

ESI

Entrapment into Charge Transfer Complexes for Resonant Raman Scattering Enhancement

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Substrate preparation: SERS-active substrates containing nanostructured silver were prepared in two simple steps. First of all, a surface of thin glass plates was cleaned with aqueous sodium bicarbonate, washed by deionized water of high purity (Milli-Q), then the plates were dipped in 0,5 M aqueous solution of sodium hydroxide and washed again with deionized water. Clean and dried glass plates were placed in aqueous solution of 0,25 M potassium hydrogen - fluoride (Aldrich, KHF₂) for 60 min at 80°C, followed by washing, drying and magnetron sputtering of metallic silver (99%) with a thickness of about 10 nm in a standard way using the Q150TES (Quorum Technologies Q150T Turbo-Pumped Sputter Coater / Carbon Coater, UK) setup.

Alternatively, spray pyrolysis deposition of aqueous diaminsilver hydroxide was used in which 0.1 M aqueous sodium hydroxide (Aldrich NaOH, high purity water, Milli-Q, Millipore) was added dropwise to freshly prepared 0.01 M aqueous silver nitrate solution until complete precipitation of a black-brown silver (I) oxide. This as - prepared oxide was thoroughly washed with deionized water and dissolved in a two-fold molar excess of a 10% aqueous ammonia solution (prepared from 30% ammonium hydroxide, Aldrich) to have 0.01 M solution of a silver (I) complex; a higher concentration deteriorates the silver ring structure formation while superstoichiometric ammonia is needed to prevent Ag₂O precipitation at the aerosol production stage. The obtained transparent silver complex solution was filtered through Millex-LCR syringe driven filter units (Millipore, 0.45 mm pores). In the ultrasonic silver rain (USR) deposition process, this initial ammonia solution of silver (I) oxide was nebulized into mist and 1–5 micron droplets were streamed onto “warm” (200–270 °C) glass with a roughened surface. [A.A. Semenova, E.A. Goodilin, A.N. Brazhe, V.K. Ivanov, A.E. Baranchikov, V.A. Lebedev, A.E. Goldt, O.V. Sosnovtseva, S.V. Savilov, A.V. Egorov, A.R. Brazhe, E.Y. Parshina, O.G. Luneva, G.V. Maksimov, Y.D. Tretyakov, J. Mater. Chem., 2012, **22**, 24530].

Solution preparation: Samples of Dibenzothiophene (DBT, 98% Sigma-Aldrich), Dibenzothiophene sulfoxide (DBTO, Santa Cruz Biotechnology), Dibenzothiophene sulfone (DBTO₂, 97% Sigma-Aldrich) and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 98% Sigma-Aldrich) were dissolved in 5.0 ml chloroform to obtain 10⁻⁴-10⁻⁶ M solution(s).

The prepared SERS-active substrates were dipped first into a solution of DDQ in CHCl₃ with a concentration of 10⁻⁴ M. Then, 10mkl of DBT or DMDBT dissolved in CHCl₃ were deposited using different concentrations of 10⁻⁴-10⁻⁶ M (Fig.1).

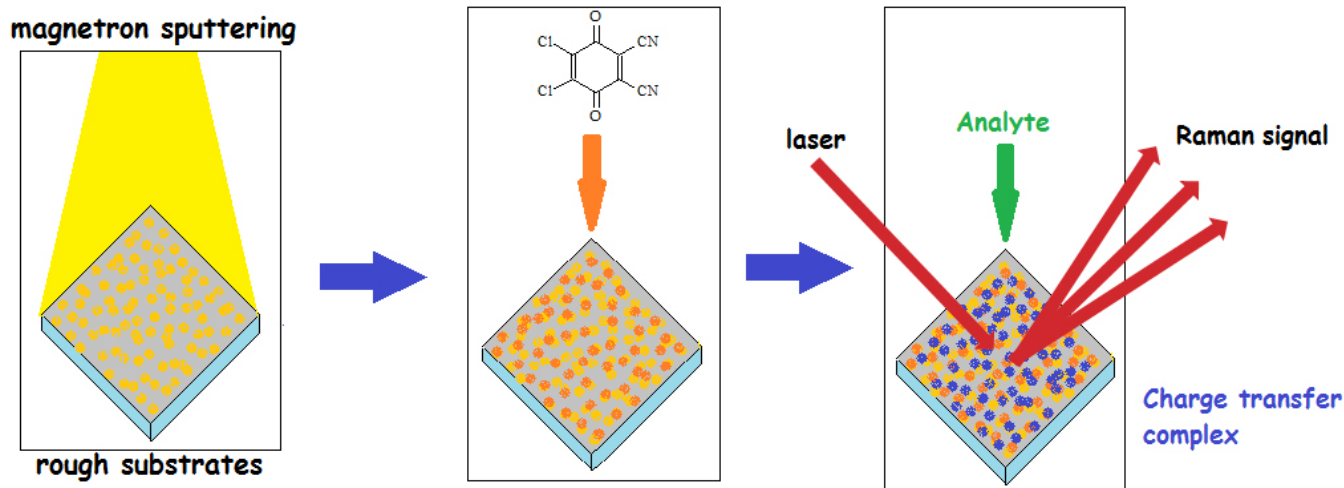


Fig.1. A scheme of sample preparation

SERS experiments were performed using an InVia Raman microscope (Renishaw, UK) equipped with a 20 mW 633 nm argon laser and power neutral density filter (10%). All the spectra were collected using a 20× objective lens and 10s of acquisition time. A silicon wafer was used for calibration.

The enhancement factors EF were counted as a ratio of corresponding peak intensities for SERS

$$EF = \frac{I_{SERS}}{I_{RS}} \cdot \frac{N_{RS}}{N_{SERS}}$$

and RS measurements divided by the ratio of corresponding concentrations

The obtained substrates were examined by XRD measurements using Rigaku D/MAX 2500 (Japan) with a rotating copper anode ($\text{CuK}\alpha$ irradiation, 5–90° 2θ range, 0.02° step). Diffraction maxima were indexed using the PDF-2 database. XRD measurements show intense reflections of the typical face-centered cubic lattice of silver (Fig.2). UV-vis absorption spectra were recorded using the UV-vis spectrophotometer Lambda 35 (Perkin-Elmer) with an attached diffuse reflectance accessory. In the absorption spectra of the nanostructured substrates there is a peak at appr. 400 nm corresponding to a plasmon band of silver. The spectrum is characterized by a long "tail" in the red region due to the hierarchical structure of the silver substrates.

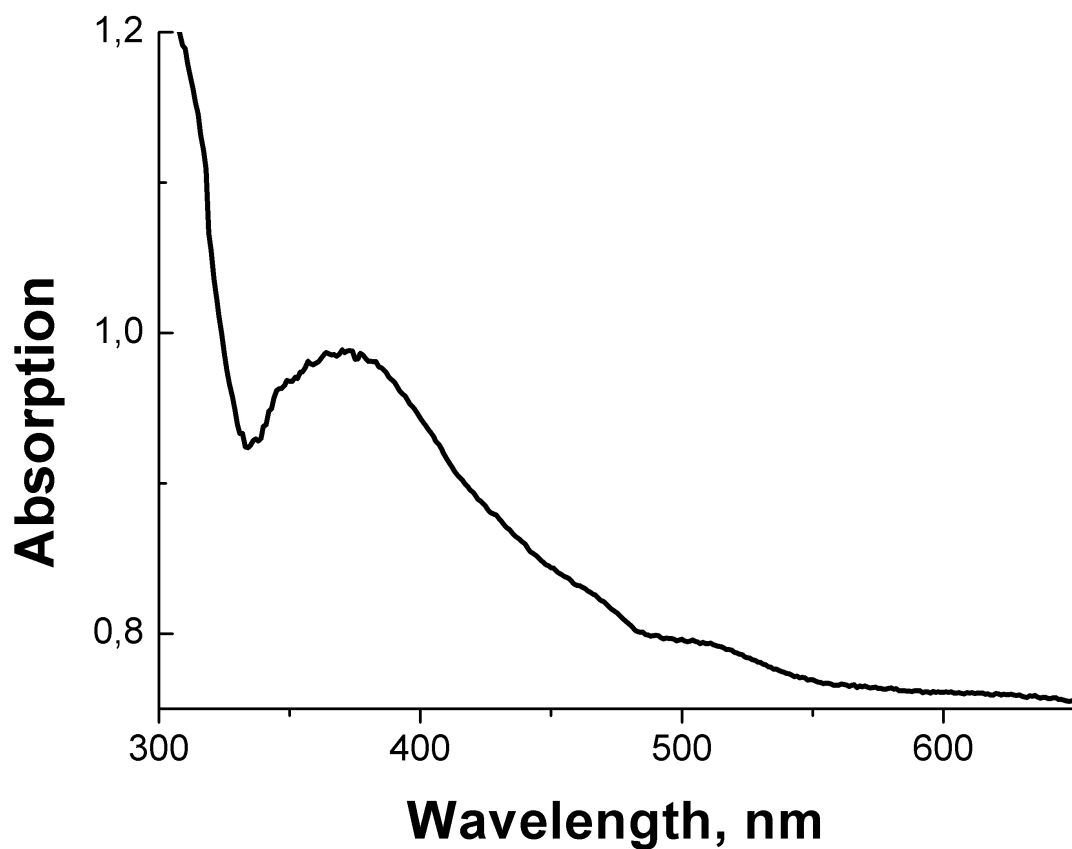
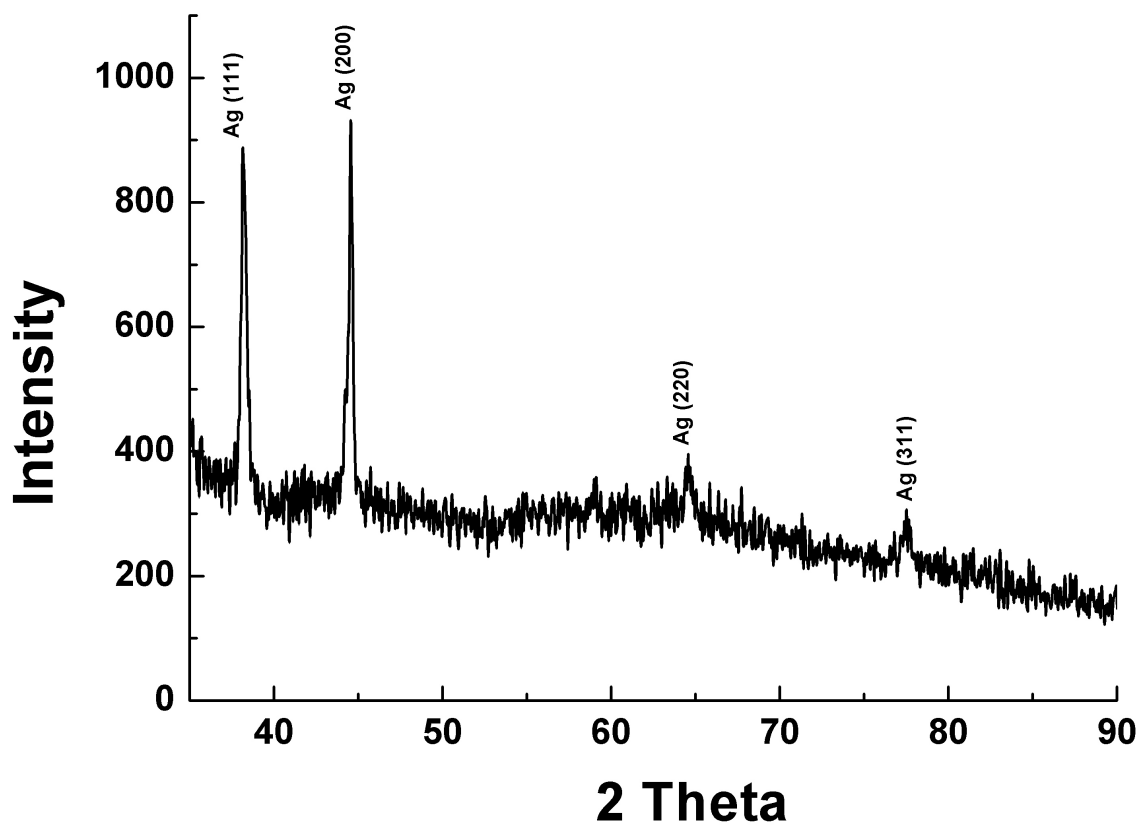


Fig.2. (1) - XRD data of the nanostructured of silver substrates, (2) - The diffusion reflectance spectra of the nanostructured silver substrates.

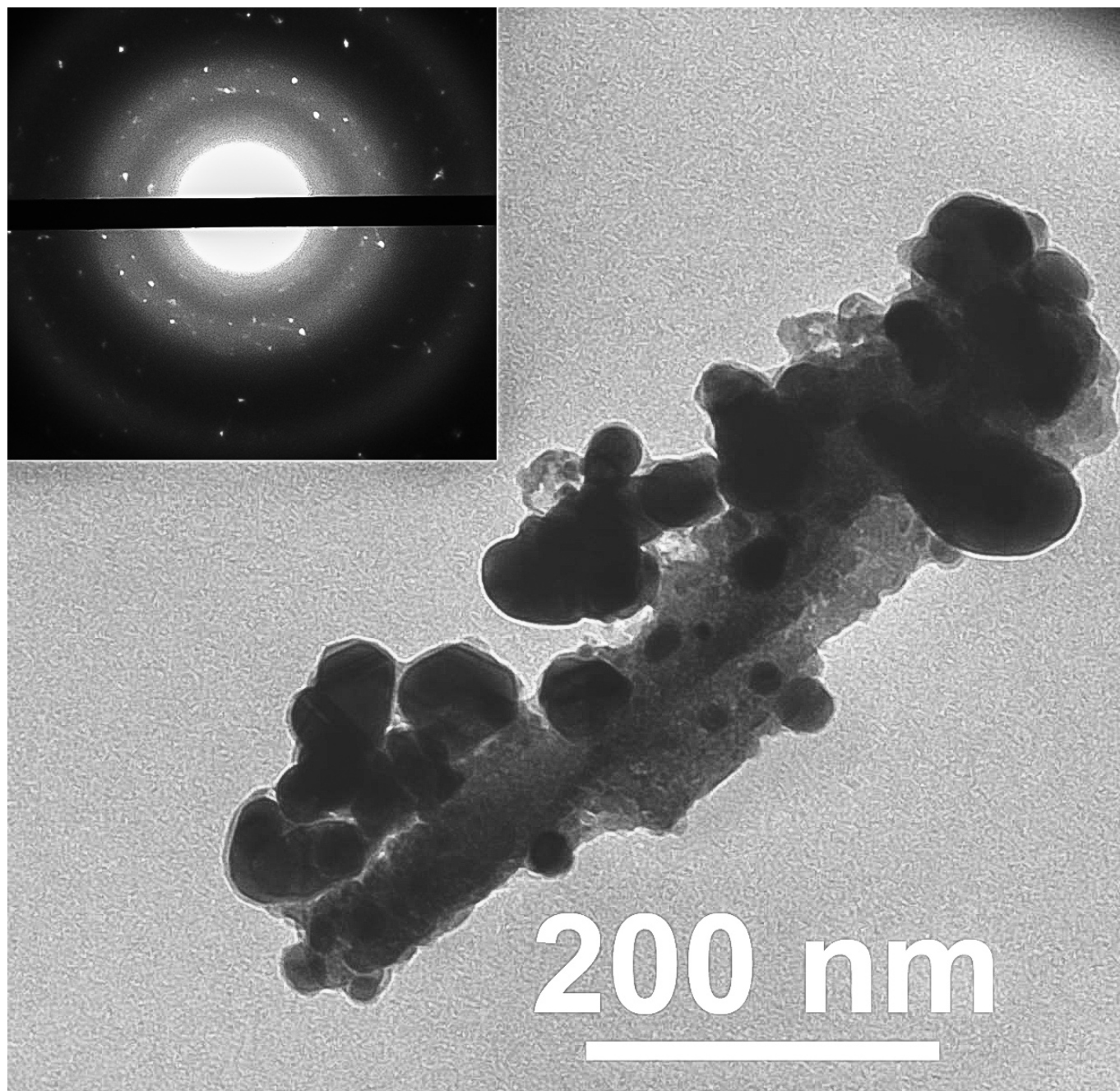


Fig.3. Typical transmission electron microscopy (TEM) images and electron diffraction (ED) of fragments of nanostructured silver substrates

The obtained nanostructured substrates were also characterized by scanning electron microscopy (Carl Zeiss NVision 40) and transmission electron microscopy (TEM) combined with electron diffraction (LEO912 AB OMEGA, Carl Zeiss). A TEM study of the samples showed that silver has a wide size distribution of nanoparticles (5 - 70 nm), that is typical of long processes of nucleation and growth. Electron diffraction shows the presence of metallic silver (Fig.3).

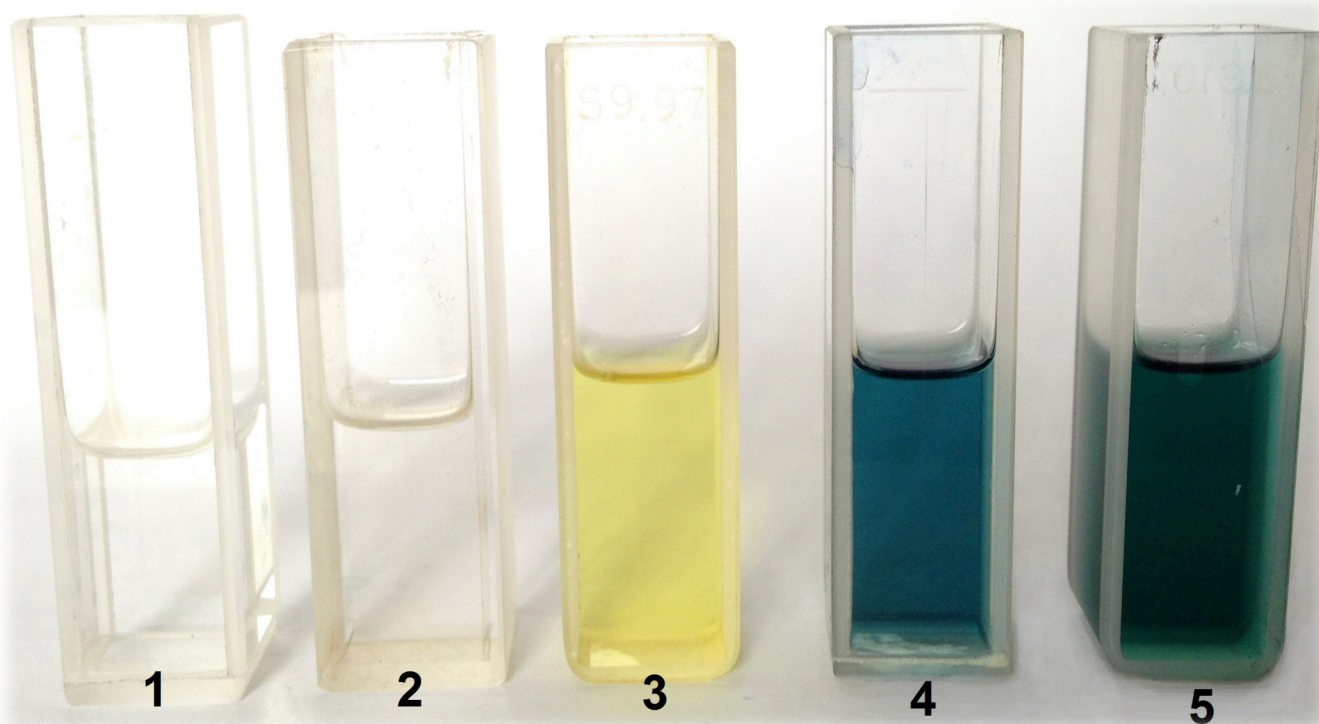


Fig.4. Optical images of analytes and charge transfer complex: 1 - dibenzothiophen (DBT), 2 – dimethildibenzothiophen (DMDBT), 3 – 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 4 – charge transfer complex of DBT with DDQ, 5 – charge transfer complex of DMDBT with DDQ

The samples prepared have different colors (Fig.4) – from transparent (1, 2), yellow (3) to intensively colored for charge transfer complexes (4, 5).