INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is a powerful technique that merges the intrinsic features of Raman spectroscopy with the high sensitivity and enhancement that allows the detection of single molecules and is widely used in many fields due to its high surface sensitivity and applicability. In SERS, the enhanced Raman scattering comes mainly from the interaction of the plasmon band of metals, in the form of either roughened surfaces or plasmonic nanoparticles, with the adsorbed molecules. Nonetheless, SERS studies were generally limited to gold, silver, and copper until 2010, when Li et al. and co-workers developed shell-isolated nanoparticles for enhanced Raman spectroscopy (SHINERS). SHINERS consists of the use of shell-isolated nanoparticles (SHINs) with a core made of metals with surface plasmon resonance (SPR) properties in the visible region (usually gold, due to a straightforward synthesis route) covered with a suitable shell that fulfills the specific characteristics for this application. In general, the shell must be 1–4 nm thick, pinhole-free, nonporous, and electrochemically inert (for most applications), to both isolate the core and allow a large enhancement factor (EF) of the Raman signal to occur. SiO$_2$ shells thicker than 4 nm reduce or even block the enhancement, and the synthesis of a thinner shell is more complex and generally results in the formation of pinholes. On the other hand, SiO$_2$ shells also present some limitations for use in catalysis and electrochemistry due to their narrow pH stability (pH 7–11.5), short shelf life (approximately 2 weeks), and stability when used at elevated temperatures above 30 °C. Therefore, the development of new shell materials to cover metals with SPR properties in the visible region is currently an active field.

Alternative oxide coatings that have been reported include Al$_2$O$_3$, SnO$_2$, MnO$_2$, TiO$_2$, or ZrO$_2$. Al$_2$O$_3$ shells have proven to give similar results to SiO$_2$ coatings with similar shell thicknesses; however, they also dissolve at alkaline pH. Ultrathin MnO$_2$ shells obtained by reducing KMnO$_4$ using K$_2$C$_2$O$_4$ have been demonstrated to achieve greater Raman enhancement.

Shell-isolated nanoparticles (SHINs) with a 37 nm gold core and an 11 nm tin dioxide (SnO$_2$) coating exhibited long-life Raman enhancement for 3 months and a wide pH stability of pH 2–13 in comparison with conventional SiO$_2$-coated SHINs. Herein, Au-SnO$_2$ is demonstrated as a more durable SHIN for use in the technique Shell-Isolated Nanoparticles for Enhanced Raman Spectroscopy (SHINERS).
enhancement and pH stability in alkaline media than SiO$_2$ and Al$_2$O$_3$ shells. TiO$_2$ coatings obtained through the hydrolysis of titanium tetraisopropoxide have also been used in catalysis and shown to be highly thermally stable (up to 400 °C). Krajczewski et al. developed ZrO$_2$ shells by decomposing zirconium (IV) propoxide for use in SHINERS, which had previously been shown to provide a high pH stability in Ag-ZrO$_2$ nanoparticles. Tin(IV) dioxide (SnO$_2$) is also another promising shell material. It does not dissolve at highly acidic and basic pH, remains stable over a wide pH range of ca. pH 0 to 12 (from the Pourbaix diagram), and is also transparent in the visible range of the light spectrum, making it a practical material for optical coatings. Indeed, Burgess and co-workers reported on SnO$_2$-Au SHINs to study steel corrosion under alkaline conditions. SnO$_2$ coatings have been demonstrated to protect metals from corrosion for the duration of the experiments, remaining stable throughout the process. The nanoparticles were stored away from light sources to cool overnight at room temperature. The obtained nanoparticles was stirred for another 20 min and then allowed to cool overnight at room temperature. The obtained nanoparticle suspensions were stored away from light sources for the duration of the experiments, remaining stable throughout the process.

**Synthesis of SnO$_2$-Coated SHINs.** The coating of the gold nanoparticles was carried out by the precipitation method described by Mulvaney et al. with slight modifications. Details of the coating of the nanoparticles are as follows. Twenty-five milliliters of the gold nanoparticles (~0.226 nM) was diluted in 50 mL of distilled water (Milli-Q, 19 MΩ), placed in a round-bottom flask under strong stirring, and heated to 60 °C for 20 min in a hot water bath. The pH of the solution was adjusted to 11.4 with 1 M NaOH (≥98%, Sigma-Aldrich) to permit the precipitation of SnO$_2$. Since bigger nanoparticles were used for this synthesis (37 vs the 15 nm NPs from the Mulvaney et al. protocol), a higher pH (11.4) was set to ensure that the pH will remain over 10.5 once the precursor was added. Different volumes of 0.2 M sodium stannate trihydrate (Na$_3$SnO$_2$·3H$_2$O) (95%, Sigma-Aldrich) were added quickly to achieve nucleation of SnO$_2$ on the surface of the gold nanoparticles. The solution was kept at 60 °C until the shell reached the desired thickness. To check the effect of temperature and pH on the shell formation process, three synthesis procedures were performed with the following details: (1) following the previous description at 60 °C, (2) at 80 °C, and (3) following the above description but skipping the pH adjustment step, giving rise to a final solution pH of 3.5.

**Characterization.** Raman measurements were carried out with a Raman microscope (Renishaw InVia), using a 785 nm laser with an exposure time of 10 sec. Raman spectra were calibrated vs the 520 cm$^{-1}$ peak of Si with a resolution of 1.1 cm$^{-1}$. For Raman pinhole tests, 5 μL of SnO$_2$-coated SHINs (~1.13 nM) was deposited onto a silicon wafer (Si(100), Agar Scientific) by drop casting. Then, 2 μL of a 10 mM pyridine (99.8%, Sigma-Aldrich) solution was dropped on top of the deposited NPs. Enhancement tests were similarly performed, but using a gold film on silicon substrates (Au(111), Platypus Technologies).

The structure, surface morphology, average particle of the SHINs, and shell thicknesses were measured by transmission electron microscopy (TEM). Images were recorded using a JOEL 2100F Cs-corrected microscope operated at 200 kV. Shell thicknesses, and nanoparticle sizes were determined using the software Gwyddion (Version 2.55). Samples were prepared from a dilute colloidal dispersion of synthesized nanoparticles (~0.226 nM), by evaporating ca. 10 μL on Lace Carbon Films on 300 Mesh Copper Grids (Agar Scientific). In all, 20–50 nanoparticles were measured in each case to obtain the shell thicknesses and nanoparticles sizes’ mean and standard deviation values.

To determine the possible influence of the pH during the synthesis on the chemical properties of the SnO$_2$ shell, X-ray photoelectron spectroscopy (XPS) was used to study the oxidation state of SnO$_2$. Measurements were performed using a Thermo Fisher Scientific NEXSA spectrometer with a micro-focused monochromatic Al K$_α$ source (1486.6 eV). Low-energy electrons and Ar ions were used for charge neutralization. Photoelectrons were measured at a pass energy of 40 eV for core levels and 200 eV for survey spectra, with an energy step size of 0.1 and 1 eV, respectively. These measurements were performed at a base pressure of 5 × 10$^{-8}$ mbar. XPS measurements were repeated using a different spectrometer and were found to be consistent. Measurements from the second spectrometer are shown here. The spectrometer consists of a SPECS monochromatic Al K$_α$ x-ray source (1486.6 eV) operating at 250 W and a hemispherical PSP Vacuum Technology electron-energy analyzer operating with a pass energy of ~10 eV. Calibration was performed using a silver sample, enabling the energy resolution of 0.4 eV to be determined by fitting the Fermi edge data. The base pressure of this system was 1 × 10$^{-10}$ mbar.
Samples were prepared from 10 μL of the core/shell nanoparticles dispersion (~1.13 nM) deposited and evaporated at room temperature until fully dry in silicon wafer (Si(100), Agar Scientific). To form a thick layer, the deposition was repeated 3–6 times to achieve greater coverage of the substrate. Peaks were simulated with combined profiles of Gaussian-Lorentzian functions, and a Shirley background was used to model the inelastic scattering of photoelectrons. The accuracy of the measurements was ±0.1 eV. In the analysis of Sn 3d XPS spectra, Sn^{2+} and Sn^{4+} oxidation states were considered. Sn 3d_{5/2} and Sn 3d_{3/2} peaks, separated by 8.4 eV, with a 3:2 peak intensity ratio, and equal full width at half maximum (FWHM) values, were represented by GL (30) functions. High-resolution spectra for O 1s were also analyzed.

Powder X-ray diffraction (PXRD) patterns were collected, and crystallite size was calculated for Au–SnO\(_2\) SHINs. \(2\theta\) patterns were collected in the angular range 20° ≤ \(\theta\) ≤ 90° in steps of 0.01° using a Rigaku SmartLab diffractometer. Samples were prepared from 10 μL of the core/shell nanoparticles dispersion (~1.13 nM) deposited and evaporated at room temperature until fully dry in plain 0.8 mm thick glass slides. To form a thick layer, the deposition was repeated 3–6 times to achieve greater coverage of the substrate. Crystallite sizes of Au and SnO\(_2\) were calculated using Scherrer equation (eq 1).

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]  

where \(D\) is the crystallite size, \(k\) is the Scherrer constant depending on the crystallite shape, \(\lambda\) is the wavelength of the X-ray source (1.541 Å for Cu), \(\beta\) is the FWHM in radians, and \(\theta\) is the Bragg angle corresponding to the peak position in radians. Three main peaks for the SnO\(_2\) shell (JCPDS 41–1445), corresponding to the (110), (101), and (211) planes were used to calculate the crystallite sizes. Correspondingly, crystallite size calculations for Au nanoparticles (JCPDS 89–3697) were performed by employing peaks relative to the (111), (200), and (220) planes. The reported crystallite sizes correspond to the average values between those calculations.

## RESULTS AND DISCUSSION

Characterization of SnO\(_2\) shell and synthesis. Tin dioxide (SnO\(_2\))-coated nanoparticles were synthesized by the hydrothermal method given in the Experimental section and described in the literature\(^{23,31}\), using 37 ± 5 nm Au NPs (See Figure S1 in Supporting Information) as nuclei for the SHINs. To study the effect of pH and temperature in the formation of SnO\(_2\)-coated Au NPs and optimize the synthesis of SHINs, SnO\(_2\) shells were obtained at pH 3.5 at 60 °C, pH 11.4 at 60 °C, and pH 11.4 at 80 °C and samples were taken at different reaction times. The TEM results in Figure 1 show images of the coated NPs after 240 min reaction time, and the characteristics of the syntheses are displayed in Table 1.

| pH     | 3.5 | 11.4 | 11.4 |
|--------|-----|------|------|
| temperature | 60 °C | 60 °C | 80 °C |
| time reaction | 240 min | 240 min | 240 min |
| Na\(_2\)SnO\(_3\) concentration | 15 mM | 8.04 mM | 1.81 mM |
| SP band position | 542 nm | 565 nm | 565 nm |
| shell thickness | 2.6 ± 1.2 nm | 23.7 ± 3 nm | 53.7 ± 5.8 nm |

A different shell morphology for all three different conditions is observed in Figure 1. The slow growth of a thin shell on the samples at pH 3.5 suggests a pH-dependent formation of SnO\(_2\) consistent with previously reported protocols\(^{31}\) for core/shell SnO\(_2\) particles where an alkaline pH is crucial for SnO\(_2\) precipitation. At pH 11.4, thicker, more porous shells are observed at 80 °C due to a faster reaction kinetics at this temperature compared to 60 °C. It has been reported\(^{45–47}\) that the position of the absorption band is directly related to the shell thickness. Thicker shells exhibit increased scattering and have larger optical cross sections and red-shifted bands. However, the absorption band also depends on the refractive index and density of the shell.\(^{31,47}\) In this framework, it would be expected that more porous shells have a lower density, and a lower shift on the absorbance peak compared to citrate-stabilized Au NPs. This is supported by the TEM images of the SnO\(_2\)-coated Au NPs (Figure 1). Despite the samples at pH 11.4 presenting the same absorption band position (~565 nm) (Figure S3), neither the thickness of the shell (Table 1) nor the granular texture under TEM agrees, proving UV–visible measurements alone to be an unsuitable method to characterize the shell thickness of SnO\(_2\)-Au SHINs.

Only those SnO\(_2\)-coated nanoparticles whose coating was synthesized at 60 °C did not present any pinholes (Figures S4 and S5), implying that the synthesis conditions are the key to achieve suitable SHINERS. A high-intensity enhancement is detected in the pinhole-free samples after a reaction time of 80 min and at an Na\(_2\)SnO\(_3\) concentration of 8.04 mM. This enhancement diminishes as the reaction time increases, suggesting an enlargement in shell thickness consistent with TEM images (Figure S3). SHINs with thinner shells obtained at pH 3.5 present a larger enhancement of the Raman signal as
the distance between the plasmonic nanoparticles is shorter, however, pinholes are detected in those cases (Figure S4). The porosity of the shell could explain the presence of pinholes even in SHINs with the thickest coatings at 80 °C.

### Surface Analysis of SHINs

Differences in shell thickness because of pH media may occur due to the amphoteric nature of SnO2 in aqueous solutions, with a point of zero charge (pzc) around either pH_{pzc} 4.3 or 6.0. Regardless of the exact value, a positive surface charge is expected at a pH <pzc, affecting the reactions taking place at the SnO2 surface. Considering the formation of the SnO2 shell by eq 2, the positively charged surface of SnO2 at pH 3.5 would be responsible for the slower shell growth under these conditions, due to the surface electrostatic repulsion of Sn^{4+} cations.

\[
\text{Sn}^{4+} + 4\text{OH}^- \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} \tag{2}
\]

The XPS signals of Na 1s and Na 2s in the survey spectra and a feature at 497.5 eV for the Sn 3d spectrum corresponding to the Na KLL Auger line are also observed at pH 3.5 (Figures S6 and S7) from the NaSnO3 precursor used in the synthesis. Changes in the surface charge have been explained according to eqs 3 and 4. An alternative proposed mechanism includes the metal reduction accompanied by the simultaneous proton intercalation into the oxideSnO2+e^- + H^+ + SnO(\text{OH})
\tag{5}

Figure 2 presents the XPS spectra of SnO2-coated gold nanoparticles synthesized at different conditions. According to the literature, commonly reported values for the binding energies (BE) and FWHM of Sn 3d_{5/2} and O 1s signals for non-intentionally doped SnO2 are 486.9 (1.04) and 530.8 (1.7) eV, respectively. Consistently, the results displayed in Figure 2 agree with the literature, confirming that the shell is exclusively composed of Sn^{4+} oxidized species (SnO2). The O 1s core-level position implies that the Fermi level (E_F) is at the SnO2 conduction band minimum. In contrast, the shift of the O 1s core-level emission of the sample synthesized at pH 3.5 can be explained by the intercalation of Na^{+} cations on the SnO2 shell as previously explained. Charge transfer from the SnO2 shell to the Au core is expected due to the large difference between the E_F of Au and that of SnO2 depending on the pH. During the shell growth around the Au cores, the charge transfer would induce a blue shift in the surface plasmon (SP) band position, as electrons are injected into the Au surface atoms. This fact may also explain the differences in the position of the SP band during shell syntheses (Figure S3) since the final position is the resultant from two, contrary, contributions: a red shift as the shell grows because of the change in the surrounding refractive index, and a blue shift due to the charge transfer from the SnO2 to Au surface.

Analysis of the PXRD patterns of SnO2 shows a crystallite size of ~2.0 ± 0.5 nm for SnO2 shells obtained at pH 3.5, while the samples at pH 11.4 present a crystallite size of ~5.6 ± 0.6 nm (Figure S8). A smaller crystallite size for the samples obtained at lower pH (3.5) reveals a lower crystallinity of the shell than for the samples at alkaline pH that could affect the growth of the shell. The lower crystallinity may also be affected by the Na+ doping that occurred at acid pH.

These results confirm the formation of SnO2 shells around the Au core and demonstrate that a high pH (11.4) is essential for the growth of the shell regardless of the temperature. A lower pH (3.5) leads to the formation of thin, Na+-doped SnO2 shells with pinholes, while at a higher pH (11.4), thicker, undoped SnO2 shells are obtained. The analysis highlights that slight changes in the synthesis protocol allow the design of SHINs targeted for each experiment, with pH 11.4 and 60 °C being the best option to obtain pinhole-free SnO2-coated Au NPs suitable for SHINERS.

### SnO2-Coated Au Nanoparticles for SHINERS

SnO2-coated Au NPs for use in SHINERS with highest enhancement were obtained at pH 11.4 and 60 °C with a precursor concentration of 8.04 mM after 80 min reaction time. The quality of the shells for use in SHINERS was studied by the pinhole test and magnitude of the enhancement in the Raman signal. For assessing these two properties, pyridine was employed as a probe molecule and the resultant spectra are summarized in Figure 3.
The adsorbed pyridine presents characteristic vibrational modes at 1016 and 1040 cm$^{-1}$, corresponding to the ring breathing mode and asymmetric stretch, respectively. In Figure 3a, no Raman signal from the adsorbed pyridine is observed in the Raman spectrum of SHINs onto a Si wafer, while high-intensity pyridine bands appear in the Au wafer consistent with a pinhole-free shell suitable for SHINERS. As previously reported, the enhancement of the Raman signal depends on the distance between the Au core and the surface, so there is a direct relationship between the intensity of the Raman signal and the thickness of the shell (Figure S9). According to the literature, SiO$_2$ shells greater

Figure 3. Raman signal of the pyridine molecule (top left) on SnO$_2$-Au SHINs (pH 11.4 at 60 °C with a precursor concentration of 8.04 mM after 80 min reaction time) absorbed on Si (black line) and Au (red line) wafers (a). Enhancement test of SnO$_2$-Au SHINs with 11 ± 3 nm (black line), 19 ± 4 nm (red line), and 24 ± 3 nm (blue line) shell thicknesses measured by TEM (b). TEM image of a 11 ± 3 nm shell SnO$_2$-Au SHIN (identical synthesis conditions as described for (a)) (c).

Figure 4. Comparison of the enhancement performance of SnO$_2$ SHINs (a) vs SiO$_2$ SHINs (b) and pinhole tests of SnO$_2$ SHINs (c) and SiO$_2$ SHINs (d) with a Raman laser wavelength of 785 nm.
than 10 nm exhibit no Raman enhancement at all. However, SnO$_2$-coated Au NPs with a pinhole-free, 11 ± 3 nm shell offer a similar enhancement to SiO$_2$-coated SHINs with a 3.2 ± 0.4 nm shell (Figures S10–S12), suitable to detect adsorbed species in electrode surfaces. Consequently, pinhole-free, functional SnO$_2$-Au SHINs are obtained at 60 °C and show Raman signal increase with shells up to 19 ± 4 nm thick when the enhancement diminishes (Figure 3b). This fact notably would facilitate the synthesis process of the SHINs, since the range of shell thickness that allows an enhancement in SnO$_2$-Au SHINs (11–19 nm) is greater than that for SiO$_2$-coated SHINs (1–4 nm).

The physical origin for the increase in the Raman signal, especially when the shell is over 10 nm thick (Figure 3c), is not yet determined. The loss of the Raman signal intensity of pyridine (Figure 3b) when the shell thickness increases confirms a strong electromagnetic field gradient$^{50}$ induced by the gold core on the SnO$_2$-Au SHINs, but this is unlikely to explain all of the observed enhancement. Beyond the independent SERS effect of Au, an enlargement of the Raman signal attributed to charge transfer (CT) between the SnO$_2$ conduction band orbital and an acceptor or donor molecular orbital of the adsorbed pyridine has also been reported.$^{51}$ Nevertheless, the contribution of each type of enhancement is complex to determine, since other factors such as porosity of the shell and size of tin dioxide particles may play an important role in the optical properties of these materials.$^{62}$

The functional shelf life of SnO$_2$-Au SHINs compared with SiO$_2$-Au SHINs was studied under different storage conditions (Figure 4 and Figure S13). When the enhancement of the Raman signal is analyzed, no significant changes in the Raman signal intensity three months after the synthesis are observed for the deposited SnO$_2$-Au SHINs (Figure 4a). An increase in the intensity of the Raman signal for SiO$_2$-Au SHINs (Figure 4b) can be explained by the adsorption of pyridine onto the Au core after pinholes are formed on the shell. Moreover, SnO$_2$-Au SHINs presented no pinholes after 90 days (Figure 4c), SnO$_2$-Au SHINs showed pinholes after 15 days (Figure 4d), indicating a greater durability for SnO$_2$ shells compared to SiO$_2$ coatings. Furthermore, a wider pH stability range for SnO$_2$-Au SHINs is observed (pH 2–13) compared to the SiO$_2$-Au SHINs (pH 4–11) (Figure S14), in agreement with the literature for SnO$_2$ coatings in core/shell nanoparticles.$^{23}$

While SiO$_2$ shells dissolve at extreme pH, SnO$_2$-Au SHINs present a full recovery of the SPR band upon pH neutralization when the negatively charged SnO$_2^-$ surface is recovered.$^{23}$ These results represent a great advancement in the development of SHINs and imply, in addition to an increase in the applicability of SHINERS for alkaline and acidic systems, a greater ease for their synthesis and a lower frequency of synthesis, increasing the reproducibility of studied systems for academic purposes, and facilitating their wider use within the industry.

The increase in the Raman intensity of the bands at 1016 and 1040 cm$^{-1}$ for SiO$_2$ SHINs 3 months after their synthesis can be tentatively explained by direct contact of the pyridine with the Au core due to the pinholes on its surface. The rise in intensity of the pyridine bands is accompanied by the appearance of numerous additional bands at 930, 1128, 1160, and 1190 cm$^{-1}$, which highlighted the degree of sensitivity to potential trace contamination once the pinholes form.

### CONCLUSIONS

Uniform, monodispersed, spherical, ca. 37 ± 5 nm Au NPs encased in SnO$_2$ with a controlled shell thickness were prepared at pH 3.5 and 11.4, at 60 and 80 °C. The preparation of SnO$_2$-coated Au NPs at pH 11.4 and 60 °C led to the formation of an approximately 11 nm thick, pinhole-free SnO$_2$ shell, which was suitable for SHINERS. The SnO$_2$-Au SHINs provided comparable Raman enhancement to the 3 nm thick SiO$_2$ shells, due to the SnO$_2$ SERS signal attributed to charge transfer and an SPR enhancement from the gold core. SnO$_2$-Au SHINs were studied after three months and showed greater durability than SiO$_2$-Au SHINs, exhibiting the same Raman enhancement as that of freshly prepared SnO$_2$-Au SHINs and, importantly, without the presence of pinholes. Moreover, SnO$_2$-Au SHINs offer higher pH stability (pH 2–13 vs pH 7–11.5 for SiO$_2$ shells) and a longer lifetime than the widely used SiO$_2$-Au SHINs, thus enabling the use of SHINERS within a wider range of electrochemical and catalytic environments.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c02432.

TEM images of citrate-stabilized Au NPs and Au–SnO$_2$ SHINs are given in the SI; pinhole and enhancement test results with both pyridine and rhodamine-6G are presented; UV–visible spectra, XPS and XRD results are shown for all different synthesis conditions used; enhancement of Au–SnO$_2$, SHINERS under different storage conditions has been measured with Raman and results are displayed in the SI; pH stability of Au–SnO$_2$ SHINERS is shown along with Au–SiO$_2$ SHINERS (PDF).

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Notes
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