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Versatile Solid Phase Synthesis of Gold Nanoparticle Dimers Using an Asymmetric Functionalization Approach

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Metal nanoparticles have received great attention due to their unique optical properties[1] and wide range of applicability.[2] In this context, controlling the particle−particle interaction is a major challenge to generate programmable assembly of nanoparticles,[3] which shows potential usefulness in device fabrication[4] and detection systems.[5] Several methods have been developed to prepare gold nanoparticle assemblies. For example, polymer single crystals,[6] organic bridged ligands,[7] DNA,[8] and solid phase approaches[9] have been used to fabricate gold nanoparticle dimer, trimer, or tetramer assemblies. Considering all of these architectures, dimers are of special interest because of their application as substrates in surface-enhanced Raman spectroscopy (SERS).[10] Theoretical calculations have shown that nanoparticle dimers produce strong electromagnetic field enhancements which contribute efficiently to the signal enhancement in SERS sensing.[11] Among the four listed synthetic methods, DNA-based assembly and solid phase approaches generate dimers with the highest reported yield. However, the DNA-based methods require electrophoretic separation to remove side products to achieve a high yield. On the other hand, the solid phase approaches have been limited to very small particles (<5 nm) and dimers consisting of nanoparticles with similar sizes.

In this communication, we report a more versatile solid phase synthesis of gold nanoparticle dimers using commercially available organic reagents through an asymmetric functionalization pathway. The method may be used to synthesize dimers for a wide size range of gold nanoparticles. In addition, we demonstrate the synthesis of dimers consisting of two particles with different sizes produced in high yield. The dimer yield varies from ∼30 to ∼65%, depending on the nanoparticle sizes. The dimers demonstrate remarkable stability in ethanol without further processing.

Gold nanoparticles (AuNPs) with different diameters were synthesized using a published procedure.[12] UV−visible absorption spectroscopy was used to characterize the surface plasmon resonance (SPR) properties of the nanoparticles both in solution and immobilized on a glass substrate, as shown in Figure 1A. The freshly prepared aqueous dispersion of 41 nm diameter gold nanoparticles produced a characteristic plasmon resonance peak (λ_{max}) at 528 nm. Generation of dimers from these nanoparticles was achieved according to Scheme 1 as follows: (1) The citrate-stabilized 41 nm diameter nanoparticles were immobilized on a silanized glass surface, and a blue shift of the resonance peak (λ_{max} of 513 nm) was observed, similar to the shift for surface-immobilized 39 nm diameter gold colloids reported in the literature.[13] (2) The nanoparticles on the silane functionalized glass surface were then reacted with 1 mM 11-mercapto-1-undecanol (MUOH) in ethanol for 2 h, resulting in the formation of a self-assembled monolayer (SAM) of thiol molecules on the outer surface of the closely packed nanoparticles. A 7 nm red shift of the SPR peak was detected (λ_{max} of 520 nm) which was likely due to a change of refractive index caused by thiol adsorption on the nanoparticle surfaces.[14] In order to remove the particles from the substrate, the MUOH functionalized nanoparticles were sonicated in 5 mL of ethanol containing 50 μL of 16-mercaptohexadecanoic acid (MHA) for 5 min to generate component **1** (λ_{max} of 532 nm) of Scheme 1. Due to the inaccessibility of MUOH to the region of the nanoparticles adsorbed on the substrate, the MHA molecules are expected to be asymmetrically bound only to the surface area of the AuNPs which were attached to the silane layer. A similar protocol was followed to functionalize the AuNPs with mercaptoethylamine (MEA), yielding component **2** (λ_{max} of 533 nm). (3) Finally, the MHA functionalized AuNPs **1** were then reacted with 100 μL of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) and 100 μL of 1-pentafluorophenol (PFP) for 2 h followed by the addition of MEA functionalized gold nanoparticles **2**, as shown in Scheme 1.

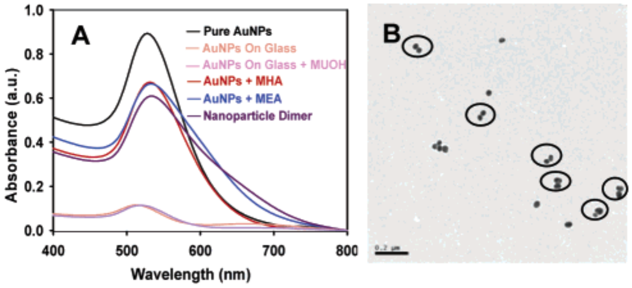
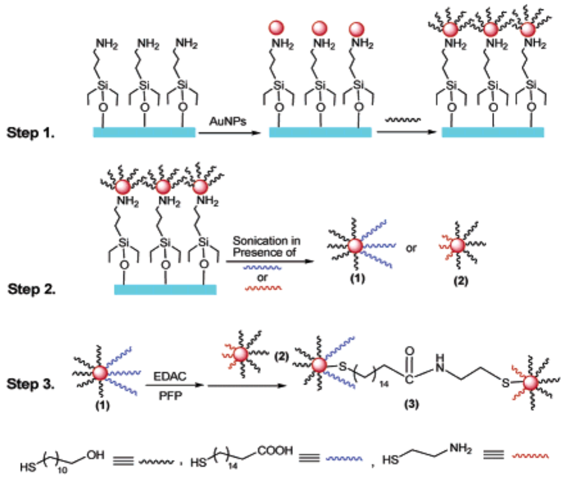


Figure 1. UV−visible absorption spectra (A) and TEM image (B) of gold nanoparticle dimers synthesized via coupling of 41 nm diameter particles. Scale bar is 200 nm.

Scheme 1. Synthesis of Gold Nanoparticle Dimers



The reaction mixture was stirred at room temperature for 4 h to produce a new component **3**, which had an SPR maximum at 533 nm. According to Mie theory[15] for gold nanoparticle dimers, when the distance between two nanoparticles becomes smaller than the sum of their radii, the surface plasmon resonance band displays a red shift, broadens, and decreases in intensity. Component **3** showed

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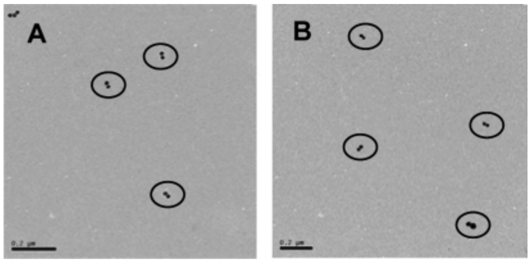

Figure 2. TEM image of gold nanoparticle dimers synthesized via coupling of 16−16 nm (A) and 30−30 nm (B) particles. Scale bar is 200 nm.

a decrease in absorbance at 533 nm and noticeable broadening of the peak, indicating the formation of nanoparticle dimers. The decrease in absorbance may also be due to concentration differences which were not accounted for in the spectrum.

Components **1**, **2**, and **3** from Scheme 1 were separately analyzed by transmission electron microscopy (TEM). The TEM analysis showed that MHA **1** and MEA **2** functionalized AuNPs produced individual nanoparticles with no traces of particle agglomeration (see Supporting Information). TEM analysis of component **3** confirmed the formation of gold nanoparticle dimers with ∼46% yield. The yield for each batch of dimers was found by counting at least 100 particles from ∼20−25 TEM images of the same sample. The dimer yield is defined as the percentage of dimers observed in the TEM images compared to the total number of structures where single particles, dimers, trimers, and other clusters were counted as unique structures. Figure 1B shows a TEM image of dimers consisting of two ∼41 nm diameter AuNPs. The formation of dimers is rationalized by our hypothesis that nanoparticle dimers would be formed when partially amine functionalized AuNPs were reacted with AuNPs asymmetrically functionalized with carboxylic acid groups in the presence of coupling reagents. To validate the hypothesis, we have performed two control experiments. In the first experiment, when components **1** and **2** were mixed together without EDAC and PFP, the TEM analysis showed the presence of individual spherical gold nanoparticles and no dimers. In a second experiment, the nanoparticles were functionalized with a 50:50 mixture of MUOH and MHA and reacted with component **2** in the presence of EDAC and PFP. After 4 h, the reaction mixture was analyzed by UV−visible spectroscopy and produced a broad maximum (λ_{max} of 550−630 nm), which was red-shifted relative to the dimer sample peak. TEM analysis confirmed that the solution did not contain nanoparticle dimers. Instead, agglomerated particles with random orientations were observed (see Supporting Information).

The syntheses of other homodimers (16−16 and 30−30 nm) also were carried out. When the dimerization reaction was used with smaller particles (16−16 nm), ∼65% of the product consisted of gold nanoparticle dimers. This yield also is higher compared to the dimers synthesized using rigid organic ligands.[7] In the case of 30 nm diameter colloids, ∼57% particles were gold nanoparticle dimers. Panels A and B of Figure 2 are TEM images of the 16−16 and 30−30 nm dimers, respectively.

The synthesis of heterodimers (41−30, 41−16, and 30−16 nm) also was carried out using the synthetic procedures described above (Figure 3). In each case, approximately 30, 50, 10, and 10% particles were dimers, trimers, tetramers, and individual single particles, respectively. The greater surface area of the larger particles (∼41 nm) that is accessible for binding of more than one smaller particle (∼16 nm) could be one reason a range of morphologies were observed.

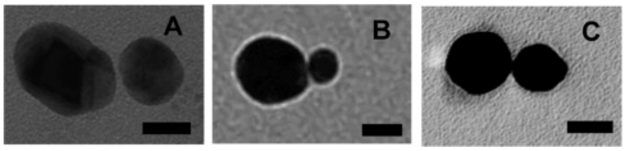

Figure 3. TEM images of dimers consisting of two AuNPs with different sizes: (A) 41−30 nm, (B) 41−16 nm, and (C) 30−16 nm gold particles. Scale bar is 20 nm.

In conclusion, we have synthesized gold nanoparticle dimers by a solid phase approach using a simple coupling reaction of asymmetrically functionalized particles. The method may be used to generate dimers with a wide size range and containing two nanoparticles with different sizes. The dimers demonstrate remarkable stability in ethanol (see Supporting Information). The process could be generalized to obtain metal−semiconductor conjugates. In addition, the distance between nanoparticles could be controlled, generating a molecular ruler,[3d] by simply varying the chain length of the linker molecules.

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Supporting Information Available: Experimental details for gold nanoparticle synthesis and additional TEM images and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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