Highly porous nanocomposites based on TiO2-noble metal particles for sensitive detection of water pollutants by SERS

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Abstract. Highly porous nanocomposites based on TiO2 aerogel and silver colloidal particles were prepared by different methods in order to study their capacity to detect pollutant species adsorbed on metallic nanoparticles surface from aqueous solution. The efficiency of the obtained composites to detect contaminants from water by means of SERS was evaluated using acrylamide and crystal violet as test molecules. It was found that the detection limits depend both on pollutant and composite type, and were determined to be in the range of $10^{-1}$-$10^{-4}$ M for acrylamide and around $10^{-5}$ M for the dye molecule. These results prove the potential of the prepared porous composites for further use in the development of new SERS-based sensors devices.

1. Introduction

Clean water is essential to human health. The world is facing formidable challenges in meeting rising requirement to clean water. Even trace pollutants can enter in human body and affect the human health. Trace detection and treatment of the pollutants become an essential problem that requires a rapid elucidation [1]. Current analysis of water pollutants include their pre-extraction using techniques such as headspace analysis, purge and trap, etc. from large quantities of water followed by chromatographic analysis. These methods are laborious, time consuming and expensive, hence unsuited for monitoring of locations where high temporal variations occur; therefore, efficient, in situ methods are desired [2, 3].

Due to its sensitivity and exceptional spectral selectivity, surface-enhanced Raman scattering (SERS) was thought to be a promising technique for the trace detection and analysis of environmental samples [4]. The primary attraction of SERS consists in its ability to provide large amounts of structural details. It can act as a molecular “fingerprint” and can allow simultaneous analysis of trace
analytes in a complex mixture without extraction and separation steps. SERS overcomes the most significant drawback of normal Raman spectroscopy for analytical applications, i.e. the inherently weak cross section, by exciting the sample in contact with a ‘plasmonic’ surface with an appropriate laser line. Under such conditions, the Raman cross section and, in turn, the signal intensity are extraordinarily enhanced so that levels of detection down to the single molecule can be reached, without loosing the structural information provided by Raman spectroscopy [5].

The development in SERS detection is related to the progress in synthesis and optical characterization of new nanostructured materials able to control both the enhancement mechanism (electromagnetic and chemical) and the adsorption of the analytes of interest [6]. The preparation of optical substrates with optimized properties is a very dynamic field of research, being developed many types of substrates: metal colloids, metal island films, self-assembled monolayer-modified metal substrates, metal-coated microsphere and metal nanoparticles entrapped in sol-gel derived matrix [7,8].

Nobel metals sealed in TiO$_2$ sol-gel matrixes present many advantages as SERS substrates: (1) the matrix isolation against aggregation leads to the stability of entrapped metal nanoparticles, (2) the porosity encourage the diffusion of analytes in the matrix and consequently the increasing the number of metal/analytes contacts, (3) enhanced adsorption capacities and selectivity obtained by matrix functionalization [9].

In a previous work [10], we obtained by different chemical routes porous nanoarchitectures based on TiO$_2$ aerogel and Au colloidal particles, annealed them at 500°C for 2 hours, and tested their capability to detect by SERS contaminant species adsorbed from an aqueous solution on metallic nanoparticles surface. The composites detection efficiency was established by using thioacetamide, crystal violet and rhodamine 6G as test molecules and the lowest detectable concentrations were found to be around $10^{-2}$ M for thioacetamide and in the range between $10^{-5}$ and $10^{-7}$ M for dye molecules off and under resonant excitation, respectively.

Having in view the affinity of some pollutant molecules, e.g. chlorates, amino and hydroxyl, to bind to the metallic silver surface, in the present work we proposed to evaluate the potential of new types of highly porous nanocomposites based on titania aerogel and Ag colloidal particles, prepared by three different methods and annealed at 500 °C for 2 hours, to detect pollutant species adsorbed from an aqueous solution on the noble metal surfaces. Prior evidencing the detection efficiency of the composites for different pollutant molecules, the existence of their porous-like structure was proved by means of scanning electron microscopy (SEM) images and specific surface area measurements. The TiO$_2$ crystalline phase that built up the composites porous network was examined by X-ray diffraction (XRD) and Raman spectroscopy.

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of silver colloid. The silver colloidal solution was prepared by the following method [11]: 100 ml of 5x10$^{-3}$ M silver nitrate (AgNO$_3$) was heated to boiling under continuous stirring. 300 ml of 2x10$^{-3}$ M sodium borohydride (NaBH$_4$) was added dropwise with vigorous stirring. The boiling and stirring of the reaction mixture was continued for another 60 min. Colloidal solution were stored in clean brown glass bottles until used.

2.1.2. Preparation of titania gel. TiO$_2$ gels were prepared with by sol-gel procedure using titanium isopropoxide (Ti(OC$_3$H$_7$)$_4$), nitric acid (HNO$_3$, 70%), ethanol (92%) and distilled water in molar ratio of 1/0.08/21/3.67. The formed gels were aged for 21 days.

- **Method 1- composite TiO$_2$-Ag1**

The aged TiO$_2$ gel was dried under supercritical conditions with liquid CO$_2$ (T = 40°C and p = 1400 psi) in order to obtain a highly porous material, named aerogel. The TiO$_2$ aerogel was
immersed into the silver colloidal solution where was maintained for three days. The aerogel impregnated with silver nanoparticles was three times washed with ethanol (92%) and then dried at 100°C.

- **Method 2-composite TiO$_2$-Ag$_2$**
  The aged TiO$_2$ gel was immersed into the silver colloidal solution and maintained there for three days. Afterward it was washed with ethanol (92%) and dried under supercritical conditions.

- **Method 3-composite TiO$_2$-Ag$_3$**
  The silver colloidal solution was added in the TiO$_2$ gel synthesis mixture instead of distilled water. The obtained gel was allowed to age and then dried under supercritical conditions.

  The aged TiO$_2$ gel was also dried under supercritical conditions in order to obtain silver metal nanoparticles free sample and was investigated only for comparison purpose. This sample will be further denoted as TiO$_2$.

  All prepared samples were subjected to a thermal treatment at 500 °C for 2 h in order to remove the organic residues.

2.2. Sample measurements

The surface area of the as prepared samples was determined by the BET method, in a partial pressure range of 0.05<P/P$_0$<0.3. The nitrogen adsorption was carried out at 77 K. Before each measurement the samples were heat cleaned at 333 K for 2 h. The total pore volume ($V_{TP}$) was obtained from the N$_2$ adsorption isotherm at a partial pressure of 0.98.

SEM measurements were performed with a Quanta 3D FEG 200/600 scanning electron microscope. A Jeol JEM 1010 TEM operating at an accelerating voltage of 100 kV equipped with a MegaViewIII CCD camera was utilized to obtain characteristic images. The samples were sonicated for 15 min and then deposited on Cu grids with carbon film evaporated on freshly cleaved mica.

  The phase content and the particle dimensions were determined using a DRON X-ray powder diffractometer linked to a data acquisition and processing facility; CuK$_\alpha$ radiation ($\lambda = 1.540598$ Å) and a graphite monochromator were used.

  SERS spectra were recorded with a WITec confocal Raman system CRM 200 equipped with a 100x/0.8 microscope objective and a 300 lines/mm grating. In the recording of the spectra, the 532 nm laser line with a power of 3 mW and a spectral resolution around 7 cm$^{-1}$ were employed. Prior to perform the SERS measurements the composites were kept 2-3 min. into aqueous solutions of contaminants of various concentrations. In order to assure the measurements reproducibility SERS spectra were collected from different points located on the composites surface and inside the samples.

  The FT-Raman spectrum of the crystal violet was recorded using a Bruker Equinox 55 spectrometer with an integrated FRA 106 Raman module, a radiation with a power of 30 mW incident on sample, and a spectral resolution of 4 cm$^{-1}$. A Nd-YAG laser ($\lambda = 1064$ nm) was employed for the recording of Raman spectra of the bulk pollutant molecules.

3. Results and discussion

The first argument that accounts for the existence of a porous structure is given by the values obtained from the BET surface area measurements presented in Table 1. It can be observed that the composite TiO$_2$-Ag$_2$ exhibits the highest BET area (157 m$^2$g$^{-1}$), while TiO$_2$-Ag$_3$ the smallest one (129 m$^2$g$^{-1}$).

One should note that the presence of silver nanoparticles induces an increase of the pores surface area.
Table 1. Textural and structural properties of the TiO$_2$ and TiO$_2$-Ag composites from BET and XRD measurements.

| Sample      | Specific surface area (m$^2$·g$^{-1}$) | Phase composition (%) | Crystallite size (nm) |
|-------------|------------------------------------|-----------------------|-----------------------|
|             |                                    | Anatase   | Brookite   | Anatase   | Brookite   |
| TiO$_2$     | 121                                 | 92.2      | 7.8        | 11        | 13         |
| TiO$_2$-Ag1 | 135                                 | 76.7      | 23.3       | 10        | 9          |
| TiO$_2$-Ag2 | 157                                 | 100       | -          | 10        | -          |
| TiO$_2$-Ag3 | 129                                 | 88.9      | 11.1       | 15        | 9          |
| Errors      | ±6                                  | ±0.5      | ±0.5       | ±1.5      | ±1.5       |

The highly porous character of the annealed aerogel like composites was tested out by SEM images. Selected images of TiO$_2$-Ag composites are illustrated in Figure 1. As can be observed the samples show a porous structure that allows the diffusion of pollutant molecules through the three dimensional structure and their adsorption on the silver nanoparticle surfaces.

Prior evaluating the composites ability to detect small concentrations of contaminant species from water by SERS, the samples were structurally examined by performing XRD measurements. XRD patterns are shown in Figure 2 and confirm the presence of anatase phase, which is accompanied for two composites by a quite important fraction of brookite phase (see Table 1).

The smallest anatase content (76.7 %), as revealed by Rietveld refinement, was obtained for the annealed composite prepared by impregnation of the TiO$_2$ aerogel with Ag colloidal suspension (sample TiO$_2$-Ag1). It was found that the sample TiO$_2$-Ag2, obtained by impregnating the aged TiO$_2$ gel with Ag colloidal suspension followed by thermal treatment, contains anatase as unique phase, while the sample TiO$_2$-Ag3, prepared by replacing the water during the sol-gel process with the Ag colloidal suspension, has a structure built up from 88.9 % anatase. By comparing the percentage obtained for TiO$_2$ sample with those derived for the composites one can infer that the preparation method of the composite TiO$_2$-Ag2 favors the anatase phase development, while the preparation of the composites TiO$_2$-Ag1 and TiO$_2$-Ag3 favors the brookite phase formation.
Figure 2. a) X-ray diffractograms of the TiO$_2$ and TiO$_2$-Ag composites; b) XRD patterns of anatase, brookite and silver based on ICSD.

The mean size of the TiO$_2$ crystallites was also derived from XRD diffractograms and is presented in Table 1. The crystallite size has been calculated by using the Scherrer equation for all reflection lines in the range of 20-70 (2θ degrees). Because of very low content (expected to be lower than 1wt %), no silver peaks were evidenced in the XRD patterns.

The obtained results were confirmed by TEM images that provided additional information related to the dimension of the Ag nanoparticles, found to be around 8.5±2.5 nm for all investigated samples (see Figure 3).

Figure 3. Selected TEM images of the TiO$_2$-Ag composites as indicated.

Our attention was further focused on the assessment of the porous composites capacity to detect various pollutant species adsorbed on Ag nanoparticles surface. Small amounts of each composite
were immersed for 2-3 min. into aqueous solution of different test molecules, i.e. acrylamide and crystal violet, and Raman spectra were recorded. Figures 4 (crystal violet) and 5 (acrylamide) show spectra recorded on porous TiO₂-Ag composites after immersion. One can recognize the most intense Raman characteristics of TiO₂ anatase phase in the low wave number region (around 144, 400, 515 and 636 cm⁻¹) that originate from vibrations of TiO₆ octahedra. Other spectral features that based on the comparison of the spectra with the Raman spectra of contaminant bulk sample can be easily associated with signals given by pollutants vibrations can be observed. Thus, in the spectra of all composites immersed in crystal violet solution (Figure 4) the bands around 1612 cm⁻¹, due to the stretching vibrations of CC from phenyl rings, and those around 1366 and 1175 cm⁻¹, attributed to the CN stretching and CH bending vibrations, respectively, occur [10,12]. The bands from the spectra of composites maintained in acrylamide solution (Figure 5) observed at 1635 and 1435 cm⁻¹ are given by CC and CN stretching vibrations, and that around 1275 cm⁻¹ was attributed to the CH₂ deformation vibration [13]. Taking into account the small concentration of pollutant molecules one can certainly conclude that these fingerprints are given by the vibrational modes of the adsorbed species. The changes in position and relative intensity of the SERS bands with respect to their corresponding Raman bands of the contaminant bulk samples further support this statement.

The detection sensitivity of the investigated porous composites was also established by using various solutions of predetermined concentration for each pollutant molecule. It was found that the detection limits depend on the sample preparation method and the pollutant type. Composite TiO₂-Ag₁ was found to exhibit the best detection sensitivity for crystal violet (10⁻⁵ M) and the worst one for acrylamide (10⁻¹ M). Composite TiO₂-Ag₂ exhibited the best detection capacity for acrylamide (10⁻⁴ M) and a good sensitivity for crystal violet (5x10⁻⁵ M), while the sample TiO₂-Ag₃ was able to detect concentrations of 10⁻³ and 5x10⁻⁵ M for acrylamide and crystal violet, respectively.

Figure 4. Raman and selected SERS spectra of crystal violet adsorbed on TiO₂-Ag samples. Note that the pollutant concentrations are also indicated.
Similar results were obtained by using noble metal nanoparticles sealed in porous silica matrix when the detected limit concentration was of $10^{-5}$ M of dye molecules [14]. In a recent study [15], we obtained porous nanoarchitectures based on TiO$_2$ aerogel and noble metal colloidal nanoparticles by using various methods of preparation, and tested their capability to detect by SERS chemical pollutants from water. The remarkably small detection limits (between $10^{-3}$ and $10^{-10}$ M) determined in the reported study were due to the missing of the heat treatment, on one hand, and to the recording of the SERRS (surface enhanced resonance Raman spectroscopy) spectra, on the other hand. However, there is a compromise between the porosity preserving and the organic residues removal, and therefore, in the present study a thermal treatment was applied. It should be noted that there are SERS-active substrates able to detect concentrations lower than those detected using our composites, but they are very unstable over time [7]. Therefore, it should be emphasized that the most important advantages of the TiO$_2$ aerogel-noble metal nanoparticles based SERS substrates over the conventional ones are their time stability and resistance to different environmental conditions.

One should emphasize that for all porous composites SERS spectra were recorded from different points inside the samples (up to 100 μm). This proves the good dispersion of the Ag nanoparticles located inside the TiO$_2$ pores and indicates once again that the recorded signals are indeed originating from molecules adsorbed on noble metal surface. Although the applied thermal treatment induces a clear diminution of the pores volume, the contaminants detection by SERS is still remarkable, when relatively large molecules like crystal violet adsorbed on Ag nanoparticle surfaces. Furthermore, since the stability of the obtained porous composites samples is higher in comparison with that of the silver colloids in liquid media [7], these samples can offer additional advantages besides those of detecting water pollutants by using SERS.

4. Conclusions

In the work presented herein we prepared three different types of porous composites based on TiO$_2$ aerogel and silver colloidal particles that are able to detect by SERS small concentrations of various pollutants adsorbed on the noble metal surfaces. Prior evidencing the detection efficiency of the composites for different pollutant molecules, the existence of their porous-like structure was proved with the help of SEM images and specific surface area measurements and, they were structurally investigated by XRD technique. The detection capacity by SERS of the porous samples obtained after
the immersion of the TiO$_2$ gel in Ag colloidal solution followed by supercritical drying and heat treatment was superior to the other types of composites for both test molecules. The lowest detectable concentrations were found to be of $10^{-4}$ and $5 \times 10^{-5}$ M for acrylamide and crystal violet, respectively. The detection limits were established and found to be in the range of $10^{-1} - 10^{-4}$ M for acrylamide and around $10^{-5}$ M for crystal violet.

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