Use of Vibrational Spectroscopic Techniques for the Characterization of Structured Particles for Chemical Robots

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This work is aimed at utilization of vibrational spectroscopic techniques for characterization of several types of structural particles suitable for the construction of chemical robots. Several case studies are presented and discussed: (i) PNIPAM-coated silica particles, (ii) surface-functionalized magnetic nanoparticles modified by citric and oleic acid, (iii) nanocomposit SERS-active substrates consisting of self-assembled monolayers of linear α,ω-aliphatic diammines with different lengths on Ag metal surface and a flat Ag electrode followed by testing of sensing activity of AD/NPs systems in the detection of the pesticide aldrin.

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1. INTRODUCTION

Chemical robots are in principle artificial cells, with the exception of the ability to evolve and self-replicate. The main components of such a synthetic cell are (i) a "body" (shell) that defines properties such a size, shape, hardness and should facilitate the exchange of molecules with the environment similarly as a cell membrane, (ii) the internal space with compartments which should process absorbed molecules and release or accumulate products of chemical reactions. Chemical robots should also have the ability to move either passively or actively in the surrounding medium, and to adhere to target substrates or objects. Chemical robots may be used for targeted drug delivery, recovery of valuable chemicals from dilute resources, environmental clean-up, as smart diagnostic devices, or other applications [1].

The adhesion of chemical robots to substrates or other robots may be affected by several parameters, such as by their shape, size, and surface properties. One possibility how to control particle size and surface properties is to use the so-called smart polymers that change their volume and hydrophilic/hydrophobic properties by external stimuli, e.g.microcapsules consisting of the thermo-responsive polymer PNIPAM and inorganic nanoparticles.

Magnetic nanoparticles have been recently extensively studied because of their extensive applications in biochemistry, bioseparation, tissue repair and in vivo drug delivery [2]. The properties of magnetic nanoparticles can be significantly altered by its physical and physicochemical characteristics, such as morphological and compositional, and the possibility of engineering the particle surface to promote specific interactions with different targets. The key to understanding the properties and stability of magnetic nanoparticles in different environments resides in the elucidation of their surface structure and its respective chemical composition. The interaction between the surfactant and nanoparticle is critical and essential for both synthesis and further applications of nanoparticles [3].

The controlled fabrication of nanostructured junctions in SERS substrates is nowadays one of the critical targets in nanotechnology [4]. The functionalization of metal nanoparticles (NPs) by bifunctional agent gives rise to the formation of highly sensitive interparticle junctions by simultaneously creating intermolecular cavities (IC) where the approaching of detected substances is possible, enabling so called single molecule detection (SMD) due to the formation of specified locations with extremely high enhancement abilities, named hot spots (HS) [5]. One of the suitable groups of substances which can serve as bifucntional linkers with promising properties for the creation of HS and IC are α,ω-aliphatic diammines (DA).

In this work several types of structural particles were analysed and characterized by vibrational spectroscopic techniques: (i) PNIPAM-coated silica particles, (ii) surface-functionalized magnetic nanoparticles modified by citric and oleic acid, (iii) nanocomposit SERS-active substrates consisting of self-assembled monolayers of linear α,ω-aliphatic diammines with different lengths on Ag metal surface and a flat Ag electrode followed by testing of sensing activity of AD/NPs systems in the detection of the pesticide aldrin.

2. EXPERIMENTAL

2.1 PNIPAM-coated SiO_2 microparticles

For the PNIPAM-coated silica particles preparation commercial microparticles based on silicium dioxide with a mean size of 5 µm (Sigma) were used. The particles were functionalized by silanization by methacryloxypropyltrimethoxysilane (MPS, Sigma). The PNIPAM coating was carried out by a conventional polymerization process [6]. The FTIR spectroscope (Nexus, Nicolet) was used to confirm the synthesis of PNIPAM-coated silica microparticles. All measurements were carried out on the ATR accessory. Each spectrum was measured with a resolution 2 cm^{-1} and 128 scans.

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2.2 Citric acid coated γ-Fe₂O₃ nanoparticles

The citric acid coated γ-Fe₂O₃ nanoparticles were synthesised using the in-situ and the ex-situ approach. The uncoated nanoparticles were formed according a procedure by Maity et al. [7]. The ex-situ citrate coated γ-Fe₂O₃ nanoparticles were synthesised using a similar procedure according to Sahoo et al. [8]. Citric acid coated nanoparticles prepared in this way could be dried, stored under atmospheric conditions, and easily re-dispersed in aqueous media to form stable ferrofluids of the desired concentration. FTIR spectra of the nanoparticles were collected using a Nicolet Nexus 670 spectrometer (Thermo, USA) in the range of 4000 - 400 cm^{-1} at 4 cm^{-1} resolution. All presented spectra are the average of 256 scans. The sample powders were mixed with KBr and compressed into a pellet. The baseline corrections were performed using OMNIC 7.0 software (Thermo,   USA).
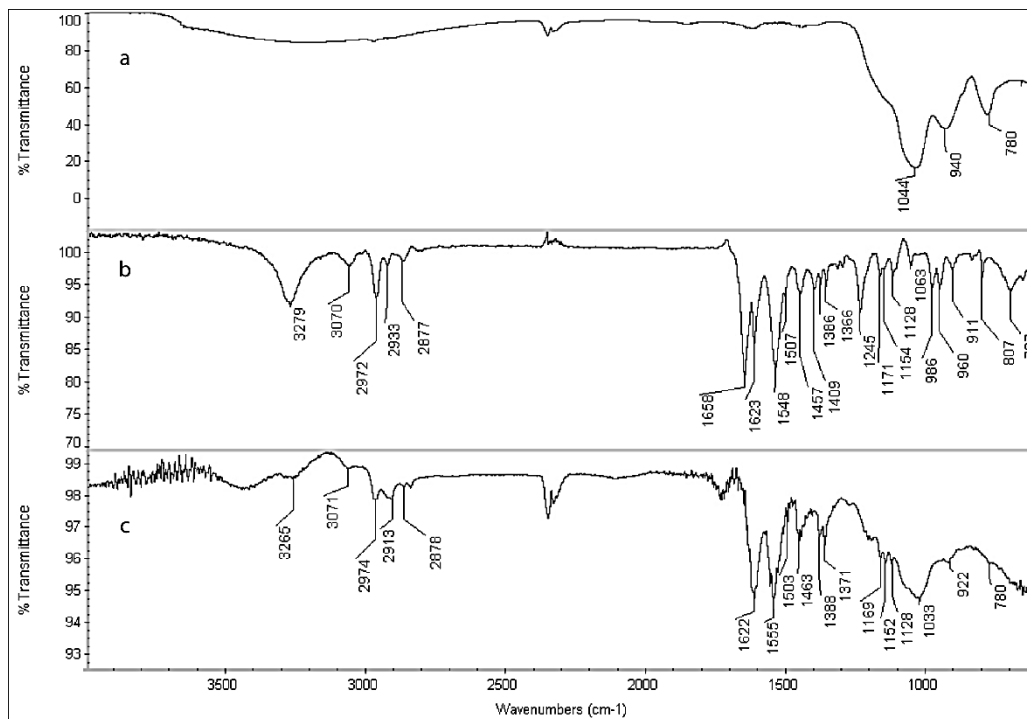

Fig. 1 – FTIR spectra of bare silica particles (a), pure NIPAM (b) and silica particles coated by PNIPAM (c)

2.3 Nanocomposit SERS-active substrates

Silver colloids were prepared by reduction of silver nitrate with hydroxylamine hydrochloride at room temperature [9]. SERS measurements on Ag colloidal suspensions were performed by adding an aliquot of aqueous chloride solution to a final concentration 2×10^{-2} M and, subsequently, by adding aliquots of and solutions up to the desired concentration. The flat electrode was subjected to the pretreatment procedure (polishing and cleaning) and afterwards to ORC treatment in electrochemical cell in order to fabricate the desired nanomorphology of the surface. The electrode was then immersed into and solution for 12 hours and then into the suspension of NPs for 2 hours. Detection of aldrin was performed after immersing the electrode with composite substrate on its surface into the solution of aldrin with concentration 10^{-4} M for 2 hours. The SERS spectra were collected with a Renishaw Raman Microscope System equipped with argon laser at 514,5 nm, a Leica microscope, and an electrically cooled CCD camera. The laser power in the sample was 2.0 mW.

3. RESULTS AND DISCUSSION

### 3.1 PNIPAM-coated SiO₂ microparticles

The successful coating procedure was confirmed by comparison of FTIR spectra of both uncoated and coated silica particles. Fig. 1 compares the infrared spectra of unmodified silica, NIPAM monomer and silica particles coated with PNIPAM. The spectra of both uncoated and PNIPAM-modified silica contain a band at 1040 cm^{-1} that corresponds to Si-O-Si stretching vibration. Besides that also bands at 933 cm^{-1} and 780 cm^{-1}, corresponding to Si-O-C and Si-C stretching vibrations, respectively, are apparent. The spectrum of PNIPAM-modified silica shows the presence of many characteristic peaks corresponding to PNIPAM: N-H group stretching band at 3265 cm^{-1}, CH₃ and CH₂ groups stretching band at 2972, 2932 and 2877 cm^{-1}, C=O stretching at 1658 resp. 1622 cm^{-1}, N-H bending at ca. 1550 cm^{-1}. All of the IR peaks have confirmed the successful grafting copolymerization of PNIPAM onto the silica.

3.2 Citric acid coated γ-Fe₂O₃ nanoparticles

Infrared spectroscopy has been used to characterize the iron oxide nanoparticles, as it is a complimentary

technique to differentiate between different oxide phases i.e. maghemite, magnetite and hematite. The FTIR spectra are summarized in Fig. 2. The broad high frequency bands between 3200 and 3600 cm^{-1} correspond to stretching vibrations of the O-H bond from hydroxyl groups or

absorbed water present on the nanoparticle surface. The peaks at 2922 cm^{-1} and 2851 cm^{-1} correspond to stretching vibrations of aliphatic groups (CH3 and CH2). The peak around 1600 cm^{-1} and 1400 cm^{-1} in the uncoated
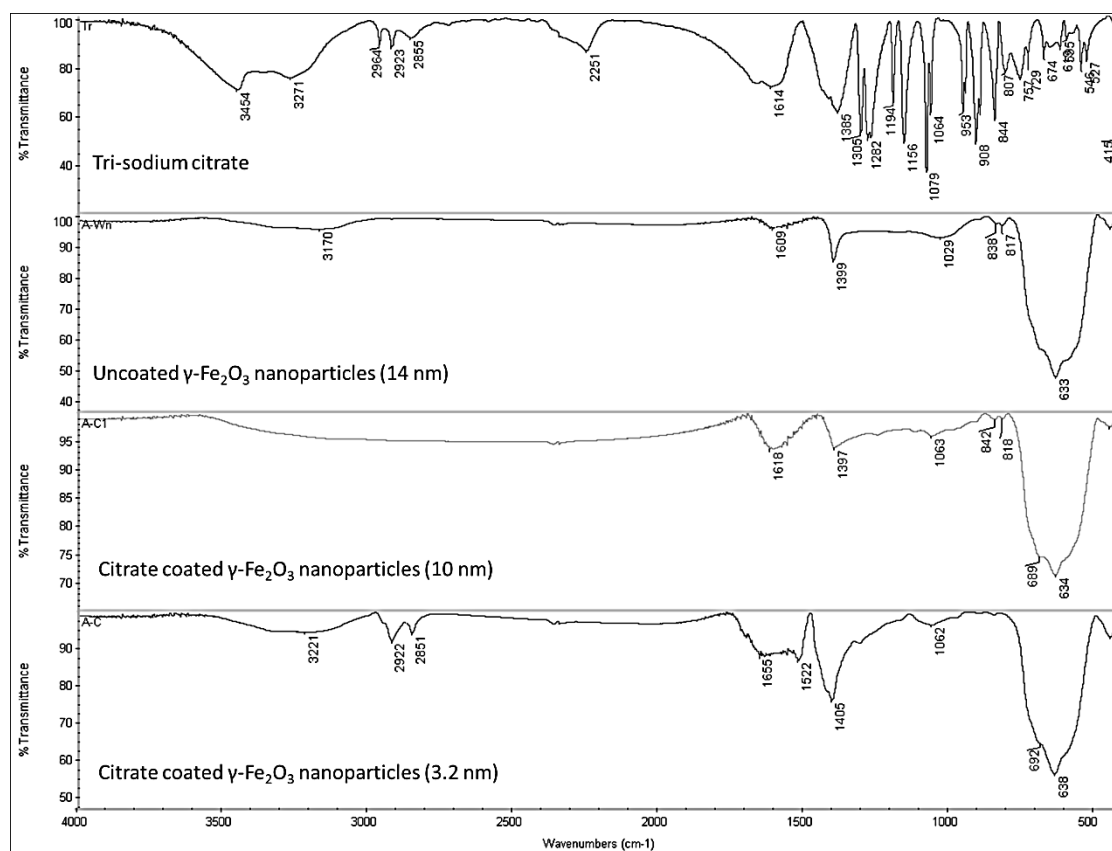
Fig. 2 – FTIR spectra of pure tri-sodium citrate, uncoated γ-Fe₂O₃ nanoparticles of 14 nm size and citrate coated nanoparticles of 3.2 and 10 nm size

nanoparticles corresponds to stretching vibrations of the O-H bond for H_2O and C-O bond for CO_2 (from air). The peaks (low frequency bands) at around 630 cm^{-1} and 446 cm^{-1} are the stretching vibration in tetrahedral site of the Fe-O bond, which is consistent with those for the maghemite (γ-Fe₂O₃) phase [7]. A small shift of Fe-O bands known for bulk maghemite may have occurred due to overlapping of bands, giving an average wave number, or due to size effects. It has been observed that the intensity of the peaks increases with the decreasing particle size, showing an increased vacancy ordering with respect to size reduction of the nanoparticles. The presence of citric acid coating is confirmed by the presence of the broad peaks between 1500-1650 cm^{-1} and around 1400 cm^{-1} which correspond to asymmetric and symmetric C-O bonds of the citric acid coated nanoparticle surface. The peaks corresponding to citric acid become more intense in the smaller (3.2 nm) nanoparticles compared to 10 nm nanoparticles, which is consistent with their larger specific surface area and therefore higher expected mass fraction of citric acid to iron oxide.

3.3 Nanocomposit SERS-active substrates

Two main spectral regions are found to be the most sensitive, giving the most useful information about the structural and dynamic properties of ADn/NPs systems. These are regions corresponding to C-C and C-H stretching vibrations. The main chain C-C skeletal stretching region from ca. 1050 cm^{-1} to ca. 1150 cm^{-1} is sensitive to the intra-molecular conformation along each chain [10]. For a long chain with all-trans structures, two intense bands appear at ca. 1050 cm^{-1} and ca. 1130 cm^{-1} , which can be assigned to symmetric and anti-symmetric C-C stretching vibrations, respectively. With decreasing number of trans C-C bonds in the chain in favor of gauche conformers, the intensity of these two bands lowers and a strong band at about 1080 cm^{-1} appears. The spectral features in the C-H stretching region at the range of ca. 2800 cm^{-1} – 3000 cm^{-1} are found to be crucially affected by the lateral packing interactions due to the re-orientation of the alkyl chains [11]. In this region all the aliphatic diammines with longer chains show a narrow band at ca. 2850 cm^{-1} corresponding to symmetric υ(C-H) mode, and a broad band at ca. 2915 cm^{-1}. The $H_{\sim 2915}/H_{\sim 2850}$ ratio can be used as an indication of inter-molecular van der Waals interactions.

The sensing ability of nanocomposit ADn functionalized substrates was tested by using the polychlorinated insecticide aldrin as an example of a probe molecule. In the absence of diammine, no SERS spectrum of aldrin could be obtained due to its low affinity toward the metal surface, whereas the fabrication of nanocomposite substrate functionalized by bifunctional linker enabled its

SERS detection due to the formation of the host/guest complex (Fig. 3). The characteristic bands of aldrin which are mainly assigned to C-Cl stretching modes can be seen in the low wavenumber region which is completely free of diammine bands. The comparison with the Raman spectrum of solid aldrin confirms its positive detection with described system.
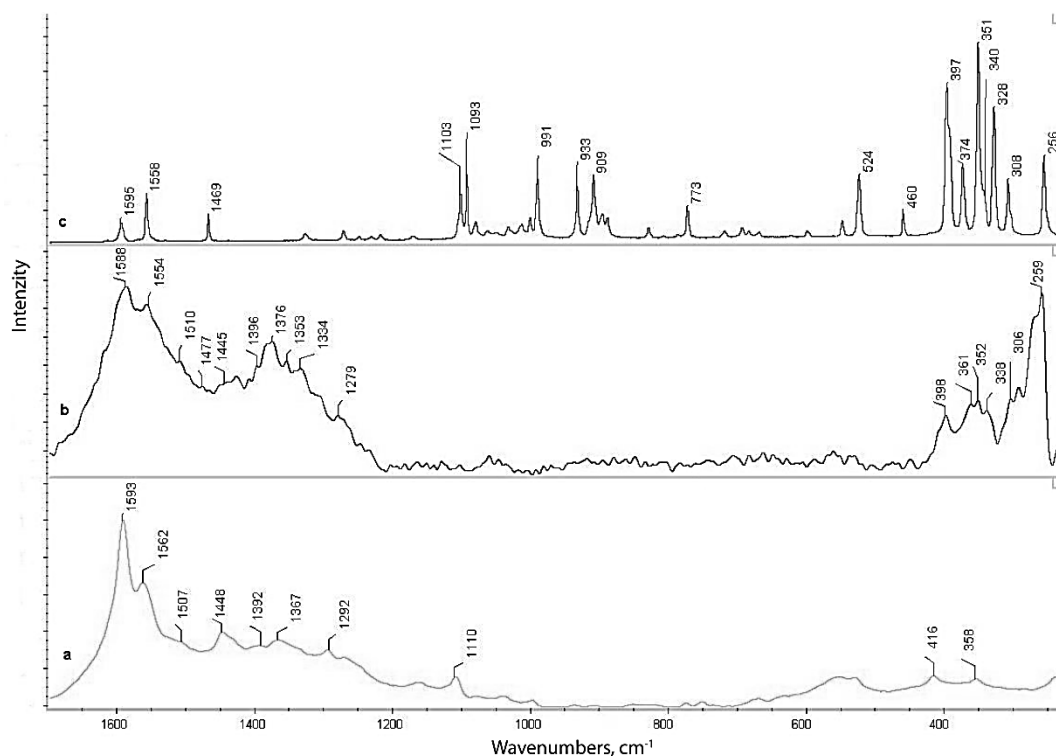

Fig. 3 – SERS spectra of DA8 (a), surface complex DA8/aldrin (b) and Raman spectrum of aldrin in condensed state (c)

4. CONCLUTIONS

It has been shown that vibrational spectroscopic techniques can be very useful in characterization of different types of structured particles which can serve as compartments for chemical robots. Within the experiments with SiO$_2$ microparticles the successful coating of microparticles with thermo-responsive polymer PNIPAM was confirmed by using FTIR spectroscopy. FTIR measurements also confirmed the coating of γ-Fe$_2$O$_3$ nanoparticles by citric acid their consistence of

the maghemite phase. Finally, in the experiments with nanocomposite substrates we have shown that ADn-functionalized Ag NPs systems can act as analyte nanosensors for SERS detection of polychlorinated pesticides.

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