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Selective SERS Sensing Modulated by Functionalized Mesoporous Films

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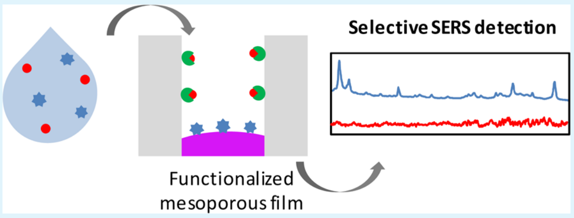
Supporting Information

ABSTRACT: A hybrid material comprising metal nanoparticles embedded in functionalized mesoporous thin films was constructed, and its use as a selective SERS-based sensor was demonstrated. The presence of specific functional groups in the pore network allows control over the surface chemistry of the pores, tuning the selectivity for specific molecules. Amino-functionalized hybrid mesoporous thin films were used in a proof of concept experiment, to discern the presence of methylene blue (MB) in mixtures with acid blue (AB), with no need for any sample pretreatment step. Selective detection of MB was possible through entrapment of AB in the mesoporous matrix, based on its high affinity for amino groups. The sensor selectivity can be tuned by varying the solution pH, rendering a pH responsive surface and thus, selective SERS-based sensing. The developed sensors allow specific detection of molecules in complex matrixes.



KEYWORDS: *SERS, gold nanoparticles, mesoporous films, hybrid materials, molecular sieves, sensors*

INTRODUCTION

Mesoporous oxides, obtained by combination of the sol−gel method and self-assembly of amphiphilic molecules, are an example of multifunctional pore systems with high surface area, large pore volume, ordered pore arrangement, and tunable pore diameters.[1] The inorganic framework can be easily modified to give rise to mesoporous hybrid organic−inorganic materials and to more complex chemical behavior, which may be particularly useful toward a wide range of applications.[2−4] Organic molecules carrying selected functional groups can be incorporated on the surface of the pores by postsynthesis treatment of the formed mesoporous material (postgrafting) or by co-condensation.[3,5,6] The postgrafting technique is useful in some cases (especially when using transition metal oxides) but the distribution of organic functions is often uneven and clogging of the pores can occur. The co-condensation method, on the other hand, involves the reaction of a functional trialkoxysilane with a nonfunctional precursor (metal salts or tetraalkoxysilanes). This approach leads to a homogeneous distribution of organic molecules within the inorganic framework, including functions available in the pores and some entrapped within the oxide walls.[7] The surface properties of the pores can be additionally controlled during the synthesis step, by incorporating suitable trialkoxysilanes including functions as diverse as phenyl, amino, thiol, alkyl chains, etc. Thus, by suitable functionalization, mesoporous oxides with different physical and chemical properties can be obtained.[8,9] Within the wide variety of mesoporous hybrid materials (powders, aerogels, fibers, etc.), thin films are especially interesting because they can be deposited on almost any smooth substrate and can thus be adapted to many existing or developing technologies such as catalysis, sensing, ion trapping, etc.[10−15]

The incorporation of metal nanoparticles in organic−inorganic oxide films results in hybrid materials with high potential as selective plasmonic sensors.[16−18] Surface-enhanced Raman scattering (SERS) spectroscopy is a sensitive, versatile, and powerful analytical technique[19] with applications in fields as diverse as chemistry, biochemistry, medicine, or environmental sciences, and the ability to reach sensitivity levels as low as a single molecule.[20] SERS is a purely nanoscale effect based on the plasmon-assisted Raman scattering of molecules adsorbed or in close proximity to metal nanostructures supporting localized surface plasmon resonances (LSPRs).[21,22] As a vibrational technique, SERS provides complete vibrational information on the molecular system under study, as well as a fingerprint for qualitative molecule detection. Application of this technique to study a particular molecule included in a complex mixture is still difficult, as the obtained spectra are complicated because of the matrix, and vibrational assignment becomes a complex task. Thus, a sample pretreatment step is

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often needed to avoid the matrix effect and allow correct interpretation of the obtained spectra. An attractive alternative is the use of selective substrates that can chemically or physically exclude matrix molecules, thereby leading to selective detection. Hybrid mesoporous thin films are particularly suitable for this purpose, since the presence of designed functional groups into the pore system allows obtaining a selective functional filter that can exclude molecular material, both by size (defined by the pores) and by chemical affinity (based on functional groups). We have recently demonstrated the ability of mesoporous thin films to act as molecular sieves by size-exclusion in biological media.[23] These porous titania thin films allowed the detection of small molecules by SERS, in the presence of serum proteins. In this work, we expand the potential of these thin films as SERS based sensors by incorporation of chemical selectivity via functionalization of the pores with organic molecules by co-condensation. The incorporation of such functionality gives rise to a sensor that can selectively detect molecules in a mixture with no need of sample pretreatment.

We thus designed a SERS active substrate comprising a submonolayer of gold nanoparticles covered with an amino-functionalized mesoporous thin film. The amino function was selected because it is very versatile and can selectively bind organic molecules[24,25] or ions.[26,27] The performance of this material toward selective detection was probed using Raman active molecules with different affinity to amino groups, so that their diffusion through the hybrid mesoporous thin film will be determined by surface modification and charge. We additionally show that pH-induced changes in amino groups[28] lead to stimuli-responsive SERS based sensors, so that detection is modulated by the solution pH in the sample. The approach presented here can be readily extended to other chemical species anchored to the pore walls, thereby leading to a wide variety of specific sensors for one-step detection of small molecules in complex mixtures.

■ EXPERIMENTAL SECTION

Chemicals. Tetrachloroauric(III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$), trisodium citrate dihydrate, titanium tetrachloride ($TiCl_4$), (3-aminopropyl)trimethoxysilane (APS), (3-aminopropyl)triethoxysilane (APTES), hydrogen peroxide 28% (H_2O_2), sulfuric acid 98% (H_2SO_4), Pluronic F127 ($HO(CH_2CH_2O)_{106}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{106}OH$), acid blue 25 (AB), and methylene blue (MB) were supplied by Sigma-Aldrich and used as received. Pure grade ethanol and Milli-Q water were used as solvents.

Gold Nanoparticles. Citrate-stabilized gold nanoparticles (GNP) with an average diameter of ~80 nm were prepared by kinetically controlled seeded growth.[29] Briefly, 150 mL of 2.2 mM trisodium citrate in Milli-Q water was heated to boiling under vigorous stirring. After 15 min, 1 mL of 25 mM $HAuCl_4$ was injected into the boiling reaction mixture, and after 10 min, the reaction mixture was cooled to 90 °C. Subsequently, 1 mL of a 25 mM $HAuCl_4$ aqueous solution was injected into the reaction mixture. After additional 30 min, 1 mL of the same $HAuCl_4$ aqueous solution was injected. After 30 min, 55 mL of the obtained solution was extracted and 53 mL of water and 2.2 mL of 60 mM sodium citrate were added. The final mixture was used as a seed solution, and the whole process was repeated again eight times, with just two injections of the $HAuCl_4$ aqueous solution, to yield 80 nm GNP.

Substrate Preparation. Glass slides were washed in piranha solution for 30 min and then copiously rinsed with pure water and stored under water until use. The surface was silanized by dipping the dry glass slides in a 0.01 M solution of APS in ethanol for 3 h and then rinsed with ethanol. The glass slides were then immersed in the GNP solution for 5 h, and rinsed with water. This treatment ensures chemical bonding between Au nanoparticles and the glass surface, so they remain firmly attached during the subsequent synthesis steps.[23,30]

Preparation of Mesoporous Films. Mesoporous thin films were produced by spin-coating, depositing 125 μL of a solution containing inorganic precursors and a nonionic surfactant template in ethanol on top of the GNP-modified glass slides, at a spinning rate of 4000 rpm.[31] Amino-functionalized mesoporous thin films (TF-NH_2) were synthesized via co-condensation of $TiCl_4$ and APTES, in the presence of a template (F127), following a well-established protocol.[32] Solutions were prepared containing Ti:APTES:H_2O:EtOH:F127 in a 0.8:0.2:10:40:0.005 molar ratio. Blank samples comprising pure titania mesoporous thin films (TF) were prepared in the same manner but with no amine precursor in the initial solution. Solutions prepared under these conditions were transparent and stable for at least 48 h at room temperature and can be reused several times if stored in a freezer at −20 °C and restored at room temperature prior to spin-coating. Freshly deposited films were submitted to 50% relative humidity chambers for 24 h, a stabilizing thermal treatment of two successive 24 h steps at 60 and 120 °C, and a final 2 h step at 200 °C. The organic template was removed by extraction in absolute ethanol for 3 days.

Characterization. UV−vis−NIR spectra were recorded using an Agilent 8453 spectrophotometer. Transmission electron microscopy (TEM) analysis was performed by using a JEOL JEM 1010 microscope operating at an acceleration voltage of 100 kV. Samples for TEM were obtained by scratching the films from the substrate and depositing them on carbon- and FORMVAR-coated copper grids. SEM images were obtained using a JEOL JSM-6700F FEG scanning electron microscope operating at an acceleration voltage of 15.0 kV. FTIR spectra were obtained from a Nicolet 5PCFT-IR spectrophotometer in the 4000−400 cm^{-1} range, to determine the presence of amino groups in mesoporous thin films. Samples for FTIR were prepared by depositing a drop of the precursor solution over a KBr pellet and subjected to the post-treatment previously described.

SERS experiments were conducted with a Renishaw InVia Reflex system. The spectrograph uses high resolution gratings (1800 cm^{-1}) with additional band-pass filter optics, a confocal microscope and a 2D-CCD camera. A laser excitation wavelength of 785 nm (diode) was used for all the measurements (10 s, 4.7 mW of power at the sample). A 50× objective was used, with a numerical aperture (NA) value of 0.75, which provided scattering areas of ~1 μm^2. SERS maps were collected out by using the Renishaw StreamLine accessory with a step size of 1.1 μm and static mode centered at 1274 and 447 cm^{-1} for AB and MB, respectively.

Diffusion Experiments. The selective diffusion properties of the ordered mesoporous films were investigated for the two different organic dyes: acid blue and methylene blue. Stock solutions (1×10^{-6} M) of both dyes were prepared with deionized water. pH was adjusted between 2 and 14 by addition of either HCl or NaOH solutions. For SERS measurements, film fragments of about 1 × 1 cm^2 were immersed overnight in the corresponding dye solution or in a binary dye mixture, rinsed with water, and air-dried.

■ RESULTS AND DISCUSSION

The design of the hybrid material presented here is aimed at the selective SERS detection of molecules in complex mixtures and comprises a submonolayer of gold nanoparticles covered with amino-functionalized mesoporous hybrid thin films. A mixed Ti−Si oxide prepared by co-condensation was chosen as mesoporous matrix, to ensure chemical stability during the measurements[23,33] and the presence of well distributed amino functional groups within the entire film.[28] In principle, selective detection can be achieved on the basis of the different affinities of molecules toward the pore surface chemistry, containing both titanol (Ti−OH) sites and amino functional surface groups. The synthetic procedure is based on a previously reported protocol, as schematically shown in Figure 1.[34] The precursor solution was prepared by cohydrolysis and

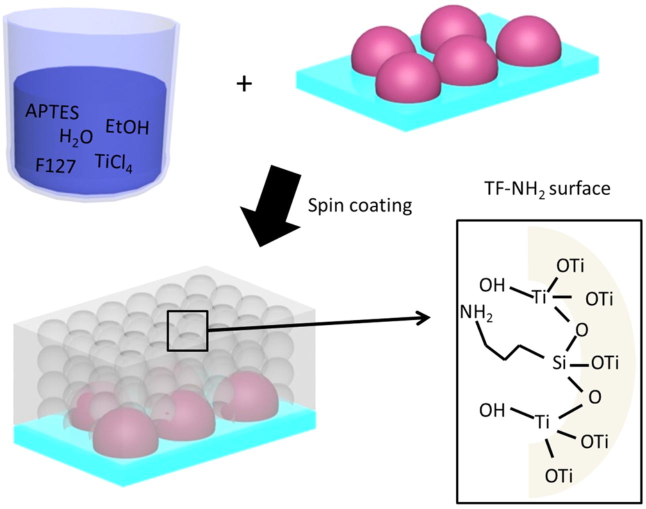

Figure 1. Schematic representation of the employed synthetic procedure. The precursor solution was spin coated over a glass slide covered with a submonolayer of 80 nm gold nanoparticles. After consolidation and condensation, a mesoporous thin film is formed, functionalized with amino groups ($TF-NH_2$).

condensation of $TiCl_4$ with a terminal trialkoxysilane [RSi(OR′)$_3$] (R = aminopropyl), in the presence of Pluronic F127 as a structure-directing agent. Spin-coating was used to build a mesoporous thin film on the glass substrate covered by gold nanoparticles. As prepared films were stored for 24 h at 50% relative humidity and subsequently consolidated by slow heating through two successive 24 h heat treatments at 60 and 120 °C and a final step at 200 °C to lock the mesostructure, removing undesired microporosity by enhancing microphase separation of the template and leading to complete condensation of inorganic material. Finally, the films were immersed in ethanol for 3 days to remove the organic template and obtain empty and accessible pores.

This procedure yields transparent crack-free mesoporous hybrid titania thin films, as determined by transmission electron microscopy (TEM). Indeed, TEM observation revealed films containing pore arrays, with no significant differences between the films prepared on pure glass slides (Figure 2A) and those containing GNP (Figure 2B). We also noticed that the LSPR band in the UV−visible spectra of the particles before and after film deposition was not altered, apart from a red-shift due to the refractive index increase around the particles (Figure 2C), indicating that no aggregation or reshaping occurred during the process. Scanning electron microsocopy (SEM) showed a homogeneous distribution of GNP on the glass slide, even when covered by the amino-functionalized mesoporous thin film (see Figure S1).

Successful incorporation of amino groups on mesoporous titania thin films is confirmed by Fourier Transform Infrared Spectroscopy (FTIR) data. Figure 2D shows the FTIR spectrum of $TF-NH_2$ compared with the spectrum obtained for unmodified TF film. Amino and/or ammonium functions are visible in the hybrid film samples, as a broad band in the 3000−3500 cm^{-1} region (ν_{NH}). This band is hard to recognize, since it is superimposed over the intense O−H stretching bands of adsorbed water and surface hydroxide groups with extensive H-bonding, which are also present in the TF sample. Also, the peak around 1590 cm^{-1} is assigned to the characteristic δ_{NH2}, which is also superimposed over the δ_{OH} bands corresponding

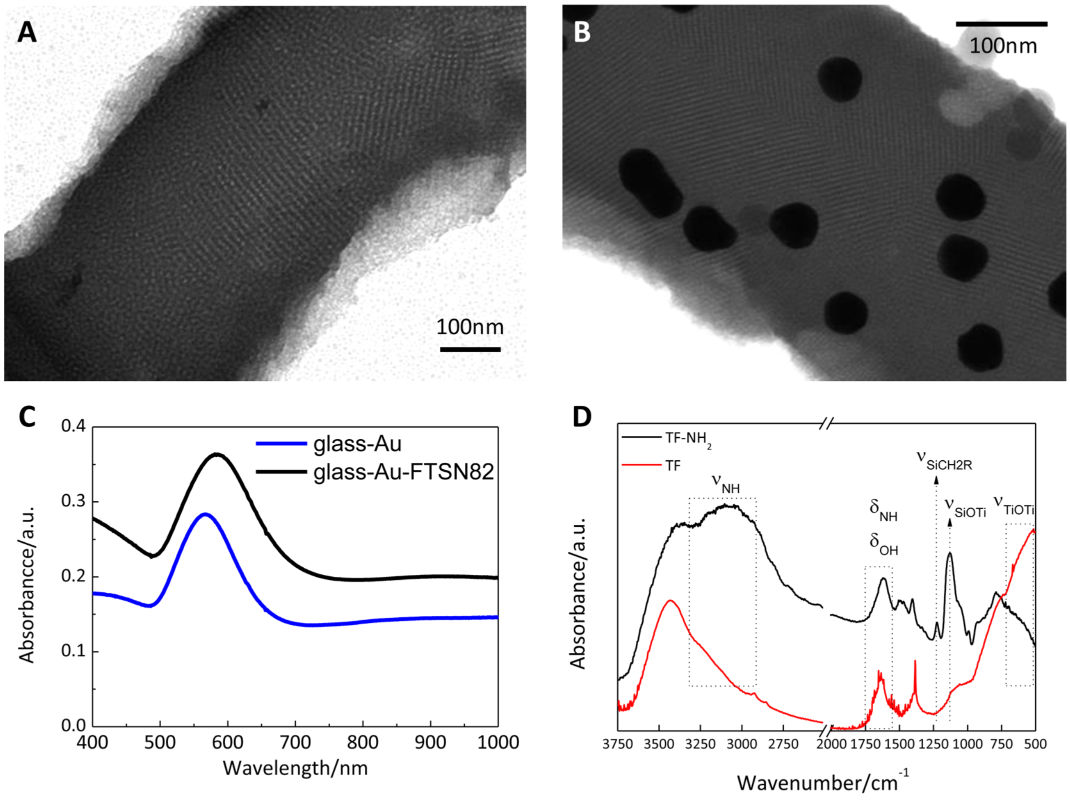

Figure 2. TEM images of a $TF-NH_2$ mesoporous thin film (A) without and (B) with 80 nm GNP. (C) UV−vis−NIR spectra of the substrate before and after $TF-NH_2$ mesoporous film deposition. (D) FTIR spectra of $TF-NH_2$ and TF mesoporous thin films.

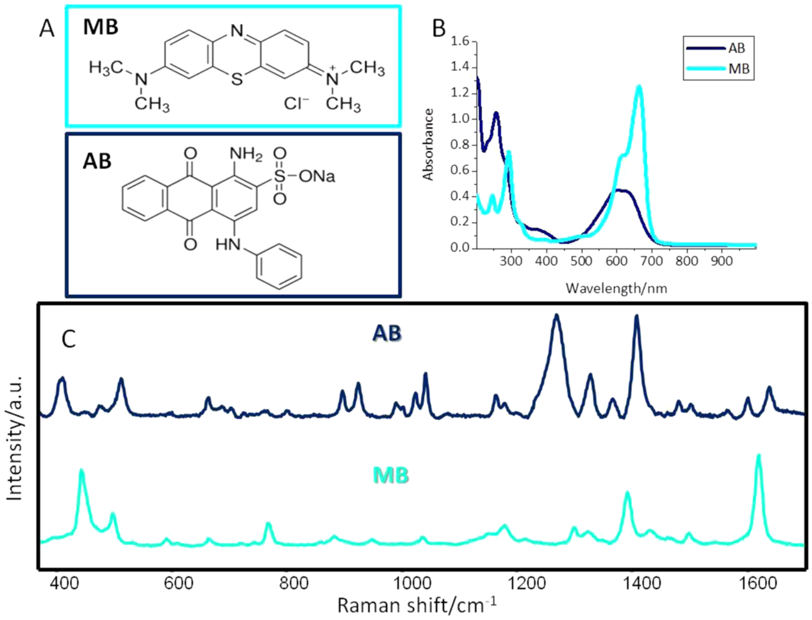

Figure 3. (A) Molecular structure, (B) UV−vis−NIR spectra, and (C) Raman spectra of acid blue and methylene blue.

to adsorbed water centered at 1650 cm^{-1}. The band at 1227 cm^{-1} corresponds with $\nu_{Si\text{-}CH2\text{-}R}$, demonstrating the presence of Si-CH_2 bonds in the hybrid material. The band corresponding to the Si−O−Ti inorganic framework can be observed at 1060 cm^{-1}, indicating a uniform distribution of the organosilane within the mesoporous matrix. These last two bands are not present in the TF sample, prepared without amino-silane. Finally, the broad band starting at 800 cm^{-1} corresponds to Ti−O and Ti−O−Ti bonds and is evident only in the TF sample, demonstrating once again the mixed oxide nature of the TF-NH_2 sample.[35]

Selective molecular diffusion through the functionalized mesoporous film was demonstrated using two different dyes: a more acidic dye, Acid Blue (AB), and a more basic dye, Methylene Blue (MB). These dyes thus present different affinity toward the amino functional groups anchored in the pores both due to electrostatic and specific interactions. In particular, it has been previously reported that amino-modified mesoporous materials have a strong affinity and a large adsorption capacity for acidic dyes like AB but not for basic dyes like MB.[36] Interestingly, the same dyes have been frequently utilized as standard probes for Raman scattering (see the molecular structures in Figure 3A). Also shown in Figure 3 are the UV−vis−NIR spectra showing the characteristic absorption bands for AB and MB, as well as the corresponding Raman spectra of pure dyes collected by excitation with a 785 nm laser line.

We first evaluated the accessibility of the embedded GNP by external molecules, through the porous film. Two pieces of the same TF sample were thus immersed in 1 μM solutions of AB and MB at pH 6 overnight and subsequently rinsed with water, air-dried and characterized by SERS. In both cases, the corresponding SERS signals were recorded, as expected (Figure S2b, d). We thus conclude that both molecules can readily diffuse through the TF pores and reach the surface of underlying GNP, where the plasmon resonance can enhance the corresponding Raman scattering. It should be noted that molecular adsorption experiments are performed within a pH range for which a slightly negative charge develops on the titania surface.[37] The observation of a clear SERS signal for AB suggests that a significant amount of these molecules are in close contact with GNP, even if an electrostatic exclusion effect could be expected for these negatively charged species, while confirming the high sensitivity of the Au-mesoporous oxide nanosystem.

Before proceeding with the selectivity experiments, the homogeneity of the substrates were tested using an aqueous solution containing AB (pH 2) and MB (pH 6), both at a concentration of 1 μM. SERS mapping of TF-NH_2 was carried out using the 785 nm laser line, which yielded a homogeneous signal intensity over the entire surface (Figure S6). This signal homogeneity, desirable for analytical applications, is in line with the one previously found for other SERS substrates based on mesoporous thin films.[38] We additionally evaluated the influence of analyte concentration on SERS signal intensity by immersing the TF-NH_2 substrate overnight in an aqueous solution of MB with different concentrations, at pH 6. As shown in Figure S7, the data could be perfectly fitted to a Langmuir isotherm. The calibration was carried out by plotting the intensity of the vibrational band at 447 cm^{-1} vs MB concentration. Each point in the plot represents the average signal from 30 spectra and the standard deviation is represented by the corresponding error bars.

Selective detection was then probed using the TF-NH_2 sample for a proof-of-concept experiment. A piece of TF-NH_2 was first immersed in an AB solution (1×10^{-6} M, pH ~6) but no SERS signal could be observed (Figure S2a), whereas immersion of a second piece of TF-NH_2 in an MB solution (1×10^{-6} M, pH ~6) followed by SERS analysis did yield the characteristic signals of MB (Figure S2c). This behavior can be explained taking into account the strong affinity of AB for amino groups,[36] which prevents its diffusion through the pores, meaning that the molecules are not able to reach the plasmonic nanoparticles surface. These experiments demonstrate that organically functionalized mesoporous films are suitable to prevent diffusion of molecules with high affinity for the functional groups present in their pores. Interestingly, as the amino groups in the material are limited by synthesis

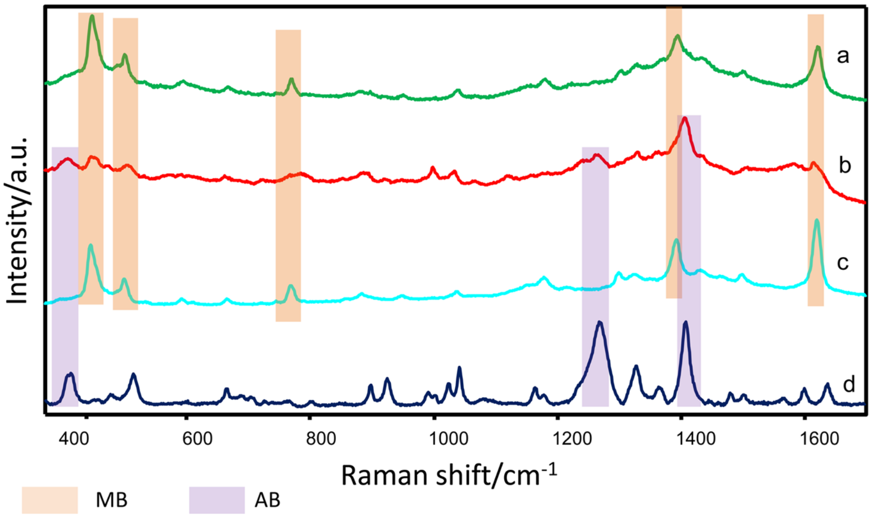

Figure 4. SERS spectra from a mixture of AB and MB in contact with (a) TF-NH_2 and (b) TF films, compared with the SERS spectra from single dye solutions of (c) MB and (d) AB.

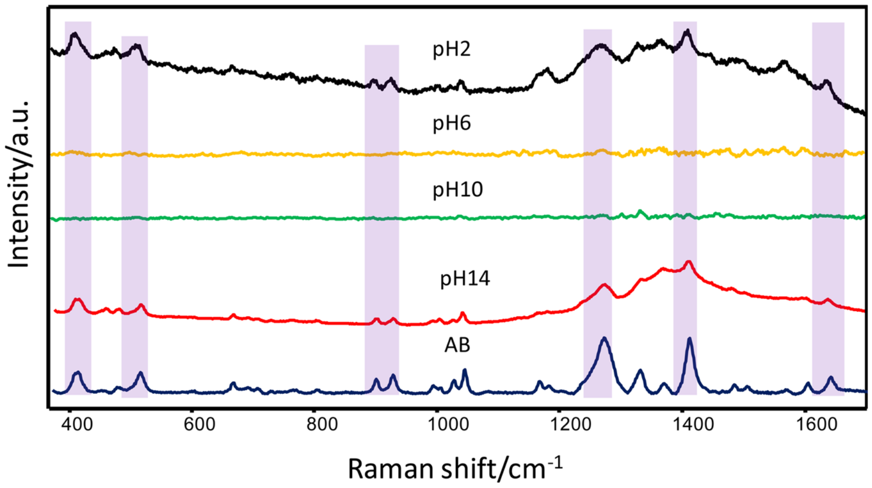

Figure 5. SERS spectra of AB at different pH values, in contact with TF-NH_2 mesoporous thin films compared with the Raman spectrum of pure AB. The most characteristic peaks are highlighted with violet bars.

conditions, there is an AB concentration ($>1 \times 10^{-4}$ M) for which part of the dye can reach the GNP and be detected. For these concentrations, all the accessible amino groups in the mesoporous film are compromised in the specific interaction with AB and thus, the extra amount of AB can be detected.

Even more interesting is the potential ability of the hybrid mesoporous thin film as a selective sensor that can differentiate individual components within a mixture by means of SERS spectroscopy. We tested this by immersing a TF-NH_2 sample in a mixed solution containing AB and MB (1×10^{-6} M, pH ~6) and the results are displayed in Figure 4a. In agreement with the above-mentioned strong affinity of AB molecules for the organic molecules present in the pores, they cannot reach the GNP surface because they are chemically trapped by the amino groups. Therefore, only the MB molecules can diffuse and reach the gold surface, so their characteristic SERS signature is recorded. As a control, the same experiment was carried out using TF films, in which case both dyes were found to readily pass through the pores reaching the gold surface, as indicated by the presence of their characteristic SERS signals in the spectrum (Figure 4b). This confirms that the presence of amino groups is responsible for blocking the diffusion of AB, so that only MB can reach the SERS active gold surface. In other words, it is possible to control the diffusion behavior of a given molecule in the pore system through rational functionalization of the pore wall with tailorable organic groups, leading to a selective SERS-based sensor.

Solution pH is an important parameter that affects the surface charge of functionalized mesoporous thin films as well as the degree of ionization of the molecules present in solution. The amino groups at the mesoporous thin film can be either protonated or deprotonated, resulting in different surface charge as a function of pH, thus becoming a stimulus-responsive surface. Amine functionalization of mesoporous hybrid thin films and their environmental response was thoroughly studied by Calvo et al. through systematic XPS studies,[7,28] which revealed the presence of two different sites corresponding to amine and ammonium groups. The corresponding molar ratio, R = $[NH_3^+]/[NH_2]$, was found to decrease when the external pH was increased.[28] We exploited such a pH dependence to demonstrate an additional example of selective detection that can be tuned by simply changing the pH of the sample. A TF-NH_2 sample was thus introduced in a solution of the corresponding dye at different pH values. In the

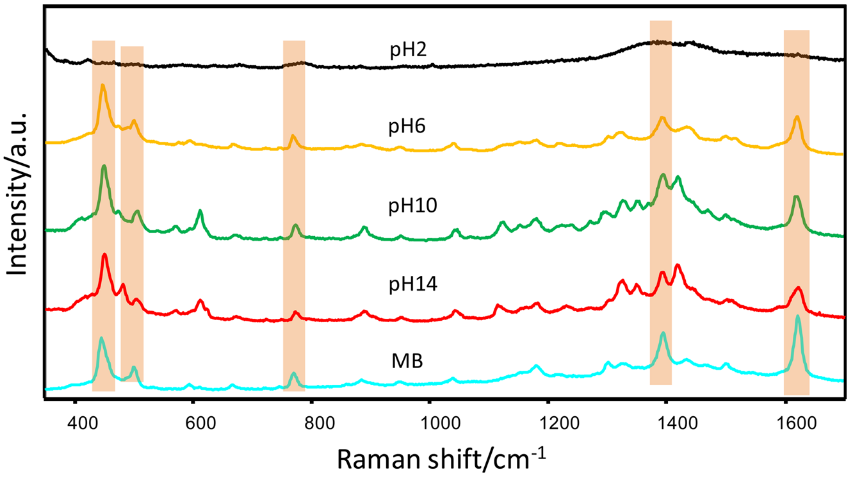

Figure 6. SERS spectra of MB at different pH values, in contact with TF-NH_2 mesoporous thin films compared with the Raman spectrum of pure MB. The most characteristic peaks are highlighted with orange bars.

case of AB, the strong affinity toward amino-containing surfaces results in SERS detection under extreme pH values only (Figure 5). At pH 2, the dye presents a positive charge due to protonation of the amino group in the molecule, but also a negative charge because of a deprotonated sulfonate group. Therefore, AB presents neutral charge at this pH and it cannot be retained by the positively charged protonated amino groups on the mesoporous thin film. The dye can thus diffuse through the pores, reach the GNP and be detected by SERS. At pH 14, the dye presents negative charge due to deprotonation of sulfonate groups and cannot be retained by uncharged pores (amine groups are present at this pH), reaching the GNP surface and also being detected. At intermediate pH values such as 6 and 10, the dye cannot be detected by SERS (Figure 5) because it is retained by ammonium groups on the pore walls, both by specific interactions[36] and electrostatic interactions between positively charged protonated amino groups on the mesoporous thin film and negatively charged sulfonate groups ($-SO_3^-$) in AB molecules. Again, a control experiment was carried out using nonfunctionalized mesoporous thin films. A TF sample was immersed in AB solution at different pH values, and the results confirmed that, in the absence of amino groups, AB molecules can diffuse through the film and reach the gold surface at all selected pH values (Figure S3). The AB characteristic vibrational bands were observed in all cases, regardless of solution pH (Figure S5).

A similar pH-dependent study was carried out for MB, which has no particular affinity toward the amino-functionalized pores. As shown in Figure 6, only for pH 2 we were unable to detect the dye. According to the acid−base equilibrium of MB represented by $MBH^{2+} \leftrightarrow MB^+ + H^+$ and its low pK_a value (3.8), at such acidic pH the dye presents a high positive charge (MBH^{2+})[39] and the percentage of positively charged adsorbent sites increases.[28] Because of the strong electrostatic repulsion between positively charged dye and the hybrid mesoporous thin film, MB cannot diffuse and, as a consequence, it cannot be detected. As the pH of the solution is increased, the ammonium/amine ratio in the functionalized mesoporous thin film decreases, leading to a decrease in the positive charge of the pores surface. Additionally, the positive charge of MB also decreases, so that the electrostatic repulsions will be reduced and the cationic dye is allowed to diffuse through the film and reach the metal surface, where the characteristic Raman scattering signals of MB are enhanced (Figure 6). As previously shown for AB, no variation of the Raman signals at different pH values was observed (Figure S5). The results for a control experiment with a TF sample are presented in Figure S4, showing that the dye can always reach the GNP, again demonstrating the key importance of amino groups on the selective character of the material.

CONCLUSIONS

In summary, we have demonstrated the performance of a hybrid material comprising metal nanoparticles embedded in functionalized mesoporous thin films as a selective SERS based sensor platform. The presence of specific functional groups in the pore network allowed us to control the surface chemistry of the pores, thereby tuning the selectivity toward specific molecules. In the present proof of concept experiments, we used amino-functionalized hybrid mesoporous thin films to discern the presence of methylene blue, in a mixture with acid blue, with no need for any pretreatment step. Selective detection was possible through entrapment of AB in the mesoporous matrix, based on high affinity for the amino groups. We additionally used the amino functionality to create a pH-responsive surface that allowed pH-selective SERS-based sensing.

By simply changing the nature of the hybrid oxide used to build the substrate, the results presented here can be readily expanded to the detection of any selected molecule in a mixture with other molecules having higher chemical or electrostatic affinity toward the mesoporous matrix. In addition, more complex systems such as polymer-modified or multilayer thin film architectures could be designed in order to attain selectivity in more complex mixtures. Thus, these results broaden the range of possibilities to design hybrid materials as versatile functional units for simple selective detection in complex matrixes using SERS spectroscopy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b10543.

UV−vis−NIR of the GNP in solution, SEM images of the obtained hybrid materials, SERS spectra of AB and MB in contact with TF-NH_2 and TF samples, SERS spectra of AB and MB in contact with TF sample at different pHs and Raman spectra of AB and MB at different pHs, SERS mapping of AB and MB on TF-NH_2 surface and SERS intensity as a function of MB concentration (PDF)

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Notes

The authors declare no competing financial interest.

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