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# Plasmon coupling between silver nanoparticles: Transition from the classical to the quantum regime

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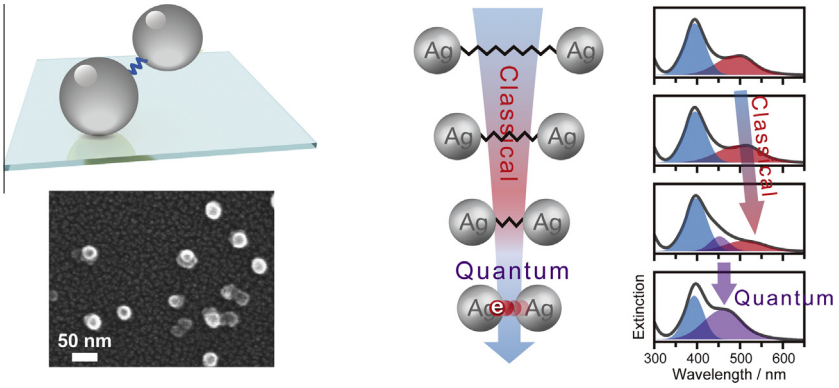
## GRAPHICAL ABSTRACT

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## ABSTRACT

We explore plasmon coupling between silver nanoparticles (AgNPs) as two AgNPs approach each other within a subnanometer distance. We prepare AgNP dimers with two 21-nm AgNPs separated by alkanedithiol linkers in high yield. Changing the length of the alkanedithiol linkers enables us to control the interparticle distance down to the subnanometer level on the molecular scale. We observe that the longitudinal plasmon coupling band, which is sensitive to the interaction between AgNPs, gradually redshifts as the interparticle distance decreases. This observation is fully consistent with the classical electromagnetic model. The redshift of the plasmon coupling, however, undergoes a drastic change when the interparticle distance reaches ~1 nm. The longitudinal plasmon coupling band vanishes and a new intense band appears at a shorter wavelength. This band redshifts as the nanogap further narrows, but crosses over to a blueshift at ~0.7 nm. A comparison of our observation with finite-difference time-domain simulations reveals that this band arises from quantum effects. Controlled assembly of AgNP dimers in combination with simulations allows us to observe the transition of the plasmon coupling from the classical to the quantum regime at the ensemble level.



## 1. Introduction

Noble metal nanoparticles exhibit unique optical properties, represented by surface plasmon resonance (SPR) [1–3]. Resonant excitation of the collective oscillation of the conduction band electrons in the nanoparticles gives rise to enormous absorption or scattering of the light far greater than their geometric cross sections [4]. It also generates a strong electric field localized around the nanoparticles [5,6].

Assembly of nanoparticles further strengthens those properties of individual nanoparticles. Plasmon coupling between nanoparti-

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cles in close proximity creates new resonances, of which wavelengths are tunable depending on the extent of the interparticle interactions [7,8]. The localized electric fields are also greatly enhanced at the gaps formed by the nanoparticles constituting the assembly [9,10]. Therefore, controlled assembly of nanoparticles enables one to tune the optical resonance wavelengths at will and focus electromagnetic fields to a desired spot with nanometer precision.

Dimers are the archetype of an assembly. The simple structure reduces the number of variables governing the plasmonic properties. The plasmon coupling is solely controlled by the change in the interparticle distance [8,11–13]. As the interparticle distance decreases, stronger plasmon coupling shifts the resonance band to longer wavelengths. This behavior is accounted for by the classical electromagnetic model [6,7]. However, the classical model breaks down as the gap distance narrows within 1 nm. Quantum effects, such as electron tunneling, or nonlocality of dielectric functions play a major role in the coupling in this regime [14–18].

Despite the significant progress on the theory side, experimental measurement of the quantum effect is very challenging [12,19–24]. Two major obstacles are the difficulties in preparing the dimers with controllable interparticle distances down to the subnanometer range and measuring the subnanometer gap distances with accuracy. Even state-of-the-art high resolution transmission electron microscopy (TEM) does not offer sufficiently high resolution and contrast for the subnanometer gaps defined by the high curvature boundaries of spherical nanoparticles [25]. Single-particle spectroscopy enables one to circumvent the first problem. Many studies on the plasmonic interaction between Au or Ag nanoparticles (AuNPs or AgNPs) have been performed at the single dimer level [12,19–21,24]. Electron energy loss spectra (EELS) or dark-field scattering spectra for a single dimer provided information on the plasmonic property of the given dimer. However, for the exact correlation of the plasmon coupling with gap distances, the optical response of a dimer must be recorded for tens of dimers and then averaged because of the distribution in the gap distances present in the ensemble of dimers and the uncertainty in the measurements of the interparticle distance. In this respect, if high-yield preparation of dimers is feasible, ensemble averaging (for more than $\sim 10^{10}$ particles) would lead to a better result [22]. In this article, we report the preparation of high-purity AgNP dimers with selected interparticle distances ranging from 1.6 to 0.7 nm. This allows us to measure the optical response of the AgNP dimers as a function of the interparticle distance at the ensemble level. Comparison of the experimental results with finite-difference time-domain (FDTD) simulations reveals that the plasmon coupling between AgNPs transitions from the classical regime to the quantum regime in the subnanometer gap distance.

In this study, we focus on the dimers consisting of two equally sized AgNPs (diameter = 21 nm). AgNPs have some unique characteristics distinguished from AuNPs although both represent the noble metal nanoparticles that support strong SPR. The SPR of AuNPs is limited to the wavelength region longer than ~520 nm because the interband transition spans from 500 nm to the UV [26]. In contrast, the optical response of AgNPs begins at ~400 nm, providing the opportunity to explore the entire visible wavelength region by exploiting the plasmon coupling. In addition, AgNPs have a higher quality factor, meaning stronger plasmon resonance, than do AuNPs across the entire range of visible wavelengths [27]. Ag is also less expensive than Au. Therefore, AgNPs are practically a better material for plasmonic enhancement and its applications such as surface-enhanced Raman scattering (SERS) [28–30], surface-enhanced fluorescence (SEF) [31], and plasmonic photocatalytic activity [32]. It is also intriguing to study how the lower work function of Ag compared to Au will influence the quantum effect when the nanoparticles are in close proximity. Therefore, studies on the plasmon coupling in AgNP dimers not only complete the studies for the family of noble metal dimers, but also provide additional values unique to the AgNP dimers.

## 2. Experimental section

### 2.1. Materials

The following chemicals and materials were used without further purification to assemble AgNPs into dimers: 1,2-ehanedithiol (TCI, >99%), 1,3-propanedithiol (TCI, >95%), 1,4-butanedithiol (TCI, >95%), 1,5-haxanedithiol (TCI, >95%), 1,6-haxanedithiol (TCI, >95%), 1,8-octanedithiol (TCI, ⩾97%), 1,10-decanedithiol (TCI, >98%), 11-mercaptoundecanoic acid (MUA; Aldrich, 95%), methanol (Duksan Chemical, ⩾99.8%), ethanol (Duksan Chemical, ⩾99.9%), water (J. T. Baker, HPLC grade), glass slides (Marienfeld, Germany), RBS detergent solution (Fluka, 35 concentrate), (3-aminopropyl)trimethoxysilane (APTMS; Aldrich, 97%), NaOH (Duksan Chemical, 93%), HCl (Duksan Chemical, 37%). Citrate-capped AgNPs were purchased from Ted Pella, Inc. (Redding, CA, U.S.A.). Transmission electron microscopy (TEM, JEOL JEM-2100F) measurements revealed that the AgNPs have a diameter of 20.5 ± 3.2 nm (Fig. S1, Supporting Information).

### 2.2. Assembly of AgNP dimers

We prepared AgNP dimers on a glass slide using the masked desilanization method that we published previously [22]. Fig. 1 illustrates the assembly procedure. **Preparation of glass slides.** We cut a glass slide (Marienfeld, Germany) to 25 mm × 12 mm. The glass slide was cleaned by immersing in a boiling mixture (1:1 v/v) of RBS detergent solution and deionized water at 100 °C for 5 min. After repeated washing and sonication (5 min) in water, the glass slide was immersed in a methanol and HCl solution (1:1, v/v) for 30 min to protonate the silanol groups on its surface. The glass slide was then washed and dried in an oven at 100 °C for 2 h. **Step 1. Amine-coating of glass slides.** We incubated the glass slide in an APTMS solution (1% v/v, 5 mL) in ethanol for 30 min, which results in amine coating of the glass surface through the silanization reaction. The residual APTMS on the glass surfaces after the reaction must be thoroughly removed by repeated washing, rinsing, and sonication (5 min) with ethanol. Otherwise, it induces the aggregation of the AgNPs in the ensuing step. The amine-coated glass slide was dried in an oven at 120 °C for 3 h. **Step 2. Adsorption of AgNPs on the glass slide.** Citrate-capped AgNPs (20.5 ± 3.2 nm) were anchored to the amine-functionalized glass slide *via* electrostatic interactions. To ensure that the amines on the glass slide were protonated, the AgNP solution (150 pM, 5 mL) was adjusted to a pH of ~4.0 by adding 10 μL of an HCl solution (2% v/v). The glass slide was then immersed in the AgNP solution for 3 h. Unreacted AgNPs were removed by washing the glass slide with water. The adsorbed AgNPs in this step are referred to as "the first AgNPs" to distinguish from the AgNPs that will be added later for dimer formation. **Step 3. Masked desilanization.** The amine-coating on the glass slide was removed by the reaction with NaOH, except for the area where AgNPs adsorbed ("masked desilanization"). The desilanization reaction was induced by immersing the AgNP-anchored glass slide in a NaOH solution (1 mM, 5 mL) for 5 h. **Step 4. Thiol-functionalization of the first AgNPs.** The adsorbed AgNPs were surface-functionalized with thiol. Immersing the AgNP-anchored glass slide in an ethanol solution of alkanedithiol [$SH(CH_2)_nSH$ with $n$ = 2, 3, 4, 5, 6, 8, and 10, abbreviated as $C_n$ hereafter; 1 mM, 5 mL] for 1 h formed a dithiol self-assembled monolayer (SAM) on the surface of the first AgNPs [33]. Extending the reaction time to