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Substantially enhanced Raman signal for inorganic-organic nanocomposites by ALD-TiO₂ capping

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Atomic layer deposition (ALD) enables conformal coating of various surface architectures with high-quality ultrathin films. Here we demonstrate how such 3–12 nm thick ALD-TiO₂ coatings can be used to substantially enhance Raman scattering of organic molecular layers embedded between thicker inorganic layers; our proof-of-concept data are for ~45 nm thick oxide-hydroquinone hybrid films.

Inorganic-organic hybrid materials are strongly emerging as a relevant option for exciting new multifunctional materials which in addition to showing e.g. different electrical, optical, magnetic, catalytic and protective properties should be environmental friendly, durable, flexible and light in weight.^{1–4} Owing to the great advances in their synthesis techniques, such state-of-the-art materials can soon be designed and fabricated with atomic/molecular level accuracy. Nevertheless, when considering hybrid materials that often consist of nano-sized components or even just atomic or molecular layers, conclusions regarding their compositions/structures are commonly based on experimental data obtained with characterization techniques working close to their resolution limits. Thus, to accelerate the pace of new-material development in the field of molecular-level engineered hybrid materials more sensitive characterization methods would be most welcome.

Raman spectroscopy is a useful tool for the characterization of a variety of materials including thin films⁵ but it is not sensitive enough to probe e.g. monomolecular organic layers embedded within an inorganic thin-film matrix, sometimes required for frontier applications of hybrid inorganic-organic thin films.⁶ Many different techniques to enhance the Raman signal have been established e.g. using colloidal nanoparticles

in the analyte solution, or choosing a proper substrate material and/or modifying the surface nanostructure.^{7–11} Different mechanisms for the signal enhancement have been identified such as surface-enhanced Raman spectroscopy (SERS), surface-enhanced resonance Raman spectroscopy (SERRS) and interference-enhanced Raman spectroscopy (IERS), the last-mentioned probably being most relevant to the case of inorganic-organic hybrid thin films. In IERS the maximal utilization of the beam intensity is achieved by enhancing the destructive interference of the incident light and the constructive interference of the scattered beams.^{12–15} Conell et al.¹³ introduced the multi-layered IERS substrate concept with the layer system, Al, SiO₂ and Te, where Al worked as a reflector, SiO₂ as a dielectric spacer layer and Te as a low-absorbing sample layer, and the low reflectivity was achieved by optimizing the thicknesses of the SiO₂ and Te layers. In IERS in general, the optimal layer thicknesses depend on the wavelength of the incident beam and the optical properties of the substrate and sample materials.¹⁴

The state-of-the-art atomic layer deposition (ALD) thin-film technique could offer new possibilities in precise modification of thin-film structures to enhance the Raman scattering. So far, there are only few ways ALD has been employed in Raman substrates, such as ALD-Al₂O₃ thin films on top of silver film-over-nanosphere substrates,¹⁶ ALD-TiO₂ thin films on polymer nanoparticles,¹⁷ as protective coatings for silver nanoparticles,¹⁸ and also as spacers that interleave metal layers;¹⁹ in all these cases, the goal was to develop better SERS substrates. At the same time, to the best of our knowledge, there are no efforts reported so far where the unique benefits of the ALD technique are fully utilized. ALD could be employed to deposit (at appreciably low temperatures in case of sensitive samples) Raman enhancing, simple or multilayer, thin films as an easily added ultrathin conformal coatings on e.g. new interesting inorganic-organic hybrid materials for which the active organic material quantities are too small to be detected with conventional Raman spectroscopy measurements. In such not-yet-realized applications, the form of the sample

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investigated should naturally not be limited to flat thin films but the coatings should be able to be applied onto essentially any imaginable sample surface architecture including (nano)particles, nanotubes, etc.²⁰

Here we report our proof-of-the-concept results for thin (~45 nm) inorganic-organic hybrid thin films fabricated by the strongly emerging combined ALD/MLD (MLD: molecular layer deposition) technique,^{21, 22} and then capped with an ultrathin (3-12 nm) ALD-grown TiO₂ coating to enhance the Raman signal of the organic species in the underlining hybrid thin film. The thus collected Raman spectra are shown to be essentially similar to the theoretical spectra predicted for the hybrid materials.

For our demonstration, we selected zinc- and titanium-based hybrid materials where the organic layer consists of benzene molecules. Such hybrid inorganic-organic thin films were grown from diethylzinc (DEZ), titanium tetrachloride (TiCl₄) and hydroquinone (HQ) precursors using ALD/MLD processes reported elsewhere in detail;^{23,24} the TiO₂ cap layer was deposited on top of a 43±2 or 46±2 nm thick inorganic-organic Ti-HQ and Zn-HQ hybrid thin film, see Figure 1. For the TiO₂ coating we used the well-established ALD process based on TiCl₄ and H₂O,²⁵ and deposited the cap layer at 170 °C, i.e. at the same temperature as used for depositing the inorganic-organic hybrid layers. It should be emphasized that this process (TiCl₄+H₂O) would work even at much lower temperatures at least down to 100 °C²⁵ such that the sample variety to be studied by our newly-developed technique could readily be extended to more temperature-sensitive materials.

The experimental Raman spectra for the two thin-film materials (Ti-HQ and Zn-HQ) and the substrate together with a theoretical Raman spectrum are displayed in Figure 2. In Panel A, we first show the theoretical Raman spectrum predicted for the TiO₂-HQ hybrid material (DFT-PBE0/SVP level of theory, see Experimental and Supporting Information). The experimental Raman spectra for Ti-HQ hybrid thin films with and without a TiO₂ cap layer of various thicknesses are shown in Panel B. Even the most intense peak (687 cm⁻¹) can be barely seen for the Ti-HQ hybrid thin film without the TiO₂ cap layer, while for the same film with an ALD-grown TiO₂ cap layer, the characteristic vibration bands of aromatic organic molecules and the C-O bond start to appear. In our experiments, we deposited 50-200 cycles of TiO₂ as a cap layer corresponding to a layer thickness of 3 to 12 nm, respectively. As seen in Figure 2B, with an increasing thickness of the cap layer the intensities of the Raman signals increase. With a 12-nm thick TiO₂ film on top of the hybrid film, the strongest Raman signal at 687 cm⁻¹ (1185 counts from the base line) can be easily observed, whereas the response of the plain hybrid thin film at the same wavenumber hardly stands out from the background.

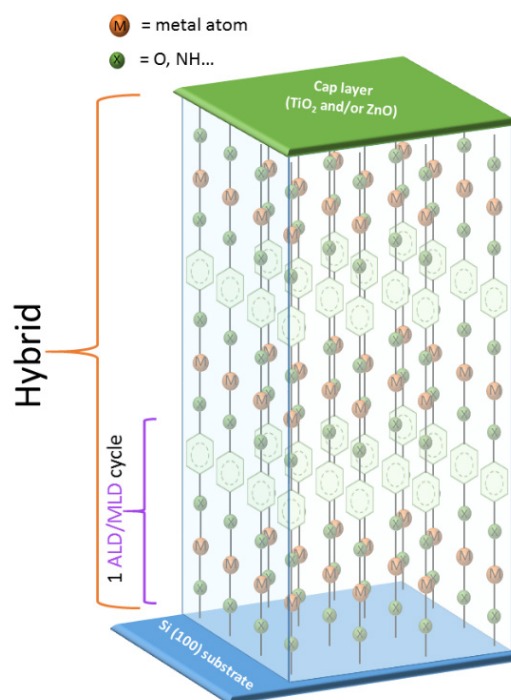


Figure 1. Schematic illustration of the inorganic-organic hybrid thin-film samples studied consisting of silicon wafer substrate, ALD/MLD-grown inorganic-organic hybrid thin film and ALD-grown oxide cap layer.

We moreover wanted to see whether the ALD-TiO₂ cap layer could improve the intensities of Raman signals from inorganic-organic hybrid thin films based on other metal constituents than titanium. For example, very recently novel ALD/MLD processes to deposit functional inorganic-organic hybrid thin films based on a number of new metal constituents such as Fe, Cu, Eu and Li have been developed for potential application in e.g. next-generation magnetic, optical and battery technologies,²⁶⁻²⁹ and Raman spectroscopy could be an important characterization technique for these layer-engineered hybrid thin films. Here, we decided to investigate the zinc-based hybrid. The 46-nm thick Zn-HQ hybrid thin film was first capped with a ZnO layer of 50 ALD cycles (~10 nm) to prevent the possible reactions of Zn-HQ with oxygen or water in the air. In Panel C of Figure 2 Raman spectra recorded for the ZnO-capped Zn-HQ film without and with an additional 6-nm thick ALD-TiO₂ cap layer are displayed. Figure 2C shows that the ZnO cap layer alone does not enhance the Raman signals of the organic molecules in the Zn-HQ hybrid thin film, whereas the TiO₂ layer does; for the TiO₂-capped Zn-HQ film the observed Raman spectrum is very similar to the theoretical Raman spectrum³⁰ predicted for the ZnO-HQ hybrid material and also to the experimental spectrum of Ti-HQ (See Table 1). Because many moisture sensitive materials require a protecting cap layer it is interesting to note that the Raman-enhancing effect of the TiO₂ coating is not deteriorated by the 10-nm thick intervening ZnO layer. Here, the Raman intensities due to the organic molecule are actually somewhat higher for the 6 nm TiO₂+10 nm ZnO-capped Zn-HQ hybrid films compared to those for the 6 nm TiO₂-capped Ti-HQ films (Figure 2 and Table 1).

Table 1. Experimental and theoretical Raman wavenumbers (ω) and measured intensities for different inorganic-organic hybrid thin films.

	Ring deformation		Ring deformation		Ring breathing		C-H bending		C-O stretching		C=C stretching	
	ω (cm^{-1})	Intensity (counts)	ω (cm^{-1})	Intensity (counts)	ω (cm^{-1})	Intensity (counts)	ω (cm^{-1})	Intensity (counts)	ω (cm^{-1})	Intensity (counts)	ω (cm^{-1})	Intensity (counts)
Cap layer												
Ti-HQ (43 nm)												
+ 6 nm TiO ₂	636	159	682	325	910	217	1154	254	1271	455	1587	308
+ 12 nm TiO ₂	634	492	687	1185	910	705	1152	850	1271	1150	1587	700
Theoretical TiO ₂ -HQ	633		678		916		1119		1353		1598	
Zn-HQ (46 nm)												
+ 6 nm TiO ₂	636	77	694	158	912	109	1152	133	1271	100	1582	111
+ 10 nm ZnO + 6 nm TiO ₂	631	184	695	369	912	239	1152	260	1264	200	1582	178
Theoretical ZnO-HQ	640		719		860		1134		1280		1610	

There are differences between the enhancing effects of the 6-nm thick ALD-TiO₂ coating depending on the growth surface. The enhancing effects obtained are greater for the Zn-HQ film samples capped with ZnO before the TiO₂ deposition than for the plain Zn-HQ hybrid. The enhancing effect between the Zn-HQ and Ti-HQ hybrid processes is more complicated to compare. In addition to different surfaces, the samples may contain different quantities of the organic molecule and titanium, the titanium content being obviously greater in the Ti-HQ hybrid material in comparison to Zn-HQ. In any case, the titanium in the Ti-HQ hybrid alone is not enough to enhance the intensity of Raman signals.

Finally, in Figure 2D we show the Raman spectrum measured for the Si substrate without and with a 36-nm ALD-TiO₂ coating (deposited at 170 °C); no features characteristic to anatase TiO₂ (639, 518, 512, 395, 198, and 143 cm^{-1})³¹ are seen. No diffraction peaks arising from the 36-nm ALD-TiO₂ coating were detected in grazing-incident x-ray diffraction (GIXRD) measurement either (data not shown), which means that the thinner TiO₂ coatings (6-12 nm) deposited on top of the hybrid Ti-HQ and Zn-HQ films should be amorphous, too.²⁵ Figure 2D shows that the ALD-TiO₂ cap layer increases the intensities of the Si substrate Raman signals as well.

The enhancing effect of TiO₂ in Raman spectroscopy has been studied previously but the mechanism is still not fully understood.^{17,32,33} For semiconducting materials such as TiO₂, the Raman enhancement is not due to surface plasmon resonance as in the case of plasmon-based SERS substrates such as coinage metals. One possible explanation is that the mechanism is related to a charge transfer (CT) from the semiconductor to the analyte.^{32,33} In the case of TiO₂ nanoparticles the specific surface area and the surface defects have been considered to affect the intensity of the Raman scattering.³³

In addition to the CT mechanism the optical properties of multi-layered thin-film structures should be noted. Alessandri et al.¹⁷ studied ALD-TiO₂ coatings on SiO₂ nano-spheres with the conclusion that the refraction index contrast between the particle and the coating may allow total reflection of the light inside the TiO₂ core shell and thus enable the enhancing effect in Raman signal by stacking the particles. In our case there is a contrast of the refractive indices between the hybrid material ($n \approx 1.95$)^{21,34} and the TiO₂ cap layer ($n \approx 2.5$)¹⁷. This would explain why ZnO ($n \approx 1.98$)¹⁷ alone does not work as a Raman-enhancing material for our inorganic-organic hybrid thin films. The reason why introducing the ZnO capping between the Zn-HQ hybrid and the TiO₂ coating seems to result in the higher intensity may lie in the different optical properties of the multi-layered systems, i.e. the thickness of the capping layer (TiO₂ vs. ZnO+TiO₂), additional ZnO layer with additional optical characteristics ($n \approx 1.98$)¹⁷ and different interface characteristics (e.g. roughness) between the sample surface and the cap layers, and between the cap layers. It is also possible that with certain thickness the TiO₂ film works as an antireflection coating providing destructive interference of the incident light.³⁵ This could explain the enhancement of the Raman signals from the silicon substrate.

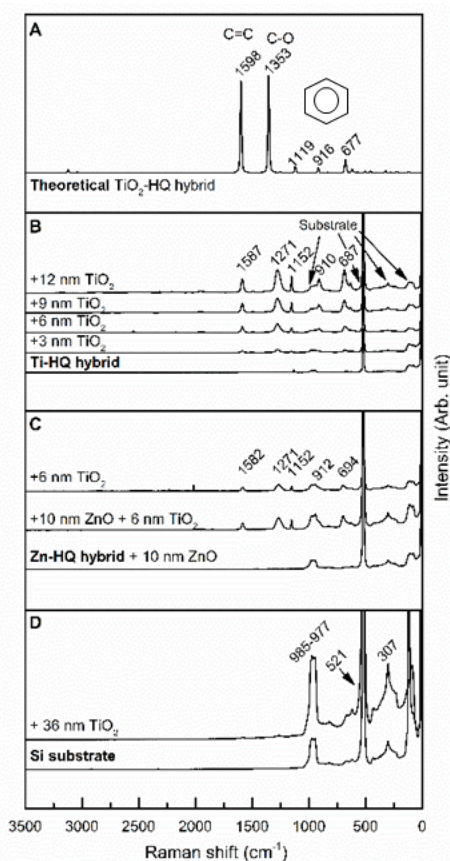


Figure 2. (A) Theoretical Raman spectrum for a TiO_2 -HQ hybrid material, and experimental Raman spectra for (B) Ti-HQ hybrid thin film (43 nm) without and with TiO_2 cap layers of different thicknesses (3, 6, 9 and 12 nm), (C) Zn-HQ hybrid thin film (46 nm) without and with a ZnO (10 nm) and/or TiO_2 (6 nm) cap layer, and (D) silicon substrate (Si(100)) without and with a TiO_2 cap layer (36 nm).

Experimental section

The ALD and ALD/MLD thin-film depositions were carried out in a hot wall ALD reactor (ASM Microchemistry, F120) at 170 °C. The hybrid thin films were deposited using titanium tetrachloride (TiCl_4 ; Sigma-Aldrich, $\geq 99.995\%$) or diethyl zinc (DEZ; Aldrich, 52 wt% Zn (minimum)) as an inorganic precursor and hydroquinone (HQ; Merck, 99.5%) as an organic precursor. The pulse sequence for the Ti-HQ and Zn-HQ hybrids were: TiCl_4 (1.5 s) : N_2 (3 s) : HQ (8 s) : N_2 (16 s) and DEZ (20 s) : N_2 (40 s) : HQ (25 s) : N_2 (50 s). The number of ALD/MLD cycles was 100 for both the Ti-HQ and the Zn-HQ depositions. The growth-per-cycle (GPC) values for the hybrid thin films were 4.3 ± 0.2 and 4.6 ± 0.2 Å/cycle. The pulse sequences for the ZnO and TiO_2 inorganic cap layers were: DEZ (1.5 s) : N_2 (3 s) : H_2O (2 s) : N_2 (2.5 s) and TiCl_4 (1.5 s) : N_2 (3 s) : H_2O (2 s) : N_2 (2.5 s). The GPC values for ZnO and TiO_2 were 1.8 ± 0.1 and 0.58 ± 0.02 Å/cycle, respectively. The GPC values were calculated from the film thicknesses determined from measured x-ray reflectivity (XRR; X'Pert MPD PRO Alfa 1, PANalytical) data using the fitting X'Pert Reflectivity software by PANalytical.

The Raman measurements were done with alpha300 R confocal Raman microscope (Witec GmbH, Germany). A doubled frequency Nd:YAG laser (532 nm, 35 mW) was focused

onto the sample using a 20X (Nikon, NA = 0.40) air objective. Integration time of 15 s was used for collecting each spectrum. Quantum chemical calculations were carried out with PBE0 hybrid density functional method using CRYSTAL14 program package and all-electron, Gaussian-type basis sets (DFT-PBE0/SVP level of theory).^{36–38} For full computational details, see Supporting Information.

Conclusions

In conclusion, we have demonstrated a new way of utilizing the ALD thin-film technique to remarkably enhance the Raman signal in the characterization of inorganic-organic hybrid materials with small dimensions, by depositing an amorphous ALD- TiO_2 coating on top of the hybrid material. Our proof-of-the-concept data were for Ti- and Zn-based inorganic-organic thin films deposited by the strongly emerging ALD/MLD technique, and it was seen that within the TiO_2 layer thickness range investigated, i.e. 3–12 nm, the Raman intensities were enhanced with increasing TiO_2 cap layer thickness. Hence it could be possible to enhance the Raman signal even more by increasing the cap layer thickness further. Moreover, the ALD- TiO_2 coating could be used not only to detect the organic species in nanomaterials but also inorganic ones as the enhancing effect was seen for the silicon substrate as well when capped with TiO_2 but this requires further studies on a number of different materials. Since the ALD technique is a relatively mild thin-film deposition method and allows depositions on various types of sensitive and/or (nano)structured surfaces, we foresee that our novel ALD- TiO_2 -based Raman enhancement technique possesses true potential to become a highly valuable standard characterization approach to the research of new hybrid inorganic-organic materials.

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