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Exploiting the Chemical Differences Between Ag and Au Colloids Allows Dramatically Improved SERS Detection of “Non-adsorbing” Molecules

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ARTICLE

Exploiting the Chemical Differences between Ag and Au Colloids Allows Dramatically Improved SERS Detection of “Non-Adsorbing” Molecules

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In colloidal SERS only analytes that can spontaneously adsorb onto nanoparticles are detected. Therefore, considerable effort has been placed on modifying the surface properties of colloidal particles, particularly Ag particles, to promote the absorption of “difficult” analytes which do not spontaneously adsorb to as-prepared nanoparticles. In contrast, much less attention has been paid to the role which the identity of the underlying metal plays in the absorption since it is widely believed that the chemical properties of Ag and Au are very similar. This leads to the assumption that molecules which do not adsorb to Ag, such as hydrocarbons, will also not adsorb to aggregated Au colloids for SERS measurements. Here, we challenge this common perception by showing that SERS detection of “difficult” aromatic targets such as naphthalene, trinitrotoluene and 3,4-methylenedioxymethamphetamine which cannot be achieved even at $>10^{-3}$ M concentrations with bare aggregated Ag colloids is possible at $\geq 10^{-8}$ M with unmodified aggregated Au colloids. For naphthalene and 3,4-methylenedioxymethamphetamine the detection limit obtained in this work with bare citrate-capped Au particles exceeds the previous best limit of detection obtained with surface-modified nanoparticles by an order of magnitude.

1 Introduction

The potential of SERS as a simple and cost-effective method for detecting low concentrations of target analytes has led to an explosion of interest in the technique and in particular the development of increasingly complex enhancing materials where the plasmonic and surface properties are controlled and optimised.^[1-3] However, Au and Ag colloids remain the most widely applied substrates in surface-enhanced Raman spectroscopy (SERS) since they are easy to prepare and give very large enhancement factors, allowing detection down to single molecule level.^[4,5] An important feature of SERS with colloidal nanoparticles (NPs) is that since enhancement is only observed when analyte molecules are within a few nanometres of the substrate material's surface, simple NP colloids can only be used to detect analytes that spontaneously adsorb to the particles in solution. It is not a coincidence that the first compounds to be studied with colloids and the most popular SERS test materials are those which have strong affinities for Ag and Au surfaces, for example thiols and charged dyes. In order to address this problem a significant amount of work has been carried out on the development of novel colloidal NPs with improved affinity and selectivity towards non-adsorbing molecules. For example,

the surfaces of NPs can be functionalized with a range of organic modifiers to achieve a required level of hydrophobicity and/or electric charge to promote analyte adsorption.^[6-8] Furthermore, NPs can also be combined with metal organic frameworks or molecular imprinted polymers to form hybrid materials with molecular specificity towards certain non-adsorbing target molecules.^[9-12] Modifying the surface chemistry has been very successful in some instances but this may have distracted attention away from the other important factor in absorption, the nature of the metal itself. Factors such as the better plasmonic properties of Ag or the higher stability of Au are often cited as a reason for choosing Au rather than Ag or vice-versa but the differences in the chemical properties of the two metals has received much less attention. Indeed, it is often assumed that the chemical properties of Au and Ag are broadly similar, so that analyte molecules that do not adsorb to Ag will also not adsorb to Au. Here, we challenge this common perception by revisiting the library of common SERS analytes and show that several analyte molecules which do not adsorb to Ag do in fact readily adsorb onto Au despite statements in the literature that this is not the case. As consequence, several analytes which have previously been studied by SERS using carefully modified Ag NPs can be directly detected down to micromolar levels using unfunctionalized aggregated Au colloids.

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2 Experimental section

2.1 Reagents and instrumentation

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All chemicals were purchased from Sigma-Aldrich and used as received. Commercial citrate stabilised Au colloid was purchased from nanoComposix Inc. and used as received. The particle diameter of the particles was ca. 50 nm. The concentration of the colloid was ca. 4×10^{10} particles/mL. All solutions were prepared from distilled, deionized (DDI) water (resistivity=18.2 M Ω), obtained from a BransteadNanopure system or from absolute ethanol. Particle concentrations were measured using a NANOSIGHT NS300 (Malvern).

2.2 Colloid preparation

Citrated reduced silver colloid (CRSC) was prepared following the exact protocol reported by Lee and Meisel.^[13] Hydroxylamine-reduced silver colloid (HRSC) was prepared following the exact protocol reported by Leopold.^[14] Citrate-reduced gold colloid (CRGC) was prepared following a variation of Fren's method.^[15] Briefly, 50 mL of DDI water with HAuCl₄ (0.05g) was brought to boil under vigorous stirring followed by the addition of 5.6 mL of 1 wt% Na₃Ct solution. The mixture was allowed to react for 15 min before being cooled down to room temperature. This yielded gold particles ca. 55 nm in diameter. After synthesis, the colloid was diluted 2 \times to match the particle concentration of CRSC and HRSC (7×10^{10} particles/mL). Surface-modified colloids were prepared by adding an appropriate amount of aqueous solution of the corresponding capping agent (KBr; polyvinylpyrrolidone PVP M.W. 30000; sodium mercaptopropene sulfonate MPS) to CRGC so that the final concentration of the capping agent was ca. 10^{-3} M. This produced stable Br⁻, PVP or MPS⁻ capped Au colloids which could be stored under room temperature for weeks.

2.3 Raman measurements

Samples for SERS measurements were prepared by adding 20 μ L of analyte solution to 200 μ L of colloid and then aggregated with 20 μ L of 1 M (NH₄)₂SO₄. Blank SERS spectra of the colloids were acquired by substituting the analyte solution with DDI water or absolute ethanol. Raman spectra were acquired using an Avalon R2 Ramanstation, equipped with a 100 mW 785 nm diode laser. Integration times of 5 \times 4 s were used for all spectra.

3 Results and discussion

Polycyclic aromatic hydrocarbon (PAH) molecules, which are widely studied because of their environmental importance, provide a good example.^[16] PAH molecules are commonly believed to have a low affinity towards Au and Ag surfaces since they are uncharged (and therefore have no electrostatic attraction) and also lack functional groups, such as amines or thiols, which typically promote adsorption to metal surfaces. Because of this, many protocols for particle surface functionalization have been developed to construct molecular traps or favourable hydrophobic environments to promote PAH adsorption onto Au and Ag particles.^[17,18] Figure 1 show SERS spectra obtained by mixing naphthalene with different types of commonly synthesised aggregated metal colloids. As shown in Figures 1A(i) and (ii), naphthalene signals could not

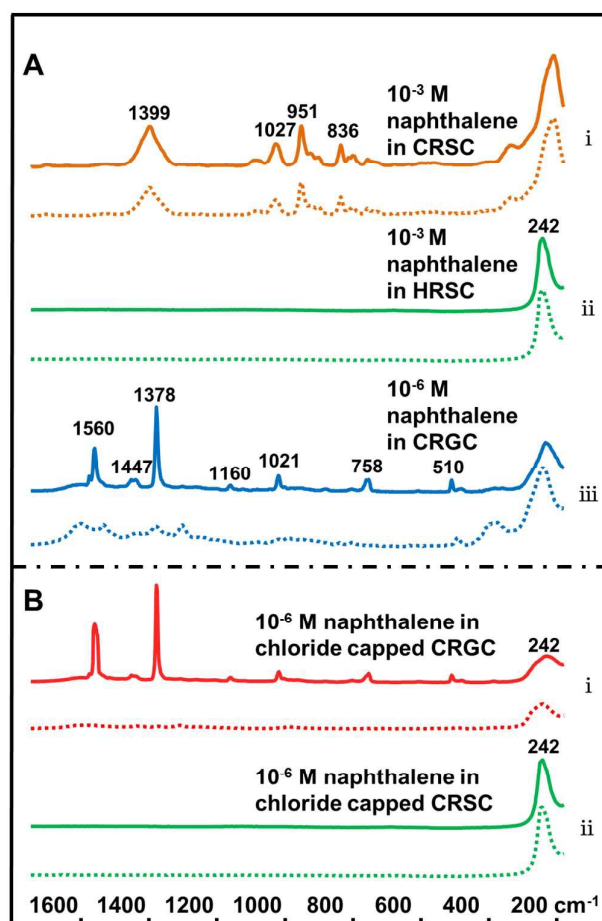


Fig. 1 A: Surface-enhanced Raman spectroscopy (SERS) signals obtained by aggregating citrate-reduced silver colloid (CRSC) (i) and hydroxylamine hydrochloride-reduced silver colloid (ii) with naphthalene at 10^{-3} M showing no signals of naphthalene. SERS signal obtained by aggregating citrate-reduced gold colloid (CRGC) with naphthalene at 10^{-6} M showing strong signals of naphthalene (iii) B: SERS signals of naphthalene obtained using chloride capped Au (i) and Ag (ii) particles. The concentrations of naphthalene were 10^{-6} M for Au colloids and 10^{-3} M for Ag colloids. The dotted spectra correspond to the blank SERS signals of the respective colloids. Spectra with different substrates have been rescaled for illustration.

be observed with aggregated HRSC or CRSC as the enhancing material. Even when the final concentration of naphthalene was as high as 10^{-3} M the resulting SERS spectra only showed the background peaks, corresponding to chloride (242 cm^{-1}) and citrate ($1399, 1027, 951, 836 \text{ cm}^{-1}$), that were initially present in the blank spectra. This is consistent with literature reports and shows that naphthalene does not spontaneously adsorb onto the surface of Ag NPs in solution. Surprisingly, as shown in Figures 1A(iii), intense SERS signals of naphthalene ($1560, 1447, 1378, 1160, 1021, 758, 510 \text{ cm}^{-1}$) could be readily obtained, even at micromolar levels when using conventional CRGC prepared by the Frens method. This suggests that although naphthalene cannot adsorb spontaneously onto aggregated Ag colloid, it does adsorb strongly onto aggregated Au. This effect is not due to the colloid that we prepared in-house having particularly favourable properties since naphthalene signals could also be obtained using commercially

available citrate-stabilised Au colloids (Fig. S1). Similarly, a range of different salts were tested to check that the effect was not due to the influence of the aggregating agents used. With different aggregating agents the level of signal enhancement and detection limit of naphthalene varied but the general observation that naphthalene signals could only be directly detected using Au colloids remained consistent (Fig. S2). As expected, NH_4^+ and SO_4^{2-} , which have a low affinity towards Ag and Au surfaces gave the best results. Therefore, $(\text{NH}_4)_2\text{SO}_4$ was used as the aggregating agent throughout this research unless otherwise stated.

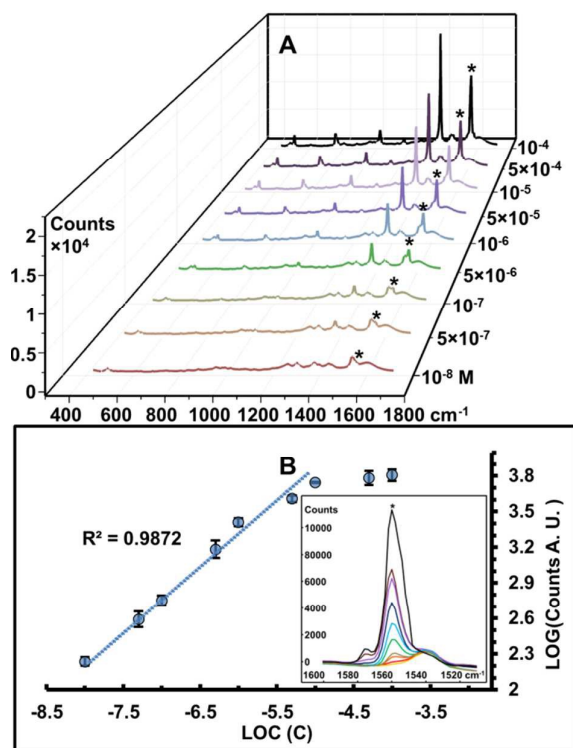


Fig. 2 A: SERS signals of naphthalene at different concentrations obtained using aggregated CRGC. B: The logarithm of the SERS intensity of the starred peak at 1560 cm^{-1} plotted against the logarithm of naphthalene concentration. Inset shows the actual spectra corresponding to the data points in the calibration plot. All spectra shown were averaged from 3 independent measurements.

Figure 2A shows the SERS signals obtained with different concentrations of naphthalene. Using as-synthesized CRGC the limit of detection for naphthalene was 10^{-8} M , which is an order of magnitude lower than the previous best detection limit of naphthalene obtained using Ag-decorated Fe_2O_3 particles.^[19] By using the peak at 1560 cm^{-1} as the marker band to plot the SERS signal intensity against the final concentration of naphthalene the experimental data can be fitted nicely with the Langmuir model for adsorption (Fig. S3). Figure 2B shows the linear quantification range between 10^{-8} M to 10^{-5} M with a R^2 value of ca. 0.99. Above this value the plot plateaued due to saturation of the surface.

We have investigated the possibility that this striking difference in the ability to detect naphthalene between CRGC and CRSC could be due to the difference in the surface capping between Ag and Au

colloids. It is widely accepted that the surfaces of citrate reduced NPs are covered in a layer of citrate ions, which provides the electrostatic repulsion that keeps the colloid stable.^[20] However, recent studies have shown that citrate can adopt various forms on the surface of NPs depending on the pH of the surrounding environment, the amount of free surface sites and which metal the particle is composed of.^[20-23] Moreover, the oxidation products generated from citrate have been shown to be different for CRSC and CRGC and these can also adsorb onto the surface of particles.^[24] This suggests that the surface properties of citrate-stabilised Au and Ag colloids could be quite different. In our case this is evidently true, since the background SERS signals of CRSC and CRGC are different from each other as shown in Figure 1A dotted spectra (i) and (iii). To remove this effect, naphthalene adsorption was also studied on CRGC and CRSC which were aggregated with NaCl so that the citrate on the surface of both CRGC and CRSC NPs was replaced by chloride ions. When the particles were pre-functionalized in this way their background SERS signals were dominated by single peaks at ca. 240 cm^{-1} , which correspond to the metal-chloride stretching vibrations (Fig. 1B, dotted spectra (i) and (ii)). With these chloride-capped particles, the SERS signals of naphthalene still could only be obtained using Au colloids (Fig. 1B, solid spectra (i)). Moreover, naphthalene could also be detected using Au NPs functionalized with other capping agents such as bromide and PVP (Fig. S4). These observations show that in this case it is the identity of the metal rather than the molecular composition of the capping layer on the surface of the particles which is important. In contrast, naphthalene signals could not be obtained with Ag nor Au colloids which had been modified with strongly covalently-bonded thiol molecules. This is consistent with a model in which naphthalene can readily displace weakly adsorbed molecules, such as chloride and citrate but cannot displace capping agents which have a stronger affinity to Au surface, such as thiols (Fig. S5). Direct evidence that the adsorption of naphthalene onto Au NPs is accompanied by desorption of the surface ions was given by experiments in which the SERS signal intensity of citrate and chloride was considerably reduced

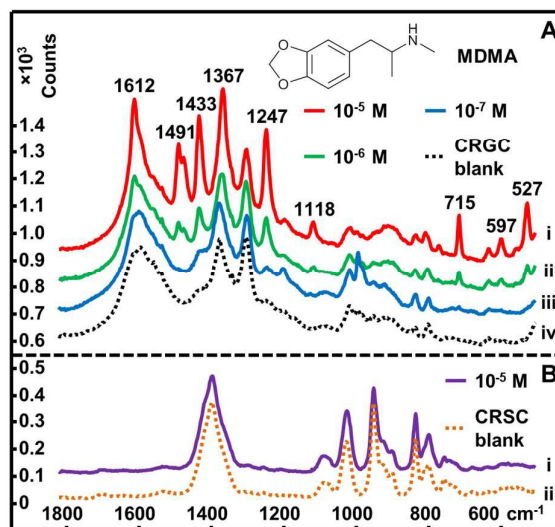


Fig. 3 Comparison between the SERS signals of 3,4-methylenedioxyamphetamine (MDMA) obtained at different concentrations using aggregated CRGC (A) and CRSC (B) as the enhancing material.

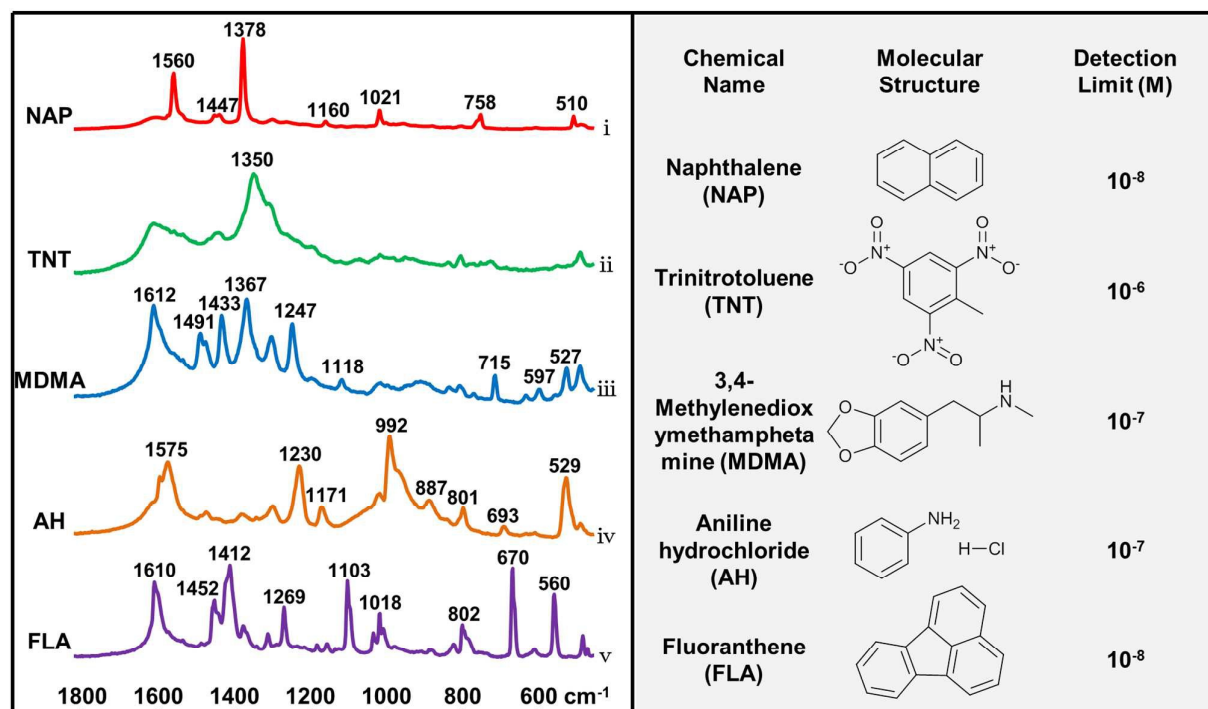


Fig. 4 SERS signals of 5 different analytes which give no SERS signals on aggregated Ag colloids because they do not adsorb but have been obtained here simply by switching to aggregated Au colloids. The table on the right shows the chemical name, molecular structure and the corresponding limit of detection using CRGC for each analyte.

when naphthalene was added to citrate-reduced Au NPs (Fig. S6).

It should be noted that this dramatic difference in SERS enhancement between Ag and Au colloidal particles is not limited to naphthalene. 3,4-methylenedioxyamphetamine (MDMA), also known as "Ecstasy" is an illicit psychoactive drug which is well-documented to be "difficult" to detect with SERS using aggregated colloids.^[25,26] Figure 3 compares the SERS spectra of MDMA obtained using aggregated CRGC and CRSC as the enhancing material. As shown in Figure 3A, when CRGC was used as the enhancing material MDMA signals could be obtained down to 10^{-7} M. Since MDMA molecules are positively charged under acidic colloidal environments, it is possible that MDMA molecules are attracted to the surface of Au NPs by electrostatic attraction from the negatively charged citrate capping layer. However, this is clearly not the case since no MDMA signals could be obtained even at a concentration which was 100 times higher when using aggregated CRSC which is also negatively charged as the enhancing material (Fig. 3B). This shows that for MDMA detection it is also the identity of the metal rather than the electrostatic attraction between the negatively charged surface capping layer on the particles which is important. Notably, the detection limit of 10^{-7} M found for MDMA in this work is one order of magnitude better than the previous best limit of detection, which was reported by our group using Ag colloids functionalised with mixed thiol monolayers.^[26]

Figure 4 shows the set of analytes which were studied here. All these compounds have previously been detected using

modified Ag colloids of various types because it was shown that they did not adsorb to unmodified Ag surfaces. In contrast using bare CRGC allowed SERS signals of not just naphthalene and MDMA but also trinitrotoluene (TNT), aniline hydrochloride and fluoranthene to be directly detected down to, or below, concentrations of 10^{-6} M (see Fig. S7 for SERS data).

The overall chemical structure and electric-charge of the five analytes studied in this work varies significantly. However, all five of the analytes have at least one aromatic ring, which suggests that in this case π -metal interactions between the analyte and the Au surface could be a crucial factor governing adsorption. Indeed, despite recent work which assumes aromatic molecules such as naphthalene do not adsorb onto gold, electrochemical studies which showed aromatic hydrocarbons adsorbing onto Au electrodes from aqueous solution at similar concentration levels to those in our SERS measurements were published by Dahms and Green in the 1960s.^[27-29] The shape of the adsorption isotherms suggested that naphthalene lies flat on the Au surface upon adsorption due to interactions of the aromatic π electrons with the metal. More recent computational results also support the model where aromatic hydrocarbons such as benzene (BZ) and naphthalene can adsorb onto coinage metals (Cu, Ag, Au) through π -metal interactions.^[30,31] Surprisingly, the calculations showed that the interaction energies of BZ between Ag and Au are nearly identical.^[31] The analyte molecules studied in this work clearly lack the proper functional groups to form strong covalent or coordination bonds with Au or Ag NPs. For charged analyte molecules such

as MDMA, we have also shown with contrast experiments between CRSC and CRGC that electrostatic interactions are not the main factor governing adsorption. These observations, particularly the similarity of the calculated interaction energies for aromatic molecules on Ag and Au, suggest that the significantly higher binding constant for naphthalene on aggregated Au colloids compared to aggregated Ag colloids is influenced by something other than the properties of the analyte. One obvious other possibility is that since the citrate and chloride surface capping agents have a much lower affinity towards Au than Ag they can be displaced much more easily from the surface of aggregated Au NPs than Ag NPs. Similar examples can be found in electro-chemical studies, where aliphatic hydrocarbons in solution prefer to adsorb onto Hg rather than Au electrodes and this is due to stronger absorption of water to Au than Hg, rather than a direct difference in the metal-hydrocarbon interactions.^[28] Indeed the only experimental reports of BZ and naphthalene adsorption onto Ag are for adsorption onto rigorously cleaned bare-surfaces under high vacuum conditions.^[32,33]

4 Conclusions

In summary, this work demonstrates the importance of the choice of enhancing metal in determining whether a given analyte will adsorb to a colloid, which is often an overlooked factor within SERS measurements. In SERS with aggregated metal colloids the particles have surface capping agents and it is the relative strength of the analyte-surface attraction versus the capping agent-surface attraction which determines whether analyte adsorption occurs. For the case of aromatic analytes simply moving from Ag to Au can shift the balance of these forces to the extent that compounds which are completely undetectable at high concentration on Ag can be detected at $\geq 10^{-8}$ M concentrations on Au. In the case of naphthalene and MDMA the detection limit found in this work using un-modified CRGC even exceeded the previous best limit of detection achieved with surface-functionalized NPs. In this work we concentrated on compounds which were known to be poorly adsorbing to emphasise the contrast between the metals but the basic concept of using unmodified Au colloids for detection of aromatic target analytes is clearly much more general than this and has broader potential applications, especially since it does not depend on specific chemical modification to promote adsorption of particular molecular targets.

Conflicts of interest

There are no conflicts to declare.

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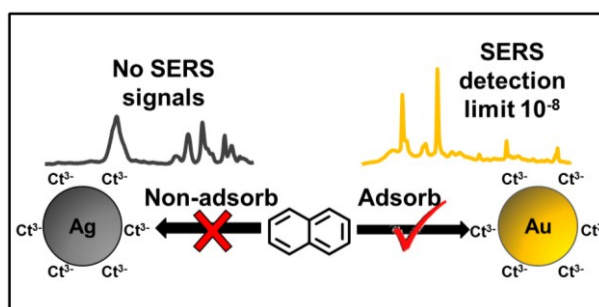
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TOC

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Switching from Ag to Au colloids allows SERS of 'non-adsorbing' analytes such as naphthalene to be detected at $\geq 10^{-8}$ M.