is bigger than 100nm, the plasmon energy is less than 3.3eV, but in the region of 10-30nm, plasmon energy does not change much, it illustrates that there is no decay in plasmon energy in this size range. [22]

For a two body system composed of two clusters, the diameters of the two clusters are 18nm and 19nm, respectively, and the space between the two clusters is 2nm. They constitute a framework of an axis of symmetry and a central point. [23] The three different locations shown in Figure 6B are parallel to the edge of center axis (blue point), perpendicular to the edge of the axis (black point), and the
central point (red point) respectively. Figure 6A shows the EELS spectra of these locations. Comparing 5B with 6A, black line shows a new peak of low energy between 2.7eV-2.9eV; central peak (red line) has a red shift to 3.6eV. Figure 6C, D, E are EELS spectra which have energy window of 2.6-2.9, 3.2-3.5 and 3.5-3.8eV respectively.

Figure 7 The plasmon coupling mode of clusters changes with the spacings among clusters. (A) The excitation spectra simulated by DDA according to two spherical modes. The dotted line gives the in-phase mode changes with the spacing diameter ratio, the incident light is perpendicular to the central axis; (B) The experiment result of in-phase mode (black) and anti-phase (blue) mode, the triangle line in the middle is the calculation result of in-phase mode, inset pictures are electric resonance of two mode.

The plasmon excitation is formed by coupling between local electric field of incident electron beam and the electric field of nanostructures. [22,24,25] The local electric field of the incident electron beam can be decomposed into three components: central axis direction, incident electron beam direction, and independent direction. They have different impacts on the plasmon excitation of two body cluster systems. The axial component (blue point) has no coupling with the system of two clusters, and its plasmon excitation response behavior likes a single cluster. The excitation component of red point symmetrically repels the dipole of two spherical clusters, generating anti-phase mode. The excitation of black point generates in-phase mode, i.e., similar to a symmetric dipole. Figure 6A shows the in-phase mode of the dipole is at 2.7eV, the anti-phase mode is at 3.6eV, in consistent with theory. [26]

We can manipulate the clusters plasmon excitation modes by adjusting the spacing among particles. Figure 7 gives the result of simulated calculation and experimental measurement. We adopt the ratio of spacing between clusters and the diameter to be a parameter. When the spacing between clusters and the cluster diameter are the same (the ratio is 1), there is no frequency shift. But when the ratio is 0.3, there is frequency shift: the in-phase mode will have red shift along with the spacing diameter ratio gets smaller; the frequency is shifted to 2.7eV when the spacing is 1.5nm; but the anti-phase mode will have blue shift when the ratio gets smaller, which cannot be observed in optical observation[20]. In-phase coupling mode is the two particle resonance mode, and exists in many particle systems, and
can be used as an extension mode of energy transport. The plasmon in-phase coupling mode in this experiment is dipole mode, so it is equivalent to the coupling mode motivated by incident light. Figure 7A is extinction spectra using DDA model to calculate the interaction between incident light beam and two particle system. [26,27,28] When the spacing diameter ratio is 1, similar to one particle spectrum, the peak is at 3.43eV. When the spacing/diameter ratio gets smaller, the low energy mode gradually appears, and an energy mode less than 3eV arises when the ratio reaches 0.05, as well as a high order mode appears at 3.2eV and 3.4eV, similar to the black curve in Figure 6A. The red shift of in-phase mode gets bigger along with the smaller spacing/diameter ratio. The black curve in Figure 7B describes this red-shift process. They fit very well within the margin of error. This proves that the in-phase coupling mode with a characteristic of red shift is the longitudinal transmission mode which can be used in optical transmission. [29,30] Here we note that an important progress has taken on STEM-EELS imaging [31], where plasmon excitation is obtained using a similar route. One can see the energy resolution is comparable to this work[18], but the plasmon peak of very small clusters reveal an interesting quantum oscillation.

In conclusion, in cluster assembling systems, we have observed electromagnetic field will change greatly when they response to light and/or electron excitation due to the coupling between clusters. For example, the enhancement of Raman scattering in the cluster array, the multi-phase plasmon excitation of Ag cluster pair and chains, etc. People can use these characteristics to manufacture a lot of new materials and quantum devices.

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