Characterisation of Novel Ag on TiO_2 Films for - Surface Enhanced Raman Scattering

A. Mills*, G. Hill, M. Stewart, D. Graham, W.E. Smith, S. Hodgen, P.J Halfpenny, K. Faulds and
P. Robertson
Department of Pure and Applied Chemistry
University of Strathclyde, Glasgow G1 1XL , U.K. (A.M., G.H., M.S., D.G., WES, S.H., P.J.H. and K.F): and
Department of Physical Science, Robert Gordon University, Aberdeen, U.K. (P.R.)

Abstract

Novel Ag on TiO_2 films are generated by semiconductor photocatalysis and characterised by UV/Vis spectroscopy, SEM, AFM as well as assessed for SERS activity. The nature and thickness of the photodeposited Ag, and thus the degree of SERS activity, is controlled by the time of exposure of the TiO_2 film to UV light. All such films exhibit the optical characteristic ($\lambda max \cong 390$ nm) of small (<20nm) Ag particles, although this feature becomes less prominent the thicker the film. The films comprise quite large (>40nm) Ag islands that grow and merge with increasing levels of Ag photodeposition. Tested with a benzotriazole dye probe, the films are SERS active; exhibiting a similar activity as that of 6nm thick vapour-deposited films. The Ag/TiO_2 films exhibit a lower residual standard deviation (ca. 25%) compared with Ag vapour-deposited films (ca. 45%), which is, however, still unacceptable for quantitative work. The sample-to-sample variance could be reduced significantly (<7%) by spinning the film during the SERS measurement. The Ag/TiO_2 films are mechanically robust and resistant to removal and damage by scratching, unlike the Ag vapour-deposited films. The Ag/TiO_2 films also exhibit no obvious loss of SERS activity when stored in the dark under otherwise ambient conditions. The possible extension of this simple, effective, method of producing Ag films for SERS, to metals other than Ag, and to semiconductors other than TiO_2, is briefly discussed.

Introduction

Surface-enhanced Raman Scattering (SERS) involves amplification of Raman scattering by interaction with surface plasmons[1]. The enhancement occurs when the frequency of the laser excitation is resonant with the surface plasmons on a rough metal surface. Silver is commonly used as the metal substrate because its surface plasmons exist in the visible region[2]. Other metals that have been used in this role for similar reasons include gold and copper. SERS is attractive as an analytical technique as it is able to combine molecular fingerprint and functional group identification with high sensitivity; in some cases down to the single molecule level[4-6]. However, in the past SERS has been dogged by the stigma of poor reliability and reproducibility, a major cause of which is the heterogeneous and easily altered nature of the surface of the metal, usually Ag, substrate[6]. Indeed, amongst recently employed SERS-active substrates there is a wide range of performance characteristics and difficulties of preparing such substrates. For example, although electrochemically-roughened Ag electrodes were the first to be used to produce SERS and have been extensively studied[7], they remain far from ideal. Surface preparation requires the use of a potentiostat and galvanostat and the cyclic oxidation/reduction process is involved[8]. Critically, the reproducibility between Ag electrodes is poor; typically exhibiting a percentage relative standard deviation (%RSD) of 40%[8]. Probably the most popular substrates for SERS are Ag colloids[6,8-11]. However, for optimal signals often an elaborate and precise procedure is required and whereas %RSD's of 6.6% and less have been reported[6], typically, the average citrate Ag colloid exhibits a batch-to-batch %RSD of ca. 41%[6]. The variation of the measured SERS intensity as a function of the age of the Ag colloid also represents a possible limitation to its application in analysis[6,12,13].

Ideally, a substrate for SERS should be a cheap, robust, stable, reproducible, active, easily-prepared and stored film[8,14]. The development of such a film would open up considerably the area of SERS in analytical chemistry and allow its use in routine, in-the-field sampling. A popular method for producing Ag films for SERS is based on vapour deposition[2,8,15,16]. However, the required vacuum-based system for producing such films is expensive and quite high maintenance. Vapour-deposited Ag films are not mechanically robust (they can be easily removed by wiping) and lose activity with time exposed to air. Batch-to-batch %RSD's for these films are typically 20-30%[8]. Many other methods of producing Ag films for SERS have been reported, including: vapour-deposition of Ag on silica stochastic-ports[1], and polymer nanospheres[17], both supported on glass, and chemically-reduced Ag on glass[18]. However, although exhibiting reasonable, albeit varying, degrees of SERS activity, most appear far from ideal, especially in terms of robustness and ease of manufacture.

In a recent paper Rowlen and co-workers compared the performance of five different Ag film substrates for SERS[8]. Included in this list was an Ag on TiO_2 film, generated by semiconductor photocatalysis. Although not found by these workers to be the most sensitive of the five films tested, - this award went to a post-deposition annealed Ag vapour film – the Ag/TiO_2 on glass film was found to be a sensitive SERS substrate[8]. The method of producing such films is simple and easily adapted for other metals. In addition, the films themselves are mechanistically robust. Prompted by these positive features, a more detailed study of this SERS-active type of substrate was carried out and the results of this work are described below.

Experimental

Reagents and Materials

Unless stated otherwise, all reagents and materials were obtained from Aldrich Chemicals in the highest purity available.

TiO_2 Film on Glass Preparation

The nanocrystalline, thin TiO_2 films on glass, used to produce the Ag/TiO_2 films used in this work, were prepared by a sol-gel process[19]. Thus, 2.5g of polyethylene glycol (MW: 600) and 7.5g of diethylene glycol (Fisher Scientific) were dissolved in 40 cm^3 of ethanol. 5g of titanium iso-propoxide (97%) were then added to the above solution and the mixture stirred for 15 minutes. This TiO_2 sol-gel solution, when covered with Parafilm™, is stable under ambient conditions for several hours. TiO_2 sol-gel films were prepared by spin-coating 6 drops of the TiO_2 sol-gel solution onto a 13 mm glass cover slip, spun at 5760 rpm for 30 s. After casting, the film was immediately transferred to a pre-heated furnace and there calcined at 450°C for 30 minutes. The product was a thin (ca. 200 nm), optically clear, robust, nanocrystalline film of anatase titania on glass.

Photodeposition of Ag onto TiO_2 Films

The Ag/TiO_2 films used in this work were prepared using the TiO_2 on glass films described above. Typically, one or more of the latter (up to five) were placed in a small petri dish, TiO_2-film side up. The films were then covered with a 1 mM $AgNO_3$ methanolic solution (75:25 v/v MeOH:H_2O). The films were then irradiated (typically 30 min) using a UVA lamp, (from VWR), comprising two 8W BLB lamps, set 11cm above the petri dish. After irradiation, the films were removed from the irradiated solution, dried in air and stored in sealed bags. Typically, the Ag/TiO_2 films appeared dark brown-black in transmitted light. A typical SEM of a deliberately scratched Ag/TiO_2 on glass film (UV illuminated for 45 min) is illustrated in figure 1 and clearly shows the three different layers, (i.e. Ag, TiO_2 and glass). From this image an initial rough estimate of the size of the Ag particles, that comprise the Ag-photodeposited film, of 150 nm was made.

Vapour-Deposited Ag Films

Vapour-deposited Ag films were generated using an Edwards Coating System E306A. The deposition source comprised a tungsten boat filled with Ag powder (99.9 + %). The thickness of the deposited Ag films on cover slip glass was monitored with an Intellimetrics IL100 thickness monitor, which utilises a quartz crystal oscillator. The films were produced at 5×10^{-5} mbar and at a deposition rate of 0.01 nm s^{-1}. All films were cooled to room temperature before the vacuum was removed.

AFM Measurements

AFM images were all taken in air using a Digital Instruments Nanoscope Multimode SPM with a JV-type scanner and a Nanoscope III controller. The type of cantilevers employed were Olympus tapping mode, silicon pyramidal, with a tip curvature < 10nm and a normal force constant of 42 N/m. For all samples both amplitude and height scans were carried out with scan sizes from 1 to 5 microns, recorded at a scan rate of 0.5 – 1.0 Hz and with a resolution of 512 scan lines per image. No image processing was carried out on the presented data.

Instrumentation

SERS spectra were collected using a Renishaw 2000 Microprobe system fitted with a Spectra-Physics model 165 argon-ion laser ($\lambda_{emission}$ = 514.5 nm, ca. 5 mW power as the excitation source). Standard 180° collection optics were used. The Renishaw has a notch filter and single-grating arrangement with a cooled charged coupled device (CCD) detector. The spectra were recorded using a x 50 objective, a 1s accumulation time and 1 μm diameter laser excitation beam. UV/visible absorption spectra were recorded using a Lambda 20 UV/Vis spectrophotometer (Perkin Elmer).

Results and Discussion

Photodeposition of Ag on TiO_2 films

The basic reaction responsible for the photocatalytic process associated with the production of the Ag/TiO_2 films can be summarised as follows[20,21]:

$$6Ag^+ + CH_3OH + H_2O \xrightarrow[TiO_2]{h\nu \geq E_{bg}} 6Ag\downarrow + CO_2 + 6H^+ \qquad (1)$$

where E_{bg} is the band-gap energy of TiO_2 (3.2 eV for anatase titania). Thus, ultra band-gap irradiation of titania generates an electron-hole pair. The photo-generated electron is able to reduce silver ions at the surface of the titania to silver metal. The photogenerated hole is able to oxidatively mineralise methanol, which acts as a sacrificial electron donor. The generic photocatalytic process can be summarised by the following equation:

$$M^{n+} + SED \xrightarrow[\text{Semiconductor}]{h\nu \geq E_{bg}} M\downarrow + SED^{n+} \qquad (2)$$

and has been the subject of extensive research, mainly using TiO_2 powders[20,22]. The photodeposition of Ag on TiO_2 films, via reaction (1), has been less well researched, compared to other metals, such as Pt and Pd, although the basic principles remain the same. Intriguingly, using this approach to metal deposition, metals other than Ag, such as Au, Pt, Cu and Hg can be photocatalytically deposited as films on a semiconductor[20,21], such as TiO_2, and used for SERS. In this work, however, the focus is on Ag/TiO_2 films. Blank experiments reveal that reaction (1) requires the presence of titania, silver nitrate and methanol, and the application of UV light, in order to proceed.

Figure 2 illustrates the typical observed changes in UV/Vis spectrum of an initially TiO_2 on glass film, in a standard $AgNO_3$ methanolic solution used for the photocatalytic deposition of Ag, upon increasing UV illumination time. From the illustrated spectral changes it is clear that as the film is irradiated the film progressively darkens since the absorbance of the film at wavelengths > 500 nm, such as that at 800 nm, Abs(800), increases. This UV-induced gradual darkening of the initially TiO_2 film is due to the UV-driven photocatalytic reduction of the $AgNO_3$ by methanol, sensitised by the TiO_2 film, i.e. reaction (1). Encouragingly, despite the broadness of the absorbance bands that emerge with increasing UV illumination, the spectra do appear also to have some features; most notably an absorption maximum at ca. 390 nm. The optical properties of sub-micron structures comprising silver particles have been studied extensively, and numerical results published elsewhere for single Ag particles with radii <20 nm predict a maximum absorbance at 390 nm[11]. Certainly, monodisperse silver colloids of this size range yield typically a λ_{max} value of 400 nm. In both cases the maximum absorbance is due to excitation of a dipolar surface plasmon in the Ag spheres. For larger sized: Ag particles (i.e. >20 nm), prolate spheroids and linear aggregates, λ_{max} is shifted bathochromically and the absorbance band is broadened[11]. Thus, the spectra associated with the photocatalytically deposited Ag/TiO_2 films indicate that the Ag films comprise a similar, polydisperse mixture of single particles and aggregates, for most irradiation times, i.e. most thicknesses of photodeposited Ag.

In order to assess the level of Ag on the above photodeposited films, for each irradiation time, from 0-45 mins, two identical films were prepared and then the photodeposited Ag stripped off, using nitric acid. The concentration of Ag^+ in the nitric acid was then measured potentiometrically, using a silver wire as the indicator electrode. This potentiometric analysis allowed the calculation of the original concentration of Ag on the surface of the two photo-deposited films ($[Ag]_f$; units: g cm^{-2}). In this work, the lower limit of detection of this technique was found to be ca. 10^{-5} g cm^{-2}.

Figure 3 illustrates the observed variation in $[Ag]_f$ for the Ag/TiO_2 films as a function of irradiation time. As expected, the levels of $[Ag]_f$ increase with increasing irradiation time, as indicated by a gradual darkening of the film and an increase in its absorbance at 800 nm. In fact, as indicated by the insert diagram in figure 3, there appears to be a reasonable linear correlation between the absorbance of a Ag/TiO_2 film as measured at 800 nm; i.e. Abs (800 nm) and the measured amount of silver on the Ag/TiO_2 film, i.e. $[Ag]_f$. This correlation indicates that the overall distribution in size of the Ag particles is not drastically altered with increasing irradiation time.

The recorded UV/Visible absorption spectra of a series of vapour deposited Ag films of different thickness, from 1-12 nm, are illustrated in figure 4. The results are similar to those reported by Van Duyen in their AFM and SERS study of Ag island films produced by vapour deposition[2]. Thus, as the film thickness is increased the position of maximum absorbance increases. As noted by these, and other workers[16], such Ag island films produced in this manner are comprised typically of a random array of individual oblate spheroidal particles. Thus, the position of λ_{max} for even the thinnest of films is significantly red-shifted compared to that associated with a monodisperse of Ag particles of radius <20 nm. In their AFM study, Van Duyne and his co-workers showed that with increasing deposition thickness, Ag island films, although still comprised of individual particles, exhibit a greater irregularity in particle shape and an increase of distribution of particle sizes and shapes[2]. Thus, Van Duyne et al report that vapour deposited films 1.8 nm thick are oblate spheroids with (major axis) *a* and (minor axis) *b* dimensions of 10 and 5 nm respectively, and that these dimensions increase to 33 and 12 nm for the 8 nm films and 100 and 10nm, for the 16 nm films[2].

The results illustrated in figure 4 are consistent with the above observations made by others[2,16] and models[10,11] relating metal particle size to their optical characteristics. Thus, the absorbance maximum can be assigned to surface-plasmon excitation along the major axis of the spheroidal particles which is red-shifted and broadened as thicker Ag films, with the particles broader in size and more irregular in shape, are deposited. The measured variation in the absorbance of vapour deposited films at 800 nm as a function of film thickness is illustrated by the results in the insert diagram in figure 4. From these results it is clear that, the absorbance of the vapour deposited films at 800 nm is not directly related to their thickness. This observation is not too surprising, given the significant shift in the wavelength of maximum absorbance (from 490 – 700 nm) as the thickness of the vapour-deposited layer is increased, indicating a significant change in particle shape and size. Indeed, as noted earlier, AFM results indicate that the oblate spheroidal nature of the Ag particles increases as the thickness of the film is increased[2]. Calculations based on the thickness and density of the vapour deposited silver films predict levels of Ag in all but the thickest (e.g. for 1 and 12 nm films, $[Ag]_f$ (calculated) = 0.1 and 1.25 x 10^{-5} g cm^{-2}, respectively), that are below the lowest limit of detection of the potentiometric technique employed to measure $[Ag]_f$ (10^{-5} g cm^{-2}); thus, no attempt was made to measure the values of the latter parameter for these films using the potentiometric technique. Instead, they were calculated from their measured thicknesses and found to be significantly (6-10 times) lower than those found for Ag/TiO_2 films (see table 1).

As part of the Ag/TiO_2 film characterisation study, a series of AFM images of the different Ag/TiO_2 films produced were recorded and the results are illustrated in figure 5. Thus, for a zero irradiation time the AGM images of the TiO_2 on glass films shows them to comprise a closely packed, continuous surface of TiO_2 particles, typically 29 nm in diameter. Other (XRD) work shows that these particles are nanocrystalline and that the titania is predominately in its anatase phase. AFM's of the blank glass cover slips reveal a perfectly smooth surface within the resolution of the AFM instrument. The 'cobbledstone' background of a non-UV irradiated titania film quickly becomes altered upon UV irradiation of the film in a standard methanolic silver nitrate solution. Thus, after 1 minute of UV irradiation of the titania film, silver island growth is apparent from the AFM image of the film. The Ag islands sparsely populate the titania film and, although of roughly similar size (ca. 44 nm), several larger particles can be seen. Within 5 minutes' irradiation, most of the surface of the titania film is covered with Ag islands, typically within an average size of 64 nm. Further irradiation appears to increase the size of the Ag particles, until, after 45 minutes irradiation, the Ag particles appear more like overlapping fish scales of significant size (ca. 163 nm).

It is generally accepted that silver roughness features required for SERS activity lie in the nanometer range. Laserna et al go so far to suggest that the 'ideal roughness for SERS activity is in the 0.1 – 1 μm range'[3]. The nanometer scale of the Ag particles or scales for all the Ag/TiO_2 films produced in this work, and illustrated by the AFM's in figure 5, suggest that such films are likely to be SERS active.

From the AFM images illustrated in figure 5, it is possible to obtain estimated values of the average diameters and heights of the Ag particles (i.e. 'd' and 'h') and the average number of particles per μm^2 (Z) as a function of UV irradiation time. If it is assumed that the particles are domed spherical segments, then it is also possible to estimate a value for the concentration of Ag on the surface of the TiO_2 film, i.e. $[Ag]_{calc}$; units: g cm^{-2}, given that the volume of a dome spherical segment, V, is given by the expression: $V = (\pi 16)(3r^2h - h^3)$. These results, along with the values of $[Ag]_{expt}$ determined experimentally, using the potentiometric analysis technique and other film characteristics, are given in table 2. From the values of $[Ag]_{expt}$ and $[Ag]_{calc}$ it can be seen that in general for most of the films the agreement between $[Ag]_{expt}$ and $[Ag]_{rate}$ is surprisingly good, even for the thicker films in which the Ag particles overlap.

The SERS activities of all the Ag films described above were then tested using the SERS probe, benzotriazole dye: 3,5-dimethoxy-4-(5-azobenzotriazole) phenylamine, which will be referred to throughout as GM19, since it was the nineteenth benzotriazole derivative synthesised by the group for work with SERS and SERRS[23-27]. GM-19 has proved highly effective as a SERS and SERRS probe dye. It is known that the benzotriazole moiety forms a polymeric silver complex with the surface of silver; indeed, benzotriazole itself is commonly used as an anti-tarnishing agent[28]. Work by our group has established that the attachment of the GM-19 dye onto silver is essentially irreversible and that the dye remains in position over a wide range of experimental conditions and concentrations, allowing highly reproducible analysis[23-27]. The dye is easily applied, typically as a weak methanolic solution (10^{-6}M in this work); adsorption is almost 100% and the observed SERS signal is usually significant on SERS active substrates, due to the large spontaneous Raman cross-section of the dye. Thus, in a typical experiment, a Ag-coated film under test was placed in a 10^{-6}M GM-19 solution of methanol for 15 minutes, removed and allowed to dry in air before being placed under the SERS microprobe microscope. The GM-19 dye has an absorbance maximum at 446 nm[27], and, therefore, in this work, there is a limited contribution to the observed SERS signal due to surface enhanced resonance Raman spectroscopy (SERRS), since an excitation laser light of wavelength 514.5 nm was used[25]. All Ag films generated as part of this work were tested for SERS activity using the above procedure.

Figure 6 illustrates the observed SERS spectra recorded for the Ag/TiO_2 films generated using different UV irradiation times. As indicated by the results, with increased levels of photodeposited Ag, the overall intensities of the observed SERS spectra increase, in a near-proportional manner, with irradiation time. Thus, a plot of the SERS peak intensities at 1615 cm^{-1} as a function of Ag/TiO_2 film irradiation times is approximately linear, as indicated by the results in the insert diagram in figure 6.

The two major set of peaks, which appear in all the SERS spectra, are the quadrant stretch of the phenyl ring at 1615 cm^{-1} and the azo stretch at 1375 cm^{-1}. DFT calculations, reported earlier have been used to assign these and the other, less prominent, vibrations[23]. Research carried out within the group shows that at 10^{-6}M, GM-19 typically forms a monolayer on most Ag surfaces[25]. Thus, using the Ag/TiO_2 films at higher concentrations the SERS signals were found to decrease whereas, at lower concentrations, 10^{-7} – 10^{-6}M, the signal was found to be approximately proportional to the concentration of GM-19. Smith et al[25] have shown that the linear region in a SERS peak signal intensity versus [GM-19] calibration graph using Ag colloids can be extended by an order of magnitude using 457.9 nm laser light, because the spectra are due to SERRS, instead of the less-sensitive process of SERS.

Vapour-deposited Ag films exhibited similar SERS spectra as those illustrated in figure 6 for the Ag/TiO_2 films. The SERS signal intensities at 1615 cm^{-1} were of the same order of magnitude as those observed for the Ag/TiO_2 films and increased, with increasing Ag film thickness, peaking at ca. 6000 counts/sec for a 6nm thick film. The film-to-film % RSD for the 6nm vapour deposited films was found to be ca. 45%, whereas with the 45 minute UV-irradiated Ag/TiO_2 films it was ca. 26%. This high degree of variation was found to exist for both types of film, from batch to batch and for single films, probed at different locations. Thus, these high % RSD's are largely due to the heterogeneous nature of the silver surfaces of these films, coupled with the small size (1μm diameter) of the laser beam probe. Additional work on the Ag/TiO_2 films, to be described in more detail in a later paper, shows that the high level of variance (26%), which renders them useless for quantitative analysis, can be reduced greatly (to <7%) and the sensitivity increased significantly (ca. 300%) by spinning the sample during the microprobe analysis, which averages and smoothes the overall observed SERS signal.

The adhesion of the Ag (and TiO_2) on the Ag/TiO_2 films was tested using the 3M Scotch Tape™ test. All films proved to be very adherent, with only the most irradiated films (60 min) exhibiting any loss of the Ag coating. These films also appear mechanically tough, resistant to scratching with pencils of softness 2H or less. In contrast, vapour-deposited films appeared easily damaged, and were removed by 3M Scotch Tape™ and gentle rubbing with a cloth. The latter films were also scratched by pencils of all hardnesses.

The Ag/TiO_2 films were tested for SERS activity as a function of storage time. Films stored in the dark, under otherwise ambient conditions, were found to retain the same SERS activity over the trial period of 3 months. Ag/TiO_2 films stored for much longer (> 1 year) also appeared not to have lost their SERS activity.

Conclusion

Novel Ag films created by semiconductor photocatalysis are SERS-active. These films, generated by UV-irradiation of a TiO_2 film on glass in a methanolic solution of silver nitrate, comprise quite large (>40nm) Ag domed spherical segment particles which grow larger and eventually overlap, like fish-scales, upon prolonged illumination. The films appear SERS active, when tested with the benzotriazole probe GM-19 and exhibit an increasing degree of activity with increasing level of Ag deposition; the latter being controlled by the UV-irradiation time. The SERS activity of these films appear similar to that of vapour-deposited films, although with a superior level of film-to-film reproducibility (cf. 26% compared to 45%). The former improved significantly (% RSD <7%), along with an increase in sensitivity (≥300%) when the film was spun during the SERS analysis. The photocatalytically generated Ag films were found to be very robust mechanically; in contrast, vapour deposited Ag on glass films were easily damaged and could be removed with the mildest rubbing. The photocatalyst Ag/TiO_2 films appeared to have an indefinite shelf-life when stored in the dark under ambient conditions.

The nature of the TiO_2 film can be easily varied, e.g. from compact to porous, thick to thin, anatase to rutile. The nature of the semiconductor can also be varied, e.g. from TiO_2 to ZnO, $SrTiO_2$ and SnO_2. The nature of the metal photodeposited can also be changed from Ag to: Au, Pt, Pb or Hg, to name but a few. Thus, given the ease of preparation and its generic nature, coupled with the mechanical robustness, long-lifetime and activity of the Ag/TiO_2 films produced by this method, it appears likely that these films have potential as a new type of SERS active substrate and thus merit further investigation.

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Figures

Figure 1: Scanning electron microscope (SEM) image of a typical Ag/TiO_2 film on glass. The film was prepared photocatalytically using a UV-irradiation time of 45 min and the standard Ag/NO_3 methanolic solution described in the Experimental section.

Figure 2: Typically UV/Vis absorption spectra recorded for TiO_2 films that had been irradiated in the standard Ag/NO_3 methanolic solution with UV light for different periods of time.

Figure 3: Plot of the measured amount of Ag photodeposited on the Ag/TiO_2 films, $[Ag]_f$, as a function of UV irradiation time. The insert plot is of the measured absorbance of the films at 800 nm (from figure 2) versus $[Ag]_f$. The solid line is the line of best fit, according to linear regression analysis.

Figure 4: UV/Vis absorption spectra of a series of vapour-deposited Ag films of different Ag thickness, ranging from 1-12 nm. The insert diagram is a plot of the measured absorbances of the films at 800 nm as a function of Ag film thickness.

Figure 5: Amplitude-based AFM images of the TiO_2 film generated after irradiation in a standard methanolic $AgNO_3$ solution for: (a) 0, (b) 1, (c) 2.5, (d) 5, (e) 30 and (f) 45 minutes, respectively.

Figure 6: Recorded SERS spectra for a series of Ag/TiO_2 films, where the Ag has been photodeposited using UV irradiation times that ranged from 1-45 minutes. The spectra are due to the GM-19 probe, which was deposited by soaking the films in a 10^{-6} M solution of the dye in methanol, before drying and subjecting to analysis using the microprobe system. The insert diagram is a plot of the

SERS intensity of the 1615 cm^{-1} peak measured for the above films as a function of UV irradiation time.

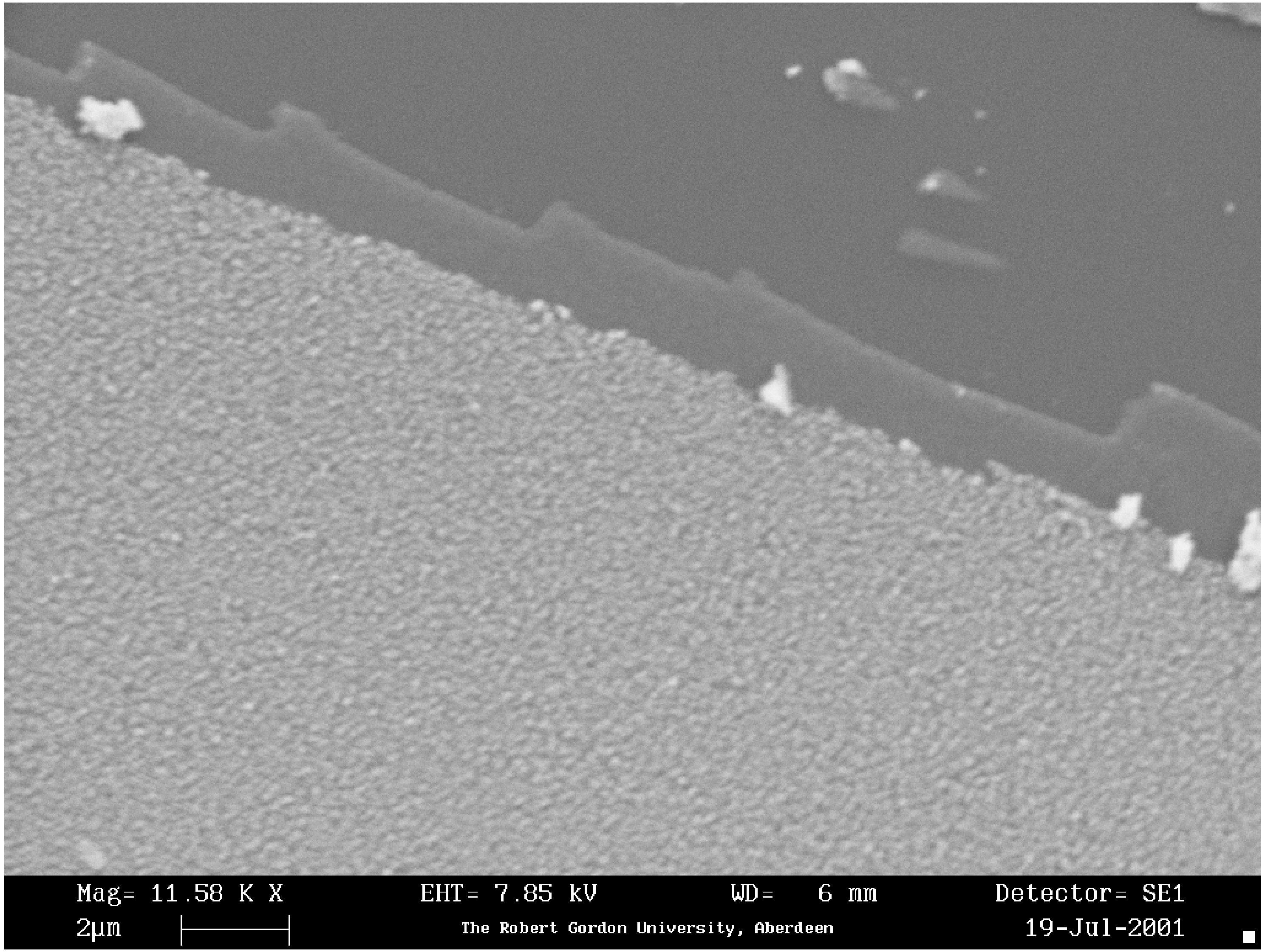
Table 1: Calculated levels of Ag and Abs(800) values for Ag-vapour deposited films of different thicknesses

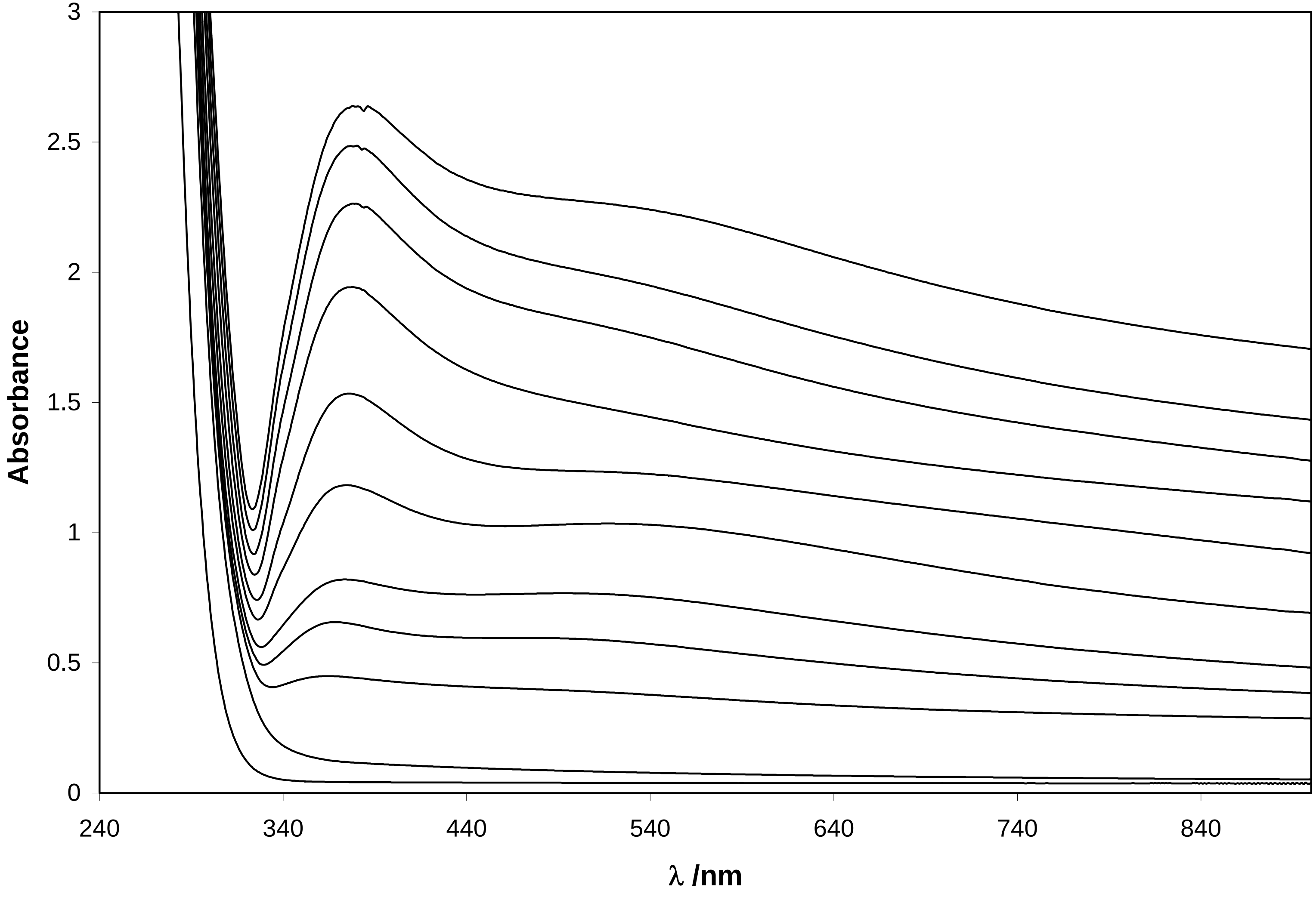
Thickness/nm	$[Ag]_{fcalc}$ / 10^{-5} g cm^{-2}	Abs(800)
0	0.00	0.036
1	0.101	0.039
3	0.32	0.073
6	0.63	0.246
9	0.94	0.588
12	1.26	0.834

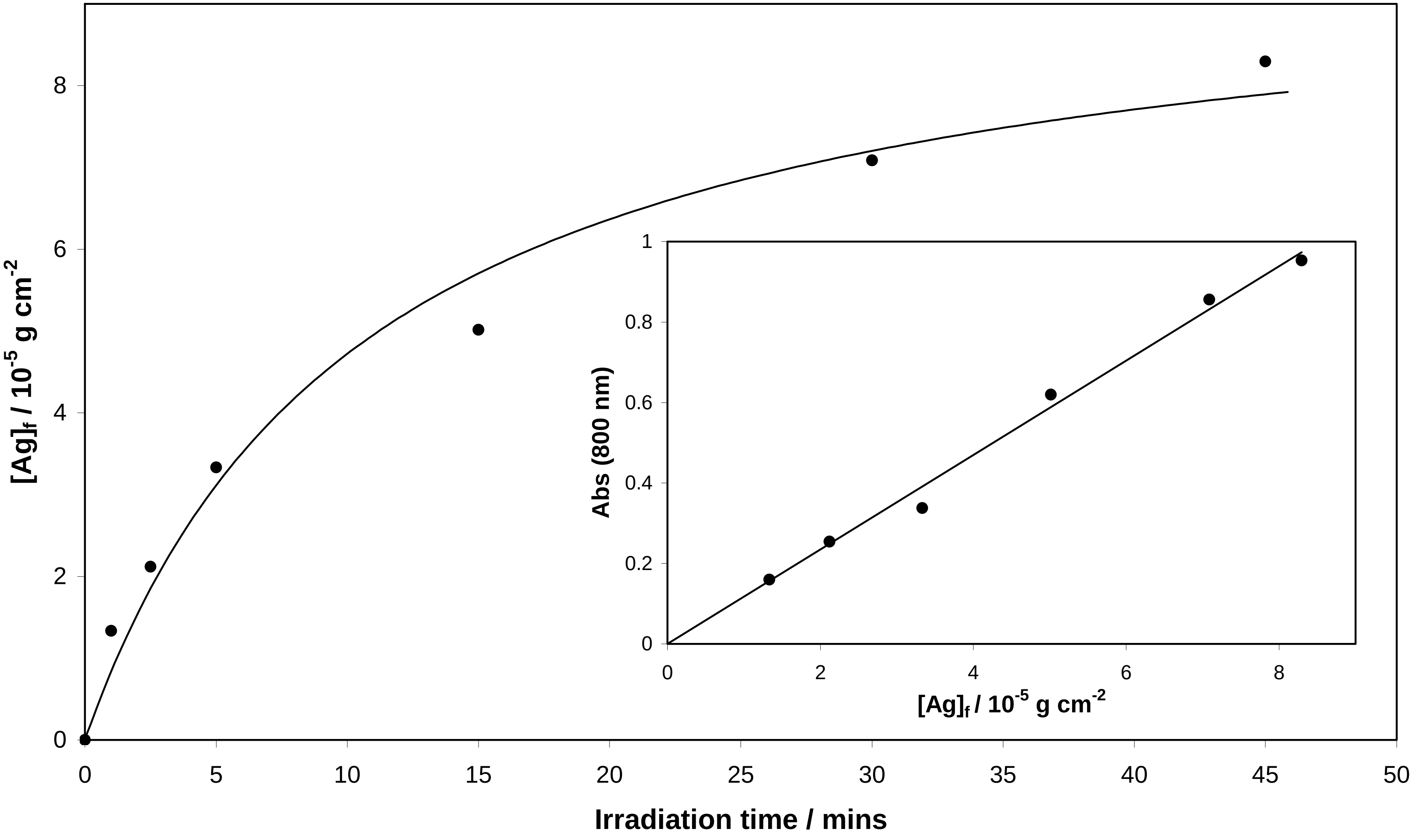
Table 2: Spectral details, Ag particle characteristics and surface concentrations for Ag/TiO$_2$ films UV-irradiated for different times

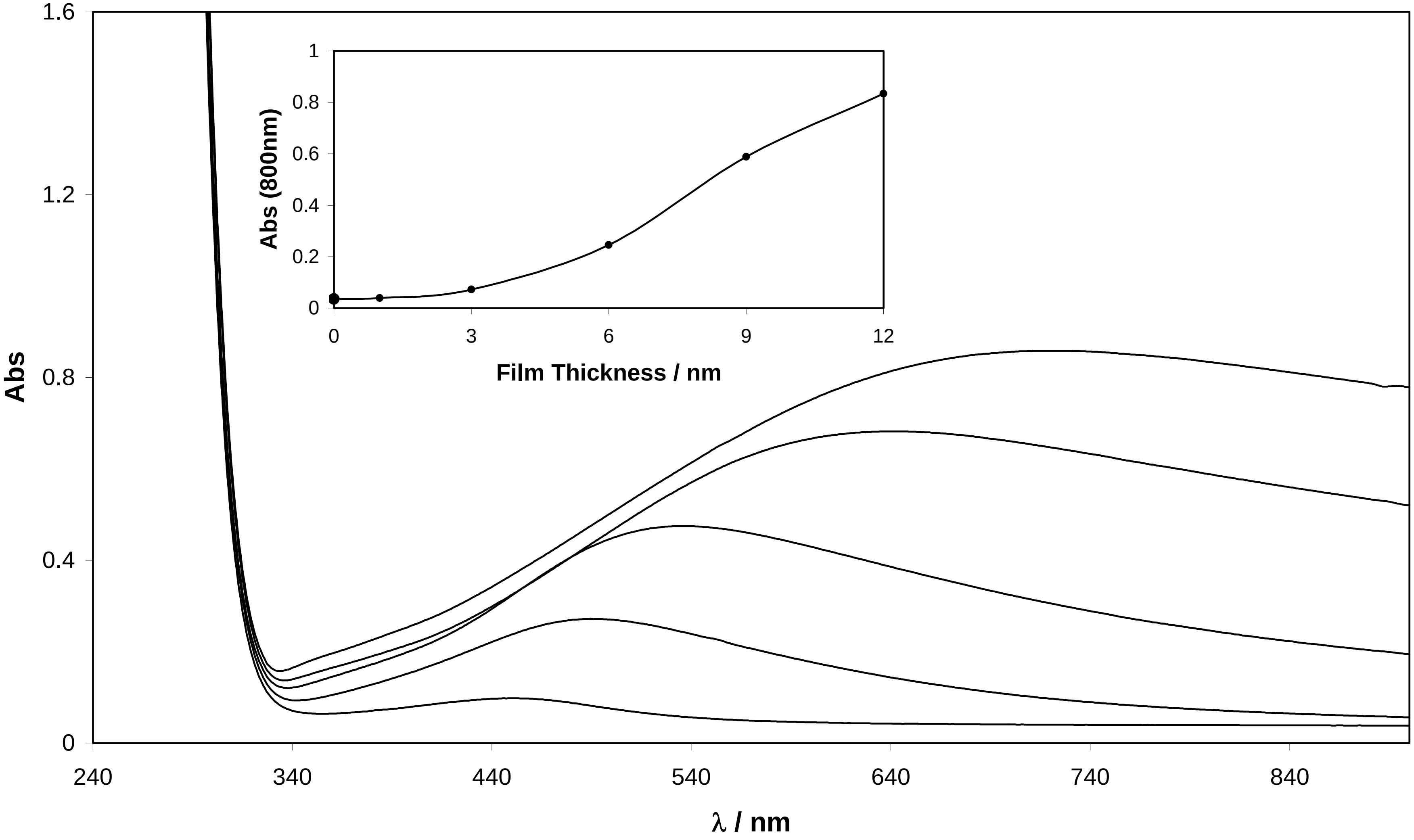
Irradiation time / mins	**Abs(800nm)**	**d* / nm**	**h* / nm**	**Z* /(No./sq micron)**	**[Ag]$_{fcalc}$ /10^{-5} mol dm^{-3}**	**¶[Ag]$_{expt}$ /10^{-5} g cm^{-2}**	**Particle type***
0	0.142	29	1.2	0	0.00	0.00	n/a
1	0.160	44	8.1	91	0.24	1.33	Single
2.5	0.254	56	20.4	167	1.84	2.12	Single
5	0.338	64	21	217	3.19	3.33	Single
15	0.620	135	20	128	7.74	5.01	Overlapping
30	0.856	152	27.6	74	7.86	7.09	Overlapping
45	0.953	163	33.7	57	8.53	8.30	Overlapping

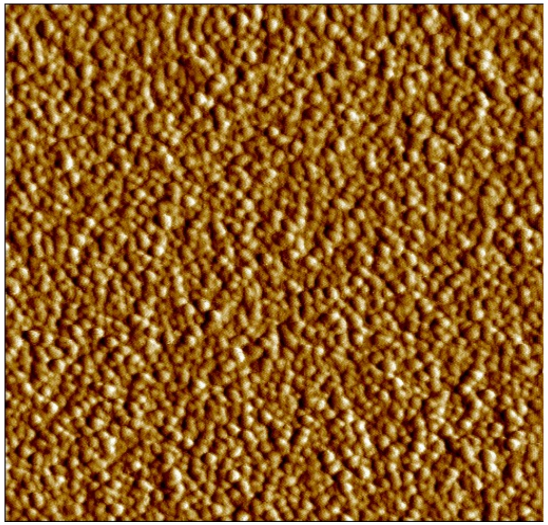
*: from AFM images; ¶: determined potentiometrically


Mag= 11.58 K X
EHT= 7.85 kV
WD= 6 mm
Detector= SE1
2μm
The Robert Gordon University, Aberdeen
19-Jul-2001

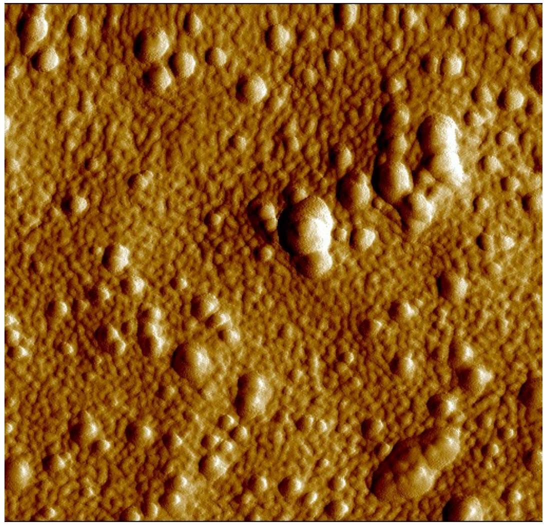

Absorbance
3
2.5
2
1.5
1
0.5
0
240
340
440
540
640
740
840
λ /nm


[Ag]$_f$ / 10^{-5} g cm^{-2}
0
2
4
6
8
0
5
10
15
20
25
30
35
40
45
50
Irradiation time / mins
Abs (800 nm)
0
0.2
0.4
0.6
0.8
1
0
2
4
6
8
[Ag]$_f$ / 10^{-5} g cm^{-2}

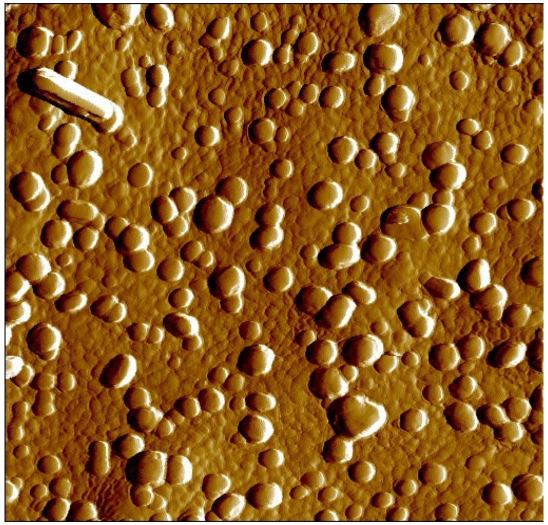

1.6
1.2
0.8
0.4
0
Abs
240
340
440
540
640
740
840
λ / nm
1
0.8
0.6
0.4
0.2
0
Abs (800nm)
0
3
6
9
12
Film Thickness / nm



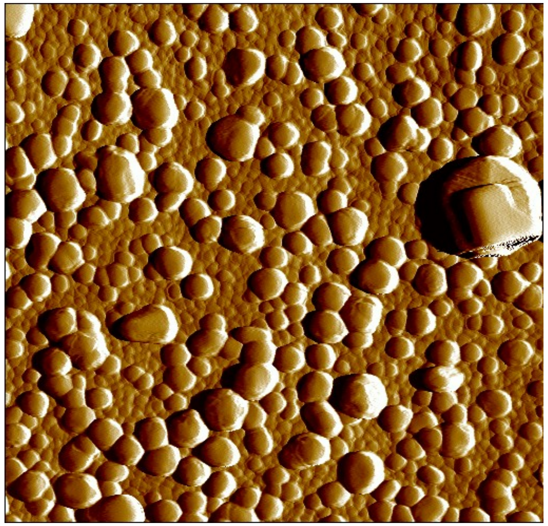
(a)



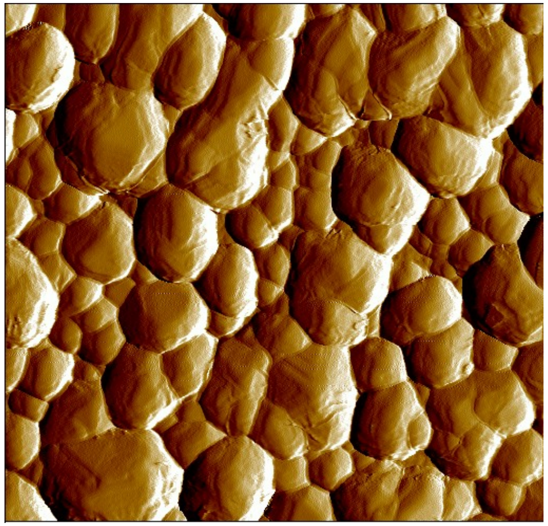
(b)



(c)

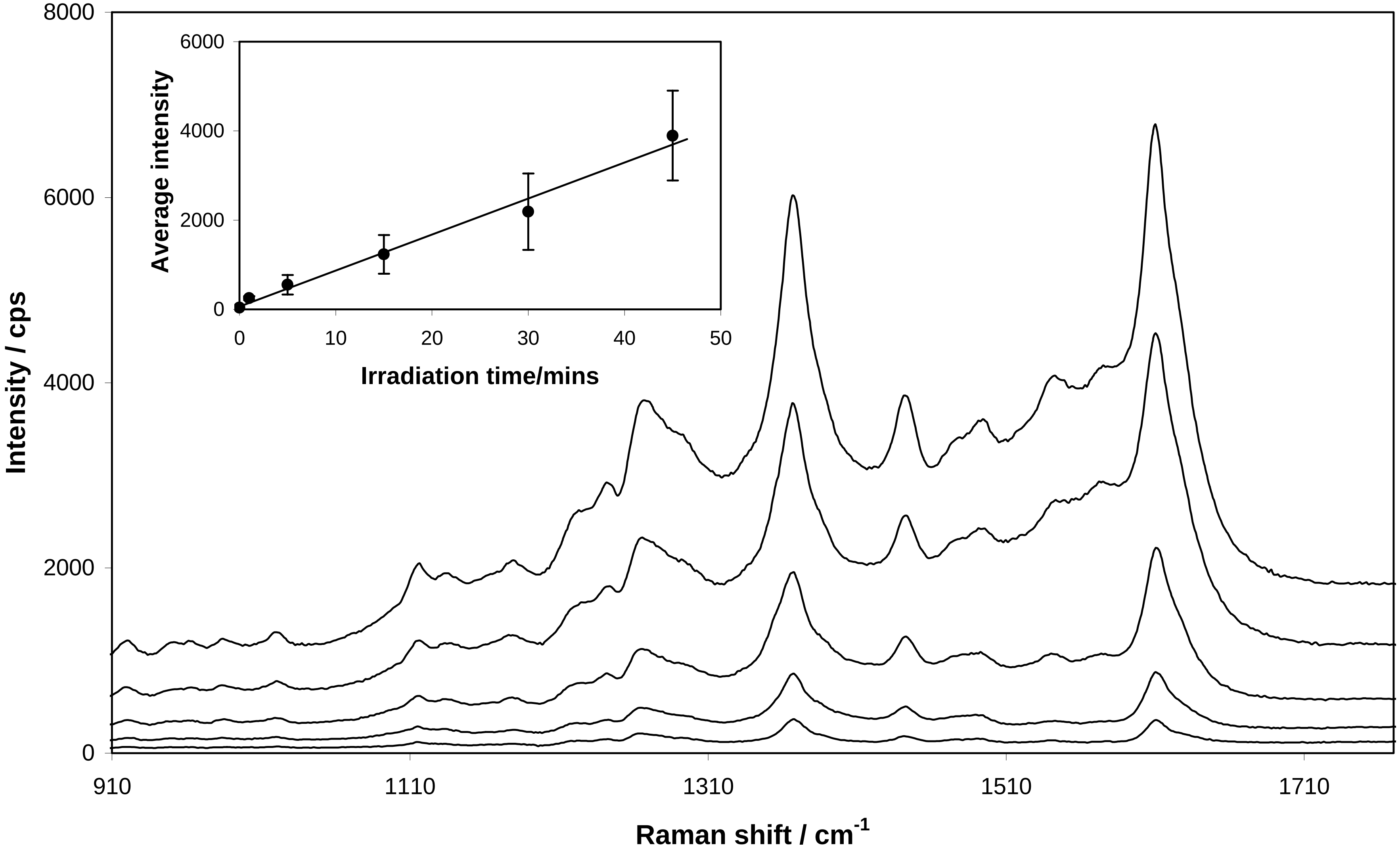


(d)



(e)

(f)


8000
6000
4000
2000
0
Intensity / cps
910
1110
1310
1510
1710
Raman shift / cm-1
6000
4000
2000
0
Average intensity
0
10
20
30
40
50
Irradiation time/mins