

Silver CD-R based substrate as a SERS active material

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Abstract A silver Compact Disc Recordable (CD-R) based substrate has been proposed as an alternative to silver colloids as active material successfully used in surface-enhanced Raman spectroscopy (SERS). Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDXS) measurements revealed that silver nanoparticles are present over the entire surface of the uncovered reflective layer of commonly used CD-R. The process of preparation of the CD-R based surface is simple, fast and repeatable. Recorded Raman spectra of 10 μM Rhodamine 6G applied to the substrate corroborate strong enhancement of Raman signal. The maximum value of EF was calculated to be about 5.76×10^6 . Raman maps are consistent with SEM micrographs and confirmed the presence of a numerous SERS hot spots occurring on the trucks of CD-R based substrate.

Keywords Nanomaterials · Raman spectroscopy · SERS technique · CD-R surface · Silver nanoparticles

Abbreviations

SERS	Surface-enhanced raman spectroscopy
R6G	Rhodamine 6G
IUPAC name	[9-(2-ethoxycarbonylphenyl)-6-(ethylamino)-2,7-dimethylxanthen-3-ylidene]-ethylazanium chloride

CD-R	Compact disc recordable
SEM	Scanning electron microscope
EDXS	Energy-dispersive X-ray spectroscopy

Introduction

The surface-enhanced Raman spectroscopy (SERS) is an extremely sensitive technique which provides amplification of the Raman signal by several orders of magnitude, thereby allowing the identification and structural characterization of small quantities of species [1–3]. This technique gives a number of additional possible applications, including: detection of single molecules [4–6] and indirect analysis of metallic surface properties [2]. Therefore, the SERS effect has been studied extensively in recent decades.

Among many theories proposed to explain the process of surface enhanced Raman spectroscopy, it is widely accepted that SERS effect consists using the large local field enhancements that can exist on the metallic surface (under the right conditions, typically by profiting from localized surface plasmon resonances) to boost the Raman scattering signal of molecules at (or close to) the surface [2, 6, 7]. Hence, the SERS process, and as a consequence enhancement factor (EF), depend on a number of parameters related not only to the analyte and excitation beam (like in normal Raman) but also on the surface. The chemical structure of the species, concentration and distance from the surface, efficiency of adsorption and possible impact on the Raman cross-section of molecules chemically adsorbed on the surface must be taken into consideration, which give the so-called chemical contribution to SERS EF. On the other hand, the most important contribution to SERS EF is brought by the electromagnetic factor that strongly depends on the properties of laser excitation (wavelength, power

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density, polarization, etc.) and on the kind of metallic structures, their shapes, size, orientation and homogeneity [2, 6, 8, 9].

Different kinds of SERS active substrates are extensively described in the literature. Mostly silver and gold nanostructures and colloids with dimension less than 100 nm are used because of their suitable optical properties to sustain plasmon resonances in the visible and near-infrared range [2]. However, in terms of the shape of the structures wide diversity is observed, from metallic colloids in solution to structures like: nanowires [10–12], nanorods [13, 14], nanocomb arrays [15], nanocluster films [16, 17], desorose-like [18] or dendritic nanostructures [19]. Although a variety of electrochemical, nanolithographic and deposition methods or synthesis have been employed with some success to fabricate SERS [20–25]. It is still in request to produce a low cost effective, reproducible, readily available and easy to manufacture substrate.

In this work new SERS-active substrate based on commercially available silver Compact Disc Recordable (CD-R) is proposed, as a new hitherto not described in the literature material, which is cheap and easy to obtain.

Experimental

Preparation of the SERS-active surface

A standard CD-R is made of polycarbonate plastic blank on the reflective layer (usually aluminium, but sometimes silver or gold). The metal is protected by a film of lacquer, normally spin coated directly on the reflective layer Fig. 1 [26].

CD-R Ultima 80 made by Kodak, with a silver reflexive layer was used for measurements after removing polycarbonate layer. A fragment of the CD-R disc was cut off and the reflexive layer was gently separated from the polycarbonate substrate. The reflexive layer was placed in toluene (MERCK) for 10 min for removing polycarbonate residues. The prepared layer was mounted on a microscopic slide by a double sided adhesive tape and dried on the air. A drop of 10^{-6} M water solution of Rhodamine 6G (R6G) (Sigma-Aldrich) was deposited on prepared substrate and left to dry on the air. The formula and structure of R6G are shown in Fig. 2. The solution was prepared using fresh deionised carbonate-free water (conductivity below $0.055 \mu\text{S}/\text{cm}$).

Microstructure analysis

SEM-EDXS measurements were performed by Scanning Electron Microscope SEM-FEI Quanta 600 equipped with PentaFETx3 Link Dispersive Energy X-ray Spectroscopy EDXS system managed by IncaOxford. A Si(Li) detector

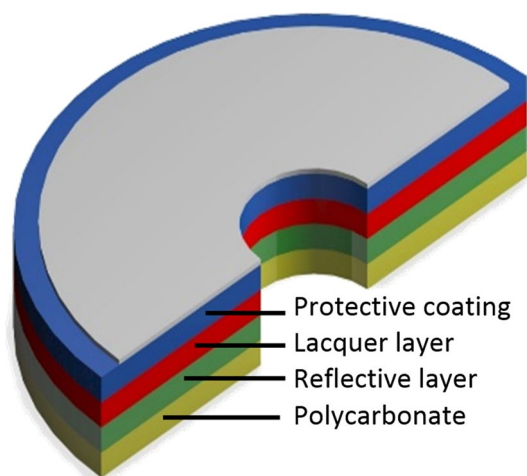


Fig. 1 The CD cross-section

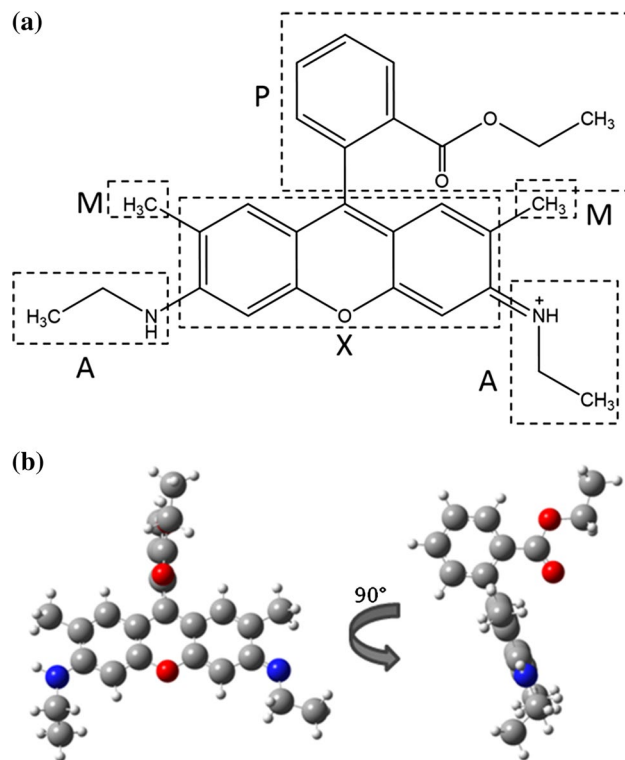
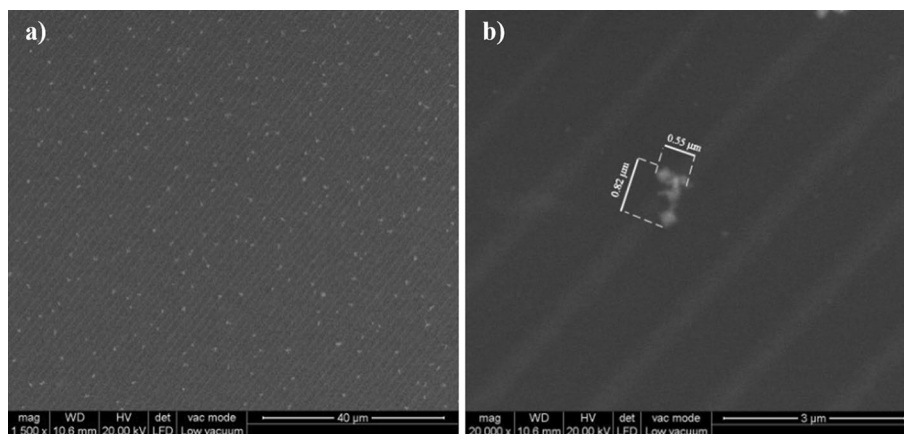


Fig. 2 Formula (a) and structure (b) of Rhodamine 6G (R6G) (*P* phenyl ring, *M* methyl group, *A* NHC_2H_5 group and *X* xanthene ring)

with a ultra-thin window ATW2, the resolution of 137 eV at 5 ($\text{MnK}\alpha 1$). The spectral data were acquired at the working distance 10.6 mm with an acceleration voltage (AV) of 20 kV.

In this work, the minimum required AV for CD-R sample was 6 kV, and all spectral data were acquired with counting time of 60 s, count for second approximately 642

Fig. 3 SEM image of CD-ROM surface recorded with magnification **a** $\times 1500$, **b** $\times 20,000$



cps with deadtime below 30 %. The results were processed by Inca software energy, which uses the XPP matrix correction scheme.

SERS measurements

All Raman maps and spectra of Rhodamine 6G adsorbed onto CD-R based substrate were recorded using Renishaw inVia Raman microscope equipped with an Argon-ion laser emitting 514.5 nm wavelength. The laser beam was reduced down to 2 μW and was focused on the sample through a long working distance of the 50x/NA 0.5 objective, thus the spatial resolution was better than 2 μm . The spectral resolution owing to the spectrometer being equipped with a 1800 g/mm diffraction grating was better than 2 cm^{-1} . The position of Raman peaks was calibrated before collecting the data using a Si sample as an internal standard. The Raman spectra of R6G were measured in 70–3200 cm^{-1} spectral range to correctly identify the dye and then, the spectral range was narrowed down to the 945–1825 cm^{-1} , in order to observe only the bands most characteristic for R6G.

Results and discussion

The surface characterisation of silver-based CD-R substrate was performed using the SEM/EDXS technique. SEM images of the CD-R surface obtained at room temperature in two different magnifications are presented in Fig. 3. The low magnification image (1500 \times) in Fig. 3a shows a typical surface of CD-R consisting of parallel tracks with a large number of bright dots. As can be observed from the high magnification micrograph in Fig. 3b (20,000 \times) the tracks are spaced apart by 1.6 μm and at the centre of the image an irregular shape of aggregated silver nanostructure of dimensions $0.55 \times 0.82 \mu\text{m}^2$ is observed.

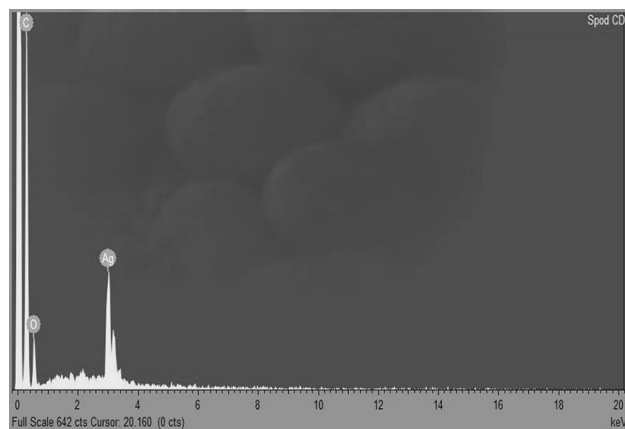


Fig. 4 EDXS spectrum of the white spots (silver particles)

Elemental EDXS spectrum acquired from a single silver particle is presented in Fig. 4. The EDXS spectrum is displayed in digitized form with the x-axis representing X-ray energy and the y-axis representing the number of counts per channel. Peaks at 0.277 and 0.525 keV correspond to carbon and oxygen, the elements which make the CD-R matrix, while the peak at 2.984 keV is attributed to the silver particles present on this matrix surface. SEM image with EDXS shows that the dark surface background in Fig. 3 is attributed to carbon and the homogeneously distributed white spots are attributed to the silver particles. Figure 3b shows a single silver particle. The EDXS semi-quantitative analysis of 10 different white spots confirmed that the composition of these particles is $97 \pm 1 \%$ silver, Fig. 4. Therefore, the prepared CD-ROM based sample contains silver nanostructures interesting from the SERS point of view.

Rhodamine 6G has been well-characterized by SERS [27], it was chosen as the model molecule to study the usefulness of CD-ROM-based sample as SERS active material. The enhancement of R6G signal by uncovered silver

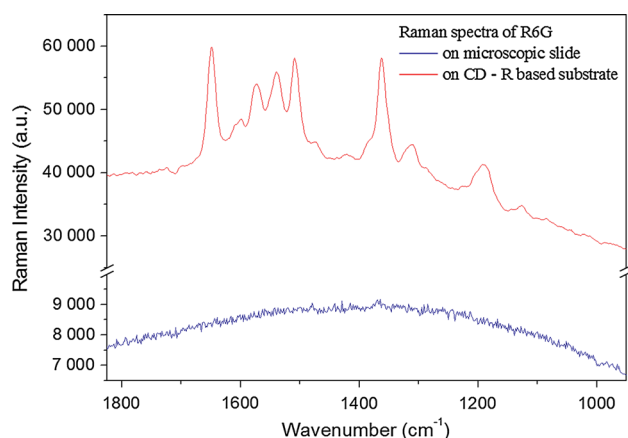


Fig. 5 Raman spectra of Rhodamine 6G

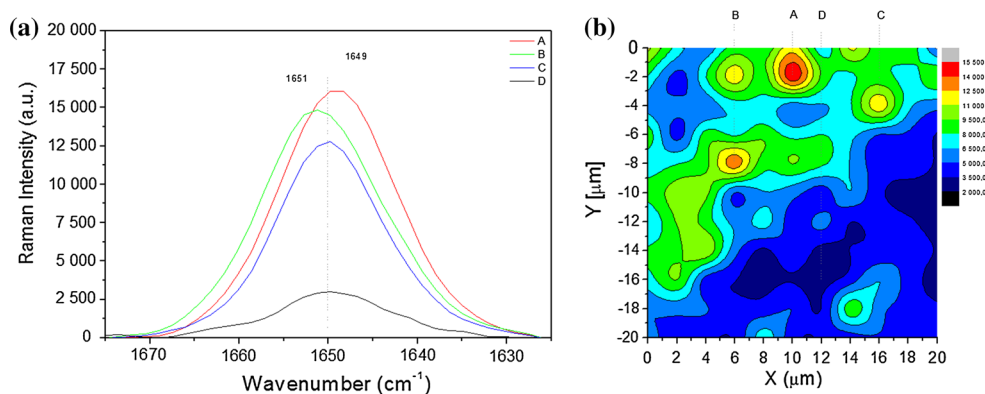
nanoparticles was analysed to define how strong enhancement is it possible to achieve in this composition. Measurements of the Raman map spectra of R6G were realized on area of $20 \times 20 \mu\text{m}^2$ with $2 \mu\text{m}$ step size. The spectral range of the SERS mapping experiment was $945\text{--}1825 \text{ cm}^{-1}$ and the exposure time 30 s per point, Fig. 5.

The full assignment of vibrational modes for R6G molecule by high-level density functional theory (DFT) calculations was proposed by Watanabe et al. [27] Rhodamine 6G molecule (Fig. 2) contains several vibrational units that can be described as “X” which represent the xanthene ring, “A” represents two NHC_2H_5 groups, “M” represents the two methyl groups, and “P” represents the phenyl ring with COOC_2H_5 group [27]. Figure 5b presents four different spectra chosen from the four different points from the area presented in Fig. 5a. The spectrum obtained from point D shows very low intensity Raman features and is typical for no enhanced signal. The spectra took from points A, B and C clearly exhibit characteristic peaks of R6G molecules at 1363 , 1508 , 1540 , 1575 and 1650 cm^{-1} . The modes recorded at 1363 and 1508 cm^{-1} are assigned to C–C stretching vibration of xanthene ring and NHC_2H_5

group. The band recorded at 1540 cm^{-1} is also attributed to vibrations of “X” and “A” part of R6G molecule. The vibrational mode at 1575 cm^{-1} is localized in the phenyl ring (“P” part) and is caused by C=C symmetric stretching. The highest intensity mode located at 1650 cm^{-1} is assigned to totally symmetric stretching vibrations of C=C bond and symmetric in-plane C–H bending vibrations of the xanthene ring “X”. The intensity of all bands changes with the position on the sample, which is correlated with the presence and the size of silver nanostructures on the surface of the CD-ROM-based substrate. In order to show the R6G Raman signal enhancement depending on the silver nanoparticles occurrence, the intensity of the strongest mode corresponding to C=C symmetric stretching vibrations of xanthene ring was presented in Fig. 6a. The estimated accuracy of the peak position of the band at 1650 cm^{-1} is equal to $\pm 1 \text{ cm}^{-1}$ and the change in the band position is not related to calibration of the spectrometer but is a physical effect. To determine correctly the intensity of the mode recorded at 1650 cm^{-1} , the background was cut off. The map of its intensity as a function of XY position is presented in Fig. 6b.

The hot-spots, where the intensity is much stronger, are not along all tracks, but occur only in some points of the surface. The intensity of the band at 1650 cm^{-1} at point A is 5 times stronger than that at point D. Furthermore, the lower intensity Raman spectrum recorded for point D demonstrates Raman features over the fluorescent background. The EF that confirms the efficiency of SERS signal has been estimated using formulae: $\text{EF} = (I_{\text{SERS}}/N_{\text{ads}})/(I_{\text{bulk}}/N_{\text{bulk}})$, where I_{SERS} is the intensity of selected vibrational mode in the SERS experiment, I_{bulk} is the intensity of the same Raman mode in the spectrum recorded for bulk material, N_{ads} is the number of molecules adsorbed and probed in SERS experiment, and N_{bulk} is the number of molecules probed in confocal volume of the optical system of Raman experiment [28–30]. The estimated number of R6G molecules on the area of laser spot N_{ads} assuming close packing is equal to

Fig. 6 R6G Raman mapping
a measurement accuracy;
b Raman map



3.12×10^5 , while the number of R6G molecules in the solid state material in the laser illumination volume N_{bulk} is equal to 19.74×10^9 . The intensity I_{SERS} of the of the Raman band at 1650 cm^{-1} at point A of Raman map (the strongest SERS signal) was about 16,000 a.u., whereas the intensity I_{bulk} of the same band recorded for bulk material was 176 a.u. Finally, substituting values of N_{ads} , N_{bulk} , I_{SERS} and I_{bulk} to mentioned above formulae, EF was calculated to be about 5.76×10^6 . The value of EF is quite comparable to values obtained by other Authors for different SERS-active substrates [28–30]. The obtained results proved usefulness of CD-R based substrate containing silver nanostructures for enhancement of Raman signal.

Conclusion

The results, presented in this work, showed that the layer rich in nanostructures of silver can be easily uncovered after removal of polycarbonate from CD-R. Moreover, the Raman signal of Rhodamine 6G adsorbed on this uncovered layer was successfully enhanced. The commercially produced CD-R with silver reflective layer was used as a SERS-active material for the first time. The polycarbonate plastic blank was removed and reflective layer was uncovered. In the SEM analysis the silver nanoparticles were lying on the horizontal line in different points of the sample, but always on CD-R tracks. The recorded SERS spectra of low-concentration of Rhodamine 6G show characteristic vibrational modes in the $945\text{--}1825 \text{ cm}^{-1}$ spectral range. The Raman maps reveal the hot-spots on the surface where the intensity of detected SERS signal is the strongest and they usually exist on tracks which complies with the SEM micrographs. The estimated EF value for the strongest signal at point A of Raman map is about 3.45×10^6 . It is very important that the preparation process of CD-R based substrate is fast, simple and repeatable.

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