Structural control of Au and Au–Pd nanoparticles by selecting capping ligands with varied electronic and steric effects

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Abstract: Weakly interacting ligands including three Gemini surfactants, didodecyldimethylammonium bromide (DDAB), and amines (RNH₂, R₂NH, and R₃N) were used to prepare Au nanoparticles (NPs). Aqueous Au NPs capped with DDAB and Gemini surfactants showed similar sizes (3–4 nm), whereas toluene-based NPs stabilized with DDAB, amines, and their mixtures range from 2.5 to 9.3 nm. Ligand effect on Au–Pd NP structure was also studied with EXAFS. These findings were consistently accounted for by considering the ligand's electronic/steric effects and mixed ligands coadsorption, and suggest useful ways to control NP structure by manipulating the two effects and using mixed capping ligands.

Key words: metal nanoparticles, capping ligands, electronic effect, steric effect, EXAFS.

Résumé : On a utilisé des ligands interagissant faiblement, dont trois agents de surface Gemini, le bromure de didodécyldiméthylammonium (BDDA) et des amines (RNH₂), R₂NH et R₃N) pour préparer des nanoparticules (NP) d'or (Au). Les tailles des nanoparticules d'or aqueuses, fermées avec du BDDA ou des agents de surfaces Gemini sont assez semblables (3–4 nm) alors que celles des nanoparticules à base de toluène et stabilisées par du BDDA, des amines ou leurs mélanges varient de 2,5 à 9,3 nm. On a aussi examiné l'effet de ligand sur la structure des nanoparticules Au–Pd par la technique de structure fine d'absorption des rayons-X étendue (SFAXE). Les observations peuvent être expliquées d'une façon cohérente en considérant les effets stérique/électronique du ligand et la coadsorption des ligands mixtes et ceci suggère des façons utiles de contrôler la structure des nanoparticules en manipulant les deux effets et en utilisant des ligands mixtes pour les fermer.

Mots-clés : nanoparticules métalliques, ligands de fermeture, effet électronique, effet stérique, structure fine d'absorption des rayons X étendue (SFAXE).

[Traduit par la Rédaction]

Introduction

Selection of capping ligands for the synthesis of metal nanoparticles (NPs) is of fundamental and technological importance.¹⁻⁶ Capping the NP surface with alkanethiols and their derivatives has become a widely used method in the past decade.¹ The availability of a large variety of commercial thiol derivatives and the advancement in thiol ligand-exchange reactions for the NPs have made such an approach particularly attractive.⁷⁻⁹ However, the primary limitation of using thiol derivatives to functionalize NP surface is that the metal-ligand interaction is too strong and this hinders some applications such as catalysis. An alternative route to control the NP surface structure is to use weakly interacting molecules (relative to thiols) such as tetraalkylammonium surfactants. A noteworthy advantage of using weakly binding ligands is that the catalytic activity of NPs can be dramatically improved relative to those of their thiol-stabilized counterparts.^{4,10} More significantly, the use of weakly interacting ligands can offer excellent control of NP structures, making possible the synthesis of NPs with flexibly controlled size and shape (e.g., nanorods and nanowires).^{3,11} In addition, weakly interacting ligands are easily replaceable/ exchangeable if strongly binding ligands are desired to surface-functionalize the NP surface.

Tetraalkylammonium surfactants are among the most widely studied weakly interacting ligands in recent years. Numerous syntheses of NPs have been reported using tetraalkylammonium ligands, such as tetraoctylammonium bromide (TOAB),¹² didodecyldimethylammonium bromide (DDAB),¹³ and cetyltrimethylammonium bromide (CTAB).¹¹ Remarkably, significant progress has also been made in understanding the binding/stabilization mechanism of NP capping ligands, which plays a critically important role in the development of more efficient NP synthetic routes.^{2,4,14} However, most of the in-depth studies on the stabilization mechanisms of weakly interacting ligands are based on ionic

Received 22 May 2009. Accepted 20 July 2009. Published on the NRC Research Press Web site at canjchem.nrc.ca on 28 October 2009.

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Scheme 1. Molecular structures of three Gemini surfactants, three fatty amines, and DDAB.

ligands.⁴ For instance, one of the widely accepted ligandstabilization mechanisms used for NP catalysis, proposed by Ott and Finke, mainly consider two effects of the ligands, i.e., the so-called electronic effect (also known as charge or DLVO effect) and the steric effect.⁴ Such a mechanism has been found to provide good interpretation of the structural and catalytic properties of high-charge ionic ligands such as (Bu₄N⁺)₉ (P₂W₁₅Nb₃O₆₂)⁹⁻. In contrast, detailed stabilization mechanisms of other types of ligands, such as neutral weakly interacting ligands, has remained largely under-explored. Such studies are particularly desirable in light of the recent remarkable findings on amine-based nanoelectronic devices.^{15–17} Herein, we report the synthesis of Au NPs with a variety of weakly interacting ligands (Scheme 1), including some novel Gemini surfactants, didodecyldimethylammonium bromide (DDAB), dodecylamine, didecylamine, tridodecylamine, and nine mixtures of DDAB/amines (DDAB mixed with three amine ligands, each with three different molar ratios). The purposes of the present work are threefold: (i) exploring how Finke's models on ligand's electronic and steric effects can be used/extended to understand the stabilization of Au/Au-Pd NPs with the abovementioned ligands (particularly the neutral amine ligands); (ii) seeking possible ways to controllably synthesize Au NPs

by selecting ligands with varied electronic/steric effects or using a mixed capping method, and (*iii*) investigating how the capping ligands influence the local structure (i.e., the bimetal mixing pattern) of Au–Pd NPs.

Experimental section

All the chemicals were obtained commercially from Alfa Aesar or Aldrich except for ligands Gem A, Gem B, and Gem C (Scheme 1). Synthetic details for the preparations of Gemini surfactants will be published elsewhere¹⁸ and can also be found in the Supplementary data. Au nanoparticles (Au NPs) were prepared by reducing HAuCl₄ in aqueous solution or AuCl₃ in toluene with sodium borohydride. Three amine capping ligands were used singularly or in combination with DDAB. For combination systems, the ratios of amine to DDAB used were 1:4, 1:1, and 4:1. In a typical procedure, 0.03 mmol gold(III) chloride and 0.45 mmol of capping ligands (gold:ligand = 1:15 molar ratio) were dispersed in 30 mL of toluene by sonication. Then, the gold(III) was reduced with sodium borohydride (0.3 mmol) in 20 μ L of water, and stirred under argon for 2 h at room temperature. The as-prepared Au NP liquid suspensions were then stored in darkness in a refrigerator without further purification. UV-vis experiments were conducted





right after the NP synthesis, and TEM measurements were done within three days. Although only as-prepared samples (ideally purified samples are preferred) were measured in the present work, the reported TEM and UV-vis results were proved to be valid by time-dependent UV-vis measurements. Indeed, the as-prepared Au NPs were found to be stable for at least one month, as shown by comparing the UV-vis spectra of fresh and one month old samples. The bimetallic Au-Pd NPs capped with DDAB/RNH₂ (80%) RNH₂) were synthesized using the same conditions as those reported recently for TOPB/RNH2-capped Au-Pd NPs.¹⁹ It was assumed that the initial Au-to-Pd molar ratio in the starting materials was maintained after the Au-Pd NPs were formed, which was supported by the XPS composition analvsis result reported for similar Au-Pd NPs in our recent publication.19

The morphology of the nanoparticles was characterized with a Technai 12 or JEOL 123 transmission electron microscope (TEM), both equipped with a CCD camera and operated at a voltage of 80 keV. One or two drops of the nanoparticle solutions were cast to carbon or formvar-coated Cu grids for the TEM measurements. The particle size information was obtained using a size-measuring program from the TEM by counting at least 100 particles. The Au-Pd NPs were purified using the centrifuge method described in our recent publication¹⁹ to obtain high-quality EXAFS data. The Au L3-edge EXAFS measurements were conducted at the HXMA beamline at the Canadian Light Source (CLS) operated at 2.9 GeV. Purified Au-Pd NPs were cast onto a Mylar tape to form a uniform film, and the samples were measured at room temperature using a transmission mode. The EXAFS data were normalized and fitted with theoretical phase-shift and amplitude generated from FEFF 8 program²⁰ using a WinXAS program, following the procedure described in our recent papers.^{19,21} The best-fit FT-EXAFS was provided in the Supplementary data.

Results and discussion

The mechanism of nanoparticle stabilization by ligands

Finke and co-workers have recently reviewed the stabilization modes of catalytic NPs with a particular emphasis on metal NPs capped with anionic ligands.^{2,4} Electronic and steric effects are proposed as the main factors influencing ligand stabilization. These two effects are schematically illustrated in Scheme 2 by inspecting the interaction between DDAB and Au NP. The electronic effect in Finke's model can be described as the Coulombic repulsive interaction between NPs due to the binding of Br^- onto Au NP surface, resulting in negatively charged NPs. That is why the electronic effect for these ionic ligands is also called the charge effect. The steric effect, on the other hand, originates from the relatively bulky ammonium groups that stay near the negatively charged NPs as counter cations. For DDAB used In the present work, the two 12-carbon alkyl chains sterically hinder direct contact between Au NPs.

When non-ionic ligands interact with Au NPs, the chargeinduced Coulombic effect used for ionic ligands does not directly apply. However, the steric effect alone is not sufficient to account for the stabilities of NPs. For instance, Au NPs stabilized with dodecylamine and dodecylthiol ligands should experience very similar steric effects, but these two types of NPs have significantly different stabilities (amine-Au < thiol-Au). A second important stabilizing effect is apparently related to the metal-ligand electronic bonding (e.g., Au-SR and Au-amine), which can be considered as another type of electronic effect. Such an electronic effect for non-ionic ligands can also play an important role in the stabilization of NPs. In a later section, it will be shown that the electronic and steric effects for non-ionic ligands, which are considered as a simple extension of the models for ionic ligands, can be used to understand the ligand-dependent NP size when Au samples were capped with primary, secondary, tertiary amines, and with amine/DDAB mixtures.

Au NPs in aqueous vs. toluene phase

Recently, it has been reported that Gemini surfactants form a unique category of capping ligands for the preparation of metal nanoparticles in the aqueous phase.^{22,23} In addition, the molecular structures of the Gemini surfactants can be altered to a much greater degree than those of the monomers, which may offer new opportunities to control the size and stability of NPs. Herein, two novel Gemini surfactants (Gem B and Gem C) together with a standard Gemini surfactant (Gem A) were used for the synthesis of Au NPs in aqueous solutions. The molecular structures of these Gemini surfactants are displayed in Scheme 1. In addition, DDAB was also used as a reference, since it has been found that DDAB can form a bilayer capping structure similar to those of the Gemini capping ligands.¹³ Figure 1 shows the **Fig. 1.** TEM images of aqueous Au NPs capped with (a) DDAB, (b) Gem A, (c) Gem B, and (d) Gem C. The average size and standard deviation are also presented in the figure.



TEM images of four Au NP samples prepared with the four ligands in water. It can be seen that all four capping ligands lead to Au NPs of similar sizes (average diameter ranging from 3.0 nm to 3.8 nm), although their molecular structures, including both the binding groups and the steric non-binding moiety, vary. It has been proposed that the double-chained structure of surfactants facilitates the formation of vesicles.^{13,23–25} The inner polar heads of the vesicles bind to the metal surface and the outer ones are exposed to the aqueous environment. The hydrophobic alkyl chains exist inside bilayers with quite dense packing through chainchain interaction. Formation of such densely packed bilayers should significantly enhance the role of the steric effect in the stabilization of NPs and thus make it dominant in controlling the NP size. The dominant role of the steric effect can be more clearly revealed by the identical size of Au NPs capped with Gem B and Gem C (3.8 nm vs. 3.6 nm), whose binding head-groups are different (bromide vs. sulfate, respectively) but have similar steric moieties.

Next, we turn to toluene-phase Au NPs prepared with DDAB and three fatty amines (primary, secondary, and tertiary) under identical synthetic conditions. The use of amines with systematically varied structures in the synthesis of NPs is particularly interesting in light of the recent remarkable findings in amine-based single-molecule circuits. Venkataraman and co-workers reported that amines bind selectively to undercoordinated Au atoms with sufficient angular flexibility for easy junction formation but well-defined electronic coupling of the N lone pair to the Au.¹⁶ It was also found that the variability of observed conductance for diamine-Au junctions is much less than that for dithiol-Au junctions.¹⁶ Therefore, amines can be considered as promising molecules for the construction of single-molecule junctions and circuits. According to recent results from theoretical studies, methyl-substituted primary, secondary, and tertiary amines almost have the same adsorption energy when binding to undercoordinated Au structures such as an adatom.²⁶ These results suggest that when the three amines stay at the same

Fig. 2. TEM images of toluene-phase Au NPs capped with (a) RNH_2 , (b) R_2NH , (c) R_3N , and (d) DDAB.



distance from Au (e.g., amines with small-sized subsituents), the electronic effects are identical. On the other hand, ionic DDAB ligand should have different electronic effects from the neutral amine ligands.

Figure 2 shows the TEM results of Au NPs prepared using DDAB and three amines. The sizes of RNH_2 -capped (2.8 nm) and R_2NH -capped (2.5 nm) NPs are very close to each other. Based on the model illustrated in Scheme 2, this observation can be easily understood. For RNH_2 - and R_2NH -capped NPs, the electronic effect is dominant; thus, the two NP samples have very similar sizes due to their identical metal–ligand bonding. On the other hand, the steric effect should play a less significant role when going from a primary to a secondary amine.

Interestingly, the sizes of R₃N-capped NPs are considerably different from those of primary- and secondary-aminecapped samples. Indeed, as seen in Fig. 2c, there exist two groups of particles for R₃N-capped NPs, one group being 3.7 nm in diameter and the other is 6.5 nm. Similar phenomena were observed from other spots on the same TEM grid. The steric effect for the bulky R₃N ligand should be more significant than the other two amines, favouring the formation of smaller NPs. However, it has been shown that due to steric hindrance, the electronic bonding between Au and amine is significantly weakened for bulky tertiary amines.¹⁵ As a result, the electronic effect for R₃N ligands should be weaker than that for RNH₂ and R₂NH ligands. Indeed, the overall low monodispersity of R₃N-capped NPs also supports the suggestion of a weaker electronic effect for the tertiary ligands.

The DDAB-capped sample has very different particle size (9.3 nm) from those capped with amines, which can be easily attributed to the pronounced difference of its stabilization mechanism from that of the neutral amine ligands. Indeed, it has been reported that amines preferentially bind to low-coordination Au sites (e.g., adatoms and corner atoms), whereas those bound to terrace-type surface atoms are not stable.^{15,26} In contrast, tetraalkylammonium bromide molecules were found to be mainly adsorbed to the terrace atoms on Au surface, although the Br alone, being separated from the ammo-



Scheme 3. An illustrative presentation of the surface-capping structure of Au NPs in aqueous (a) and toluene phase (b).

nium counterions, can strongly bind to low-coordination Au sites.²⁷ Therefore, the considerable NP size increase when going from amines to DDAB can be accounted for by considering their different ligand-binding mechanisms. The use of amines resulted in much smaller NPs which contain higher percentage of low-coordination surface atoms (i.e., adatoms, corner, and edge atoms) that can be bound by the ligands; the use of DDAB produced bigger NPs where the terrace-type surface atoms are more abundant.

One may also consider the possibility that the size difference among amine- and DDAB-capped NPs observed in Fig. 2 might be caused by different reduction rates of gold compound in toluene phase by aqueous NaBH₄. Since DDAB is a phase-transfer agent, the absence of DDAB in the three amine-capped samples may cause a slower reduction rate. However, the fact that Au NPs capped with 100% RNH₂ and those capped with a mixture of 80% RNH₂ and 20% DDAB (see next section) have very similar sizes (2.8 nm vs. 2.4 nm) suggests that such a possibility can be ruled out. Note that the presence of Cl- anions from AuCl₃ starting materials can also bind to the NP surface. However, the possibility that the chloride anions play an important role in determining the NP size can be ruled out in this work. This argument is supported by the following two facts. First, it is well-known that bromide (from DDAB) can bind to gold surface more strongly than chloride. Therefore, in the presence of DDAB, the anion adsorption effect associated with Br- should be more significant. Second, even in the absence of bromide, the above argument seems still true as the Au NP size was found to be largely determined by the molecular structure of amines (Fig. 2). It is also noted that different sizes for DDAB-capped Au NPs have been reported in the literature.²⁸ This could be attributed to differences between the synthetic procedures. Indeed, the stability of weakly bound NPs is largely kinetic in nature, thus causing the NP size to vary in different reports.²⁹ In the present work, it is still valid to make a comparison between the amine- and DDAB-capped NPs, as they were prepared under identical conditions.

Overall, a comparison of the syntheses of Au NPs in aqueous and toluene phases highlights the very different roles that the steric and electronic effects of the ligands play, which is schematically illustrated in Scheme 3 using DDAB as an example. Due to the existence of densely packed bilayer capping structure in aqueous solutions, the steric effect is dominant, whereas in toluene, the electronic effect is more important than the steric effect.

Au NPs with mixed ligands

To further study the interplay between the electronic and steric effects of the ligands as well as to explore the possibility of manipulating the two effects to control NP size, we next used a combination of amine and DDAB to synthesize Au NPs. Nine NP samples (3×3) were prepared using mixed ligands of RNH₂, R₂NH, or R₃N with DDAB, each series having 20%, 50%, and 80% amines, respectively. Figure 3 shows the TEM images of these nine NP samples. UV-vis results of the three series of Au NPs (i.e., NPs capped with DDAB/RNH₂, DDAB/R₂NH, and DDAB/R₃N) with systematically varied concentration of amines (0%, 20%, 50%, 80%, and 100%) are also displayed in the figure. A few interesting observations are noted. Firstly, the three samples capped with mixed DDAB and RNH₂, shown in Figs. 3a-3c, all have similar sizes (2.4 nm to 2.8 nm in diameter) to that of pure RNH₂-capped NPs (2.8 nm), which are considerably different from that of DDAB-capped samples (9.3 nm). The UV-vis spectra in Fig. 3j show that all the amine-capped NPs exhibit diminishing surface plasmon resonance band, indicating the small sizes for these NPs and consistently supporting the TEM data. Secondly, the DDAB/R₂NH-capped NPs displayed in Figs. 3d-3f exhibit nearly the same particle size (6.8 nm to 7.1 nm in diameter), which are very different from pure R₂NH-capped Au sample (2.5 nm), consistent with the UV-vis results in Fig. 3k. Thirdly, the size of DDAB/R₃N-capped NPs increase gradually with the concentration of DDAB, from 5.7 nm (80% R_3N) to 6.7 nm (50% R_3N) and then to 7.6 nm (20% R_3N). The UV-vis spectra of NPs in this series in Fig. 31 all exhibit fairly intense surface plasmon resonance bands. A close inspection of Fig. 31 reveals that the surface plasmon resonance band of Au shows a noticeable blue shift when DDAB is present, even if the concentration of DDAB is low (20%).

The use of cosurfactants adsorbing onto Au 2D surfaces has been reported.³⁰ Generally, the existence of a cosurfactant can either reduce the adsorption of the primary surfactant due to a competitive adsorbing mechanism or enhance the adsorption caused by a collaborative adsorption of the two surfactants. The results of DDAB/RNH₂-capped NPs in Figs. 3a–3c suggest a competitive adsorbing process between DDAB and RNH₂ ligands and indicate that stabilization of Au NPs by the latter is dominant. A plausible reason is that RNH₂ is much smaller in size than DDAB, making the former more competitive in the coadsorption process. This is consistent with the reported results in the literature **Fig. 3.** TEM images of Au NPs (in toluene) prepared using mixed amines and DDAB: (a) 80% RNH₂, (b) 50% RNH₂, (c) 20% RNH₂, (d) 80% R₂NH, (e) 50% R₂NH, (f) 20% R₂NH, (g) 80% R₃N, (h) 50% R₃N, and (i) 20% R₃N. (j)–(l) are UV–vis spectra of RNH₂ series (j), R₂NH series (k), and R₃N series (l).



on Au 2D surface where cosurfactants of smaller sizes even at low concentration (e.g., 1%-2%) greatly reduced the amount of adsorbed primary surfactants.³⁰ The results of DDAB/R₂NH-capped NPs, however, seem to be very different from the case of primary amine. The sizes of the three NP samples (\sim 7 nm) shown in Figs. 3d–3f are close to that of pure DDAB-capped NPs (9.3 nm), but quite different from that of pure R₂NH-stabilized sample (2.5 nm). Interest-

Fig. 4. TEM images of (a) $Au_{0.25}Pd_{0.75}$ NPs, (b) $Au_{0.50}Pd_{0.50}$ NPs, and (c) $Au_{0.75}Pd_{0.25}$ NPs. Au L₃-edge FT-EXAFS is presented in (d) using *k*-space EXAFS data of 3–13 Å⁻¹. Idealized local structure models of the three NPs are also shown in (d).



ingly, the size of the three DDAB/R₂NH-capped NPs, which are all slightly smaller than that of DDAB-capped ones, does not change as the concentration of DDAB increases. A possible explanation will be discussed in conjunction with the discussion of DDAB/R₃N-capped NPs. The results of DDAB/R₃N-capped NPs clearly indicate that both DDAB and R₃N ligands play an important role in the NP synthesis. As a result, when more DDAB ligands were used, the NP size was closer to that of pure DDAB-capped NPs. As was discussed in a previous section, R₃N has the weakest electronic effect among the three amine ligands. Therefore, it is understandable that the adsorption of DDAB is significant even at low concentration (20%). Supporting evidence is provided by the UV-vis results presented in Fig. 31. However, the secondary amine (R₂NH), whose electronic effect is stronger than the tertiary amine, seems to be less competitive than R₃N in the coadsorption process with DDAB. Considering their very similar molecular structure (see Scheme 1), we propose that R₂NH and DDAB were collaboratively adsorbed onto the NP surface.³⁰ Since the NP surfaces mainly consist of terrace atoms, it can be easily understood that DDAB ligands are the ones that mainly determine the NP size, as amines cannot form stable bonds with the terrace Au atoms.²⁶ This notion can also explain why the particle size of DDAB/R2NH-capped samples (~7 nm) is close to that of pure DDAB-capped NPs (9.3 nm) and remained almost unchanged when the concentration of DDAB was increased from 20% to 80%.

In summary, the particle-size data of Au NPs capped with mixed amines and DDAB ligands indicate that the coadsorption mechanism of ligands determines the NP size. RNH₂ is more competitive than DDAB in the coadsorption process; thus, the NPs capped with 20%-80% RNH₂ are all very small (<3 nm), similar to that of pure RNH₂-capped NPs. R₂NH may be coadsorbed onto Au in a collaborative way with DDAB, making the NP size close to that of pure DDAB-capped ones. R₃N and DDAB, whose competitive abilities in the coadsorption process are comparable, are similarly important in determining the NP size. Consequently, the NP size increases with the concentration of DDAB. Overall, these results suggest that by selecting ligands with desired molecular structure (and thus the electronic and steric effect), one can possibly control Au NP size with this mixed-capping method. Although further experimentation is needed to rigorously evaluate the effectiveness of this mixed-capping method, the results presented in Fig. 3 do show some promise of more flexible control of NP size than using a single type of ligands.

Au-Pd NPs with mixed ligands

We have recently reported the use of this mixed-capping method to prepare Ag-Pd and Au-Pd NPs.^{19,21} Herein, we present results on bimetallic Au-Pd NPs capped with mixed DDAB (20%) and RNH₂ (80%) ligands. These results can be considered as an extension of the work on Au monometallic NPs presented in the above sections. Moreover, the effect of weakly binding ligands on the structure of bimetallic NPs is even more interesting, as not only the particle size but also the bimetal mixing pattern can possibly be influenced by selecting the ligands. We have recently reported EXAFS results on the local structure of Au-Pd NPs capped with a mixture of 20% tetraoctylphosphonium bromide (TOPB) and 80% n-dodecylamine, which show alloying-structuredependent physical and chemical properties.¹⁹ In the present work, we intend to compare the local structure of Au-Pd NPs capped with 20% DDAB and 80% n-dodecylamine (RNH₂) with the previous results with an attempt to study the effect of different type of bromide ligands (DDAB vs. TOPB) on the bimetal mixing pattern of Au-Pd NPs.

Figures 4a-4c depict the TEM images of Au-Pd NPs with varied concentrations of Au. The average sizes for $Au_{0.75}Pd_{0.25}$, $Au_{0.50}Pd_{0.50}$, and $Au_{0.25}Pd_{0.75}$ are 4.3 ± 0.7 nm, 3.3 ± 0.5 nm, and 3.7 ± 1.0 nm, respectively. The fact that these NPs are all bigger than their pure Au counterpart (2.4 nm) implies that the metal-ligand binding differed after Pd was introduced. To investigate the ligand effect on the mixing patterns of Au-Pd NPs, Au L3-edge EXAFS measurements were performed. The FT-EXAFS and fitting results were presented in Fig. 4d and Table 1, respectively. A comparison of the experimental EXAFS data and first-shell best fit is provided in the Supplementary data. The information about Au-Pd mixing pattern can be obtained by analyzing the coordination numbers (N_{Au-Au} , N_{Au-Pd} , and N_{total}) in the table. It has been established^{19,31-33} that if N_{Au-Au}/N_{Au-Pd} is equal to Au/Pd molar ratio, a homogeneous alloy was resulted. If N_{Au-Au}/N_{Au-Pd} is considerably greater than Au/Pd

Sample (% Au)	M-M bond	N ^a	N _{total}	R (Å) ^b	$\Delta\delta^2$	ΔE (eV)
25	Au–Au	7.4	11.8	2.830	0.0088	0.88
	Au–Pd	4.4		2.804	0.0082	2.28
50	Au–Au	7.8	11.8	2.827	0.0090	-1.14
	Au–Pd	4.0		2.797	0.0093	0.63
75	Au–Au	10.4	12.4	2.810	0.0088	-3.29
	Au–Pd	2.0		2.793	0.0079	3.28

 Table 1. Au L3-edge EXAFS fitting results for three Au–Pd NP samples.

Note: The uncertainty is ~20% for N and ~0.02 Å for R.

^aNearest-neighbor coordination number.

^bFirst-shell metal-metal bond distance.

molar ratio, then Au-core Pd-shell NPs were formed. Moreover, N_{total} is useful to obtain the information about the location of Au atoms. If N_{total} is 12, which is the first-shell coordination number for a bulk fcc metal, Au atoms cannot be found on the NP surface (i.e., all the neighboring sites for Au are occupied). If N_{total} is less than 12, some Au atoms should be located on the surface, as the surface atoms of a metal with fcc crystalline structure have a coordination number less than 12. The results of N_{Au-Au} and N_{Au-Pd} in Table 1 indicate that all the three Au-Pd NPs have core-shell structures. In addition, all the three N_{total} values are nearly 12, indicating that the particle surfaces are essentially all covered by Pd atoms. Based on the above analysis, the structural models for the three Au-Pd NPs are schematically illustrated in Fig. 4. The core-shell structural models are consistent with the TEM results, which show that Au-Pd NPs are all bigger than pure Au NPs, since the surface metal-ligand bonding in the Au-core Pd-shell NPs is different from that of pure Au NPs. It is interesting to note that the present structural results of Au-Pd NPs capped with DDAB/RNH2 (80% RNH₂) differ from those capped with TOPB/RNH₂ (80% RNH₂) we recently reported.¹⁹ For the TOPB/RNH₂capped NPs, core-shell structures were found only for the $Au_{0.50}Pd_{0.50}$ and $Au_{0.75}Pd_{0.25}$ NPs, whereas the $Au_{0.25}Pd_{0.75}$ NPs showed a cluster-on-cluster structure. Therefore, a comparison of the bimetal mixing patterns of these two series of samples indicates that the Au–Pd bimetallic mixing pattern can be modified by varying the type of ligands used in this mixed-capping method. We are in the process of systematically investigating the correlation between the Au-Pd mixing pattern and the structure/concentration of the two types of ligands (e.g., TOPB, DDAB, amines, and so forth) used in the mixed-capping synthesis.

Conclusion

To conclude, we have reported results of Au NP synthesis using a variety of weakly interacting ligands. Aqueous Au NPs capped with DDAB and three Gemini surfactants were found to have very similar sizes (average diameter of 3– 4 nm), whereas in toluene, the use of DDAB, amines, and their mixtures as capping ligands led to Au NPs with average sizes ranging from 2.5 nm to 9.3 nm. The ligand effect on the bimetal mixing patterns of Au–Pd NPs was also studied with EXAFS. These results can be accounted for by considering the electronic and steric effects of capping ligands and the ligand coadsorption mechanism when mixed ligands (cosurfactants) were used. The experimental findings presented in this work suggest that manipulation of the electronic and steric effects of weakly interacting ligands and the use of mixed capping ligands can offer useful routes to control NP size and bimetal mixing patterns.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5287. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/ unpub_e.shtml.

Acknowledgements

We thank the financial support for this work by Dalhousie University, the Natural Sciences and Engineering Research Council of Canada (NSERC), the Atlantic Innovation Fund, and Canada Foundation for Innovation (CFI). The CLS is funded by NSERC, the Canadian Institutes of Health Research (CIHR), the National Research Council Canada (NRC), and the University of Saskatchewan. The EXAFS technical support from CLS staff scientist, Dr. Ning Chen, is also acknowledged.

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