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Philip, Anish; Ghiyasi, Ramin; Karppinen, Maarit

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Visible-Light Absorbing TiO₂:Curcumin Thin Films with ALD/MLD

Anish Philip, Ramin Ghiyasi and Maarit Karppinen*

Abstract: Curcumin is known for its antimicrobial effects. Here we use the atomic/molecular layer deposition (ALD/MLD) thin-film technique to embed monomolecular curcumin layers within photocatalytic TiO₂ matrix into different superlattice structures with the anticipation of intriguing synergistic effects. We demonstrate the extension of the light absorption to the entire visible range which could pave the way for the use of these films for light-driven destruction of pathogens.

Curcumin—chemically a diarylheptanoid—is a major constituent of the spice turmeric (a member of the ginger family) obtained from the plant *curcuma longa*.^[1–3] In the curcumin structure, the two phenol rings with additional methoxy groups (–OCH₃) are connected by a β -diketo group (O=C–CH₂–C=O), see Fig. 1.^[4] The recent interest in this natural product originates from its capability to modify the protein structure of viruses and act as a pharmaceuticals against viral infections;^[1,3,5] literature highlights include the positive effects of curcumin against HIV-1,^[6] hepatitis B^[7] and even COVID-19.^[8] At the same time, various adverse effects have been observed from the high doses of curcumin intake, such as DNA damage to both mitochondrial and nuclear genomes in human hepatoma G2 cells,^[9] and also the destruction of DNA-repair proteins in the NCI-H460 cells.^[1,10] Hence, new ways to utilize curcumin externally need to be developed. Here we imagine e.g. protective masks with thin curcumin-bearing coatings.

From another perspective, some metal oxides have been found antimicrobial, and TiO₂ in particular is known as a photocatalyst towards the disinfection of viruses,^[11,12] bacteria,^[13,14] cancer cells,^[15] and other microbes.^[16,17] Titanium dioxide is moreover chemically stable, non-toxic and composed of earth-abundant elements only.^[18,19] However, as a wide-bandgap semiconductor, TiO₂ works only under UV light,^[15,20,21] which comprises only 3% of the solar spectrum. Activation of TiO₂ for visible light has been investigated utilizing various doping and dye-sensitization schemes; in many cases though the disadvantage is the need to use precious metals (e.g. Pt, Au, Ag).^[19]

Recently, we demonstrated the possibility to tune the optical bandgap of different semiconducting metal oxide thin films through precise film thickness control (CuO),^[22] or insertion of monomolecular organic layers within the metal oxide matrix (TiO₂, ϵ -Fe₂O₃).^[23,24] These thin films were grown through ALD (atomic layer deposition) and MLD (molecular layer deposition) cycles, for the inorganic and organic layers, respectively. Inspired by these positive results, we now challenge the combined ALD/MLD technique to fuse nanoscale curcumin and TiO₂ layers together for various superlattice (SL) structures,^[25–27] anticipating their synergistic effects^[28,29] towards visible-light activation and even antipathogen functionality.

Both ALD and MLD – the state-of-the-art industrial technology for inorganic thin films and its less explored counterpart for organic films – are based on vaporized precursors sequentially pulsed into the reactor.^[30–32] The films grow through self-limiting gas-surface reactions with atomic/molecular level precision; this allows precisely layer-engineered inorganic-organic multilayer thin films for which the layer insertion pattern can be arbitrarily chosen.^[33] As an additional bonus, this technique is compatible with a wide variety of demanding substrate materials such as textiles.^[34,35]

Here we report the successful preparation of TiO₂:curcumin and also hetero-organic TiO₂:curcumin/hydroquinone superlattices with different layer sequences, and the remarkably enhanced visible-light absorption for these SL thin films. The films were fabricated by combining the ALD cycles of titanium isopropoxide (TTIP) and water for the TiO₂ layers with the ALD/MLD cycles consisting of TTIP and curcumin (Cur) or TTIP and hydroquinone (HQ) for the Ti-Cur and Ti-HQ layers, respectively (Figure 1). Out of these three unit processes, the TTIP+H₂O process is well known from previous literature,^[36–38] and also HQ is a common organic precursor in prototype ALD/MLD processes.^[23,33,39] Here, our first task thus was to develop the entirely new ALD/MLD process for the Ti-Cur layers such that it would be compatible with the TTIP+H₂O and TTIP+HQ processes; see details in Supporting Information (SI Fig. 1). In short, we fixed the deposition temperature to 300 °C, and optimized the precursor evaporation temperatures to be: TTIP 30 °C, H₂O 20 °C, HQ 80 °C, Cur 260 °C. The pulse lengths were accordingly (N₂ purge length in parentheses): TTIP 15 s (N₂ 30 s), HQ 10 s (N₂ 20 s), Cur 6 s (N₂ 15 s). For TiO₂ the pulse and purge lengths were: TTIP 6 s (N₂ 15 s) and H₂O 3 s (N₂ 7 s). The film growth rates (GPC: growth per cycle) were: 1.0 Å/cycle for TiO₂, 2.5 Å/cycle for Ti-HQ, 3.9 Å/cycle for Ti-Cur. The higher growth rate observed in case of TiO₂ could be attributed to the possible presence of excessive hydroxyl groups on the active surface sites of catalytic crystalline TiO₂.^[40]

[*] Dr. A. Philip, Mr. Ramin Ghiyasi, Prof. M. Karppinen
Department of Chemistry and Materials Science, Aalto University
P.O. Box 16100, FI-00076 Aalto (Finland)
E-mail: maarit.karppinen@aalto.fi
Supporting information and the ORCID identification numbers for the authors of this article can be found under: xxxx.

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Figure 1. Molecular structures of the precursors: curcumin (Cur), titanium isopropoxide (TTIP) and hydroquinone (HQ).

We first deposited for reference both bare TiO_2 films without the organics, and hybrid Ti-org (Ti-Cur and Ti-HQ) films without distinct TiO_2 layers, using our unit deposition cycles of TTIP+ H_2O (TiO_2 films), TTIP+Cur (Ti-Cur films) and TTIP+HQ (Ti-HQ films). Then the actual superlattice sample sets of TiO_2 :Cur and TiO_2 :Cur/HQ films were deposited by appropriately combining the three unit deposition cycles; in these SL films the overall number of organic layers (n) within the TiO_2 matrix varied from 5 up to 30. It should be noted that in the TiO_2 :Cur films n thus denotes the number of curcumin layers, while in the hetero-organic TiO_2 :Cur/HQ films the curcumin and hydroquinone layers were introduced alternately such that the total number of layers for each was $\frac{1}{2}n$. The total number of ALD and MLD deposition cycles was fixed in such a way that the thickness of the SL films was ca. 100 nm. As an example, the TiO_2 :Cur/HQ ($n=20$) sample was deposited using the precursor pulsing process: $20 \times [22 \times (\text{TTIP}+\text{H}_2\text{O}) + 1 \times (\text{TTIP} + \text{HQ}) + 22 \times (\text{TTIP}+\text{H}_2\text{O}) + 1 \times (\text{TTIP}+\text{Cur})] + 22 \times (\text{TTIP}+\text{H}_2\text{O})$.

All other films except the parent TiO_2 film were found amorphous; this was expected due to the relatively thin (TiO_2 :org SLs) or non-existing (Ti-org hybrids) TiO_2 layers in our organic-inserted films. The diffraction pattern for the TiO_2 film (SI Fig. 2) perfectly matched with the anatase crystal structure.

Judged from the XRR (x-ray reflectivity) data, the surface roughness somewhat increased with increasing number of organic layers. From SEM analysis, aggregates of grains were seen for the parent TiO_2 film (SI Fig. 3), but not for the organic-containing films. For the TiO_2 :organic SL structures the intended layer sequences could be readily confirmed from the XRR data; representative XRR patterns are shown in Figure 2 and SI Fig. 4. The sharp and intense SL peaks resulting from the constructive interference of different layers in the structure are seen for the TiO_2 :Cur and TiO_2 :Cur/HQ films but neither for TiO_2 nor Ti-Cur, as expected. Also seen is the increase of the smaller fringes between the larger SL peaks with increasing number of organic layers.

Figure 2. XRR patterns for representative TiO_2 :Cur and TiO_2 :Cur/HQ SL films with different n values; for comparison XRR patterns for Ti-Cur and TiO_2 (62 nm) films are also shown.

We carried out systematic FTIR (Fourier transform infrared) analysis to investigate the bonding between the TiO_2 and organic layers in the TiO_2 :Cur and TiO_2 :Cur/HQ superlattices; in Figure 3 also the spectra for the Ti-Cur and Ti-Cur/HQ films are shown for

reference. First of all, the spectra confirm the presence of aromatic rings (1488 cm^{-1})^[23] in all the samples due to the curcumin and/or hydroquinone moieties. The specific features confirming the presence of curcumin in the films are: the para C–H bending of a para-substituted aromatic ring at 833 cm^{-1} , the aliphatic C=C stretching at 1650 cm^{-1} , and the C=O stretching related to the β -diketo ($\text{O}=\text{C}-\text{CH}_2-\text{C}=\text{O}$) group at 1700 cm^{-1} .^[41–43] On the other hand, the presence of HQ moieties in the TiO_2 :Cur/HQ and Ti-Cur/HQ films is best seen from the appearance of the 1209 cm^{-1} peak due to the C–O stretching resulting from the bonding of aromatic ring to the titanium ion; the tiny deviation of the peak position from the literature values^[23] is presumably due to the presence of the secondary linker (Cur) in the structure. The weaker intensities of all the aforementioned spectral features in the TiO_2 :Cur and TiO_2 :Cur/HQ films compared to the Ti-Cur and Ti-Cur/HQ films are explained by the lower concentration of the organics in the SL films.

Figure 3. FTIR spectra for representative TiO_2 :Cur and TiO_2 :Cur/HQ SL films in wavenumber regions of $400\text{--}2000 \text{ cm}^{-1}$ (for the signatures of Cur and HQ) and $2900\text{--}3100 \text{ cm}^{-1}$ (for the signatures of $-\text{OCH}_3$ groups); for comparison spectra for Ti-Cur and Ti-Cur/HQ are also shown.

As for the way curcumin is bonded to titanium, we can first of all see features characteristic to Ti–O bonds below 500 cm^{-1} . Also, the broad C–O stretching peak at 1261 cm^{-1} confirms the formation of Ti–O bonds similar to the Ti–O bond formation with HQ.^[23] It seems that the Ti–O bonding occurs primarily via the original hydroxyl groups of curcumin, since the sharp peak at 3508 cm^{-1} (SI Fig. 5) due to free $-\text{OH}$ groups is absent in the Cur-bearing thin films. On the other hand, the bands observed at 2945 and 2980 cm^{-1} (due to symmetric and asymmetric C–H stretching of the $-\text{OCH}_3$ unit)^[42] indicate that the methoxy groups remain intact upon the film formation, i.e. they do not participate in the bonding. Hence, our FTIR analysis has confirmed not only the presence of the β -diketo ($\text{O}=\text{C}-\text{CH}_2-\text{C}=\text{O}$) groups, but also the methoxy ($-\text{OCH}_3$) groups in our Cur-bearing thin films. It should be emphasized that the former groups in particular are suspected to be crucially important for the prospective antiviral functionality of curcumin.^[44,45]

Finally, we characterized the SL films for their optical properties using UV-Vis spectroscopy; representative spectra are displayed in Figure 4. It is evident that the curcumin layers activate TiO_2 for the visible light absorption such that the absorption in the organic-bearing films comprises nearly the entire Vis light range up to 650 nm . Also seen was (not shown here) that the Vis-range absorption increases with increasing number of Cur layers.

Figure 4. UV-Vis absorption spectra for representative $\text{TiO}_2\text{:Cur}$, $\text{TiO}_2\text{:HQ}$ and $\text{TiO}_2\text{:Cur/HQ}$ SL films; for comparison spectrum for a TiO_2 film is also shown.

In Figure 4 we show the spectra for $\text{TiO}_2\text{:Cur}$ and $\text{TiO}_2\text{:HQ}$ films with $n = 10$, and also for the hetero-organic $\text{TiO}_2\text{:Cur/HQ}$ films with $n = 10$ and 20 . Interestingly, while the curcumin layers and hydroquinone layers alone do enhance the Vis-range absorption moderately, the effect is clearly amplified for the combination of the two organic components, Cur and HQ. Indeed, for the hetero-organic $\text{TiO}_2\text{:Cur/HQ}$ SL film highly promising UV-Vis absorption characteristics are seen. In this $\text{TiO}_2\text{:Cur-TiO}_2\text{:HQ}$ piling the individual TiO_2 layers are $1.5\text{--}4.6$ nm thick. Quite promisingly, the absorption enhancement observed for the $\text{TiO}_2\text{:Cur/HQ}$ SL film with $n=20$ is comparable or better compared to spectra reported for e.g. $\text{TiO}_2\text{-Au}$ composite aerogels or C/S/N co-doped sol-gel synthesized TiO_2 thin films.^[46,47] Finally, it should be mentioned that the presence of TiO_2 in the SL structures is an essential component for the visible light absorption; we also measured the UV-Vis spectra for several Ti-Cur and Ti-Cur/HQ films without the TiO_2 layers (SI Fig. 6), but the Vis-range absorption was nearly negligible.

In conclusion, we have demonstrated an exciting way to combine nanoscale UV-active TiO_2 layers with monomolecular curcumin and hydroquinone layers into superlattice structures, to significantly extend the absorption range to the visible light. Interestingly, even though both the curcumin and hydroquinone layers alone enhance the Vis-range absorption, the simultaneous presence of curcumin and hydroquinone is highly beneficial to cover the entire visible light range and reach the superior absorption characteristics. We believe that these $\text{TiO}_2\text{:Cur/HQ}$ thin films fabricated with the currently strongly emerging and industry-feasible ALD/MLD technique with atomic/molecular level accuracy could be exciting new materials for photocatalytic applications. Another unique feature of our superlattice thin films is that they contain curcumin moieties that are believed to show antiviral properties. In that respect, it is important to emphasize we could confirm that the curcumin moieties are bound to TiO_2 in a way which leaves the β -diketo and methoxy groups intact; note, that these groups are believed to play a key role in the antiviral efficiency of curcumin. Unfortunately, the antiviral tests could not be realized within the scope of this work. Optimally, we imagine that the fact that the curcumin moieties are intimately combined with UV-Vis photoactive TiO_2 pharmaceutical functionality. Having the eye on possible wearable applications, it is important

to note that we utilized here the significantly less reactive TTIP instead of the more common TiCl_4 as the precursor for titanium, to rule out the possibility of unwanted side reactions between the highly reactive TiCl_4 and textile/cellulose.

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Author(s), Corresponding Author(s)*

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Here in the current research, we demonstrate the fabrication of curcumin based superlattice thin films with unprecedented accuracy using an industrially feasible atomic-molecular (ALD-MLD) deposition technique. The presence of HQ as a secondary linker in the thin film have shown a positive impact on the absorbance indicating the possibility of using them as visible light harvesters, especially for light driven destruction of pathogens.