

10<sup>th</sup> International Conference on Solid State Chemistry, Pardubice, Czech Republic

## The catalytic behaviour of nanoAg@montmorillonite composite materials

Martina Karlíková<sup>a\*</sup>, Libor Kvítek<sup>a</sup>, Robert Pucek<sup>a</sup>, Aleš Panáček<sup>a</sup>, Jan Filip<sup>b</sup>,  
Jiří Pechoušek<sup>b</sup> and Nathaniel F. Adegboyega<sup>c</sup>

<sup>a</sup>Department of Physical Chemistry, Faculty of Science, Palacky University, 17 Listopadu 12, Olomouc, 771 46, Czech Republic

<sup>b</sup>Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Palacky University, Olomouc, 771 46, Czech Republic

<sup>c</sup>Chemistry Department, Florida Institute of Technology, 150 West University Boulevard, Melbourne, FL 32901, USA

---

### Abstract

The preparation of nanoAg@montmorillonite composite materials and their catalytic activity is reported in this article. The nanoAg@montmorillonite composite materials were prepared by the adsorption of silver NPs, with an average size about 30 nm, from their aqueous dispersion onto two types of montmorillonite with different chemical composition. Silver NPs were prepared via modified Tollens process, which involves the reduction of  $[\text{Ag}(\text{NH}_3)_2]^+$  complex cation by maltose. The amount of silver NPs anchored onto the MMT surfaces was determined by UV-VIS spectroscopy; the decrease in absorbance of the dispersion after the adsorption was monitored. Prepared nanocomposite materials were subsequently characterized by means of transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). The reduction of 4-nitrophenol by sodium borohydride was chosen to examine the catalytic properties of the synthesized silver nanocomposite materials.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Selection and/or peer-review under responsibility of the Organisation of the 10th International Conference on Solid State Chemistry.

*Keywords:* Adsorption; Clay; Montmorillonite; Nanoparticles; Silver

---

### 1. Introduction

Nanoparticles of noble metals are intensively studied due to their unique electrical, optical, catalytic and biologic properties, which are different from the properties of the “bulk” materials. They can be used in different fields in chemistry as effective catalysts, excellent antibacterial and antifungal materials, and also in the construction of new sensors for analytical applications. In recent times, however, discussions concerning the usage of nanoparticles are often linked with their potential ecological risk. In order to keep their application potential and simultaneously prevent their release into the environment, NPs can be

anchored on the solid macroscopic substrates. In recent years, silver NPs have been intensively studied due to the high antibacterial [1] and catalytic activity [2–3]. This unique property is as a result of the huge surface area of nanoparticles, and their specific interactions with some organic molecules. Clay minerals can be used as suitable materials for anchoring silver NPs taking advantage of their large surface area, sorptive and ion exchange properties and good economic accessibility [4].

The integration of metal nanoparticles onto solid macroscopic substrates involves two methods. The first, based on the direct reduction of the metal ions leads to the incorporation of NPs on both the surface and in the pore of solid substrates. In this regard, the size and shape of the prepared nanoparticles is largely dependent on the size and shape of the pore. This method most often results in the preparation of small particles with relatively wide size distribution. For example, very small particles with size range from 3 to 13 nm were prepared by simple reduction of silver ions intercalated to the structure of montmorillonite by sodium borohydride [5]. Similar method was used for preparing a highly stable silver NPs in n-hexanol [6]. Darroudi et al. developed a simple method for the preparation of silver NPs using UV-irradiation of  $\text{AgNO}_3$  in the interlamellar space of clay without any reducing agent or heat treatment. In this case, the particle size decreased from 30 nm to 6 nm with increase time [7]. The second method is based on the deposition of pre-prepared metal nanoparticles from their aqueous and non aqueous dispersions onto the surface of an inert carrier. Various methods for the synthesis of metal nanoparticles exist, but the chemical method based on metal salt solution reduction by inorganic and organic reducing agents such as  $\text{NaBH}_4$  [8], citrate [9] and ascorbate [10] predominate in practice.

In the present work, the preparation of composite materials containing silver nanoparticles anchored onto solid surfaces of the two different forms of montmorillonite and the study of their catalytic activity is described. As a model reaction to verify the catalytic activity of the aforementioned nanocomposite materials the reduction of 4-nitrophenol by sodium borohydride was chosen.

## 2. Experimental

The aqueous dispersion of silver NPs was prepared by modified Tollens process [11], which involves the reduction of  $[\text{Ag}(\text{NH}_3)_2]^+$  complex cation by maltose in alkaline media. The initial concentration of the reaction components in the mixture were as follows:  $1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  of  $\text{AgNO}_3$  (Tamda, ČL 2009) and  $5 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  of ammonia (Lach-Ner, p.a.). The resulting diamine silver(I) complex was reduced by  $1 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$  maltose solution at pH about 11.5 achieved by adding appropriate amount of  $\text{NaOH}$  ( $1 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ). The average size of the prepared particles was about 30 nm with narrow size distribution, as determined by dynamic light scattering on a Zeta Plus instrument (Brookhaven Instr. Co., USA).

Two different kinds of montmorillonite; concretely MMT-1 and MMT-2 obtained from Institute of geonics AV ČR in Ostrava were chosen as an inert carrier for the adsorption of silver NPs from their aqueous dispersion. The composition of used carrier, expressed in weight percentage was as follows: **MMT-1**:  $\text{SiO}_2$ : 70.1,  $\text{Al}_2\text{O}_3$ : 16.0,  $\text{TiO}_2$ : 0.22,  $\text{Fe}_2\text{O}_3$ : 0.65,  $\text{FeO}$ : 0.15,  $\text{MnO}$ : 0.009,  $\text{MgO}$ : 3.69,  $\text{CaO}$ : 1.59,  $\text{Na}_2\text{O}$ : 0.27,  $\text{K}_2\text{O}$ : 0.078, F:0.084,  $\text{P}_2\text{O}_5$ : 0.026, S: 0.04, **MMT-2**:  $\text{SiO}_2$ : 62.9,  $\text{Al}_2\text{O}_3$ : 19.6,  $\text{TiO}_2$ : 0.090,  $\text{Fe}_2\text{O}_3$ : 3.35,  $\text{FeO}$ : 0.32,  $\text{MnO}$ : 0.006,  $\text{MgO}$ : 3.05,  $\text{CaO}$ : 1.68,  $\text{Na}_2\text{O}$ : 1.53,  $\text{K}_2\text{O}$ : 0.53, F: 0.111,  $\text{P}_2\text{O}_5$ : 0.049, S: 0.05. The values of specific surface area determined by static adsorption of inert nitrogen gas on Sorptomatic 1990 (ThermoFinnigan) was respectively  $96 \text{ m}^2 \cdot \text{g}^{-1}$  and  $26 \text{ m}^2 \cdot \text{g}^{-1}$  for MMT-1 and MMT-2.

The nanocomposite materials were prepared by dispersing 0.5 g of clay mineral in 150 mL of silver NPs dispersion with concentration of  $108 \text{ mg Ag} \cdot \text{L}^{-1}$  and stirred for three hour - until equilibrium was established. The mixture was filtered and the prepared nanoAg@MMT composite materials were dried at  $105 \text{ }^\circ\text{C}$  for 24 hours. The amount of anchored silver NPs was measured on a UV-Vis spectroscopy (spectrophotometer Specol S600, Analytic Jena AG, Germany) by monitoring the decrease in absorbance

of dispersion after adsorption at wavelength of 415 nm. The results were confirmed using a Perkin Elmer 3300 atomic adsorption spectroscopy. The structures of nanoAg@MMT-1 and nanoAg@MMT-2 composites were characterized by means of transmission electron microscopy JEM 2010 (Jeol Ltd., Japan) and powder X-ray diffraction (XRD).

Catalytic activities of nanoAg@MMT-1 and nanoAg@MMT-2 composite materials were studied on a model reaction based on the reduction of 4-nitrophenol to 4-aminophenol by an excess of sodium borohydride in aqueous solution. Typically, 300 ml of  $1 \cdot 10^{-4}$  mol·L<sup>-1</sup> 4-nitrophenol (Sigma-Aldrich) was mixed with appropriate amount of nanoAg@MMT to create a final silver concentration of 0.012 mol·L<sup>-1</sup> in the mixture. Thereafter, sodium borohydride (Sigma-Aldrich) to the final concentration 0.01 mmol·L<sup>-1</sup> was added to the mixture. The reaction progress, from which the rate constant was determined, was monitored on a UV-Vis spectroscopy by observing the spectral changes for the absorption peak of 4-nitrophenolate ions at 400 nm over time. The spectra were taken every 30 s in range of 250-600 nm. Subsequently, in order to compare the rate constants, the same reduction reaction of 4-nitrophenol catalyzed by the “free” silver nanoparticles in dispersion was also performed.

### 3. Result and discussion

NanoAg@MMT composite materials were prepared via a simple adsorption of silver NPs from their aqueous dispersion onto the surface of MMT-1 and MMT-2. The amount of anchored silver NPs, determined from the decrease of absorbance of dispersion after adsorption at wavelength of 415 nm and expressed as a value of the silver NPs adsorbed on the surface of 1 g of inert carrier was, respectively, 20.31 mg and 17.63 mg Ag for MMT-1 and MMT-2. The presence of silver NPs on the surface of MMT was confirmed by an XRD analysis (Fig. 1 and Fig. 2), which showed a Bragg reflections at  $2\theta = 44.7^\circ$  corresponding to the existence of captured silver particles on the clay.

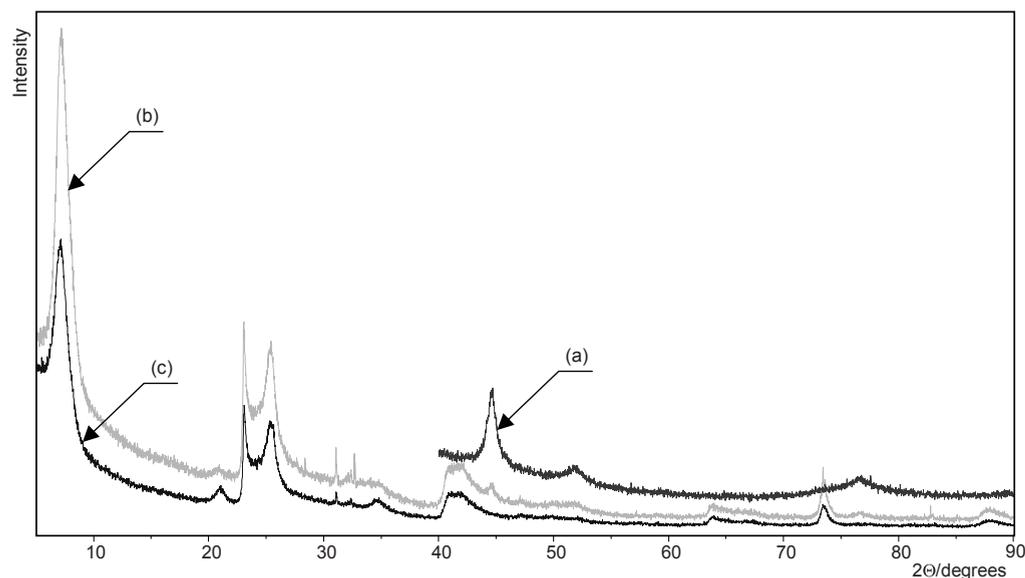


Fig. 1. XRD patterns of (a) silver NPs; (b) nanoAg@MMT-1 nanocomposite and (c) pure MMT-1

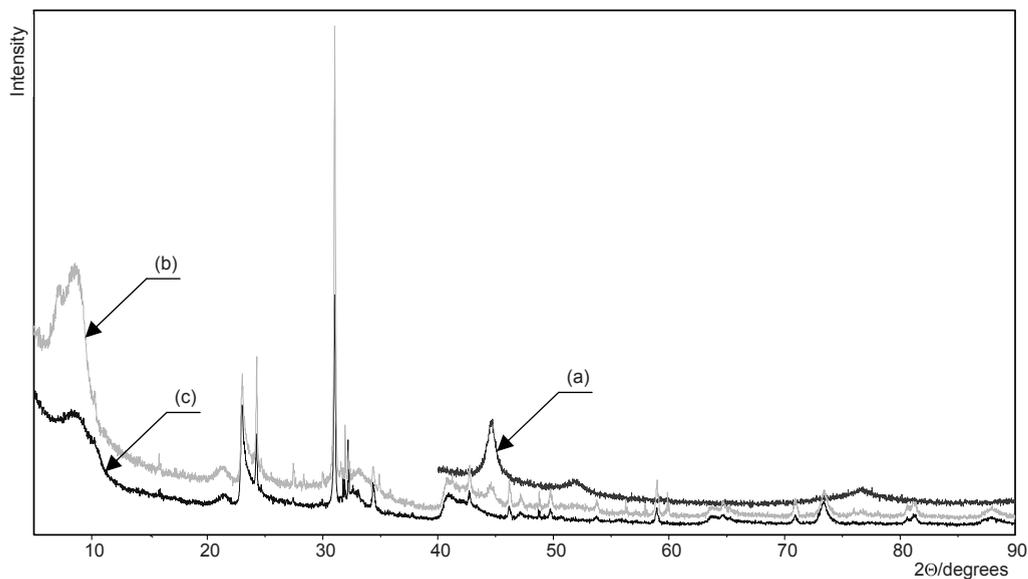


Fig. 2. XRD patterns of (a) silver NPs; (b) nanoAg@MMT-2 nanocomposite and (d) pure MMT-2

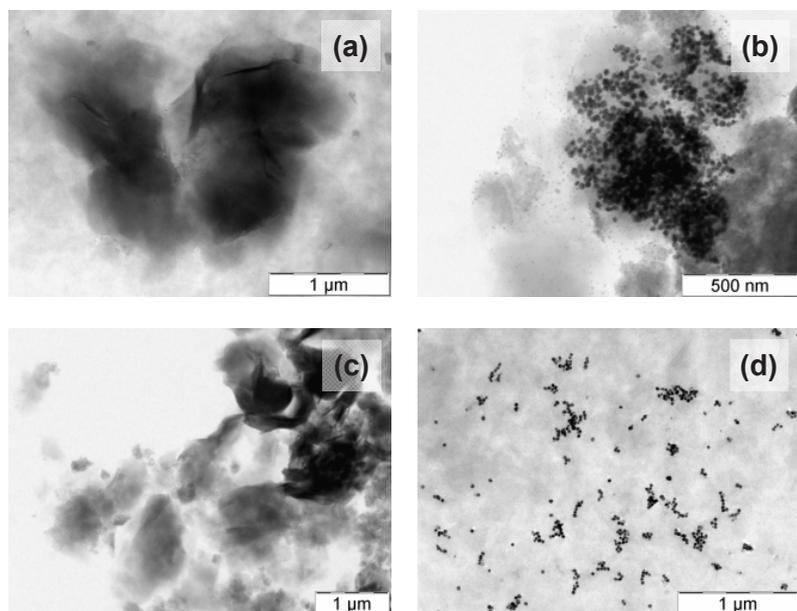


Fig. 3. TEM images of (a) pure MMT-1 (b) nanoAg@MMT-1 composite and (c) pure MMT-2 (d) nanoAg@MMT-2 composite

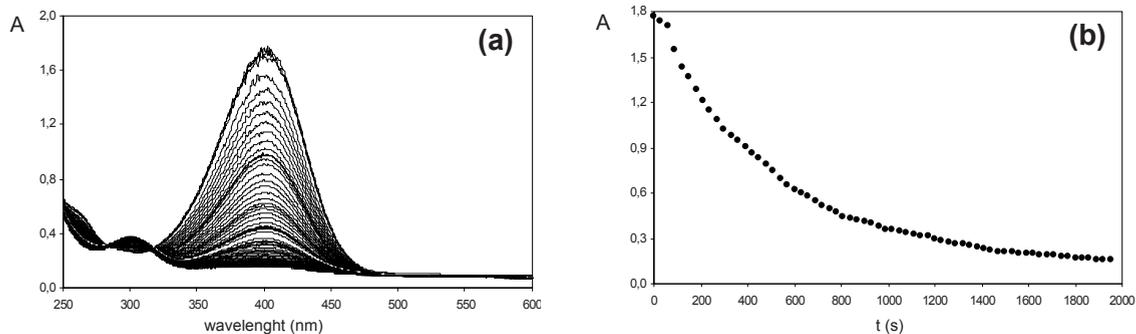
The TEM images of nanoAg@MMT composites (Fig. 3) showed the distribution of silver NPs onto inert carrier surfaces, without any trace of agglomerate formation. Moreover, because the average size of

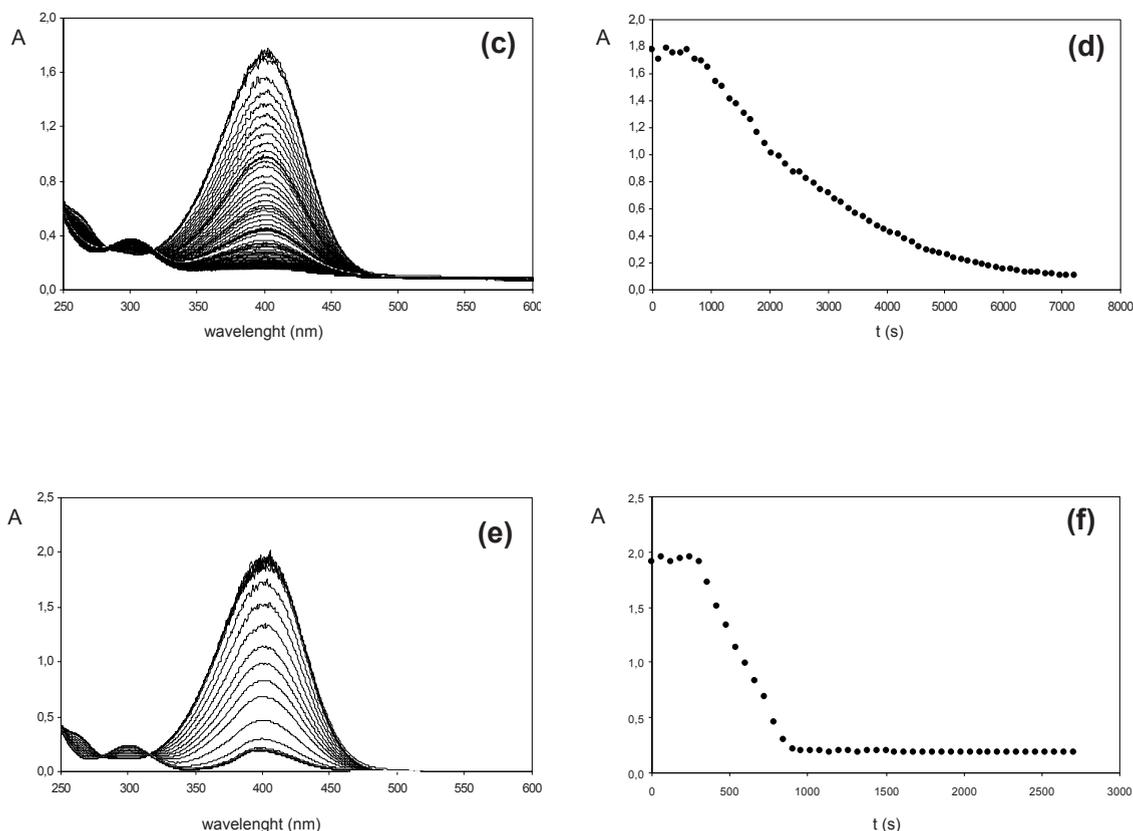
anchored silver NPs was about 30 nm, it is unquestionable that they are not able to penetrate into the structure of pores of clay and thus they are adsorbed only on the surface of the supporting material.

In order to investigate the catalytic activity of nanoAg@MMT-1 and nanoAg@MMT-2 composite materials the model reduction of 4-nitrophenol to 4-aminophenol by an excess of sodium borohydride in aqueous solution was used. The reaction progress was measured on UV-Vis spectroscopy by monitoring the gradual decrease in the peak intensity of 4-nitrophenolate ions at 400 nm over time. Simultaneously the appearance of a new peak at 290 nm attributed to 4-aminophenol was also observed. Two isosbestic points at 280 and 315 nm (Fig. 4) indicate that 4-aminophenol is the unique product of the above mentioned reaction. The obtained rate constants for reactions catalysed by nanoAg@MMT-1 and nanoAg@MMT-2 composite were compared with the value of the rate constant acquired from reduction reaction catalysed by the “free” silver NPs prepared the same way. The obtained rate constants were consequently recalculated to apparent rate constants ( $k_{app}$ ), which are normalized to 1 gram of the catalysts (mean to 1 g of silver) in the unit volume of the system.

Whereas, the course of the reaction process for nanoAg@MMT composite catalysts is controlled by the first order kinetics, a zero order kinetic was observed for “free” silver NPs. The initial constancy of the time dependence in Fig. 4 is probably caused by the previous reduction of the thin layer of the silver(I) oxide, which usually covered surface of metal particles in a medium containing oxygen. Firstly, after adding of sodium borohydride to the system the thin layer of oxide has to be reduced back to the silver(0) and afterwards the catalytic reaction on the surface of metal can be started.

The obtained rate constant values showed that the “free” silver NPs exhibited the highest catalytic activity. The apparent rate constant determined for this type of catalyst was equal to  $2.231 \text{ s}^{-1} \cdot \text{g}^{-1} \cdot \text{L}^{-1}$ . In the case of nanoAg@MMT composites, the reaction rate of the studied reduction reaction was lower as evidenced by the normalized rate constants, determined respectively for nanoAg@MMT-1 and nanoAg@MMT-2 as  $0.384 \text{ s}^{-1} \cdot \text{g}^{-1} \cdot \text{L}^{-1}$  and  $0.923 \text{ s}^{-1} \cdot \text{g}^{-1} \cdot \text{L}^{-1}$ . This fact can be explained from the results provided by the subsequent desorption study of the silver NPs from the nanocomposite materials in demineralized water. For this purpose, the 1% (w/w) aqueous dispersions of these composite materials were prepared and shaken for 3 hours. The dispersions were filtered and the amount of the released silver in the filtrate was determined using atomic absorption spectroscopy. In case of MMT-2 as the carrier of the silver NPs, it was determined that half of the whole content of adsorbed silver NPs is released while only 17 % of silver NPs was released when MMT-1 was used. These results reinforce the conclusions obtained by the kinetic studies, which pointed out that the released amount of silver nanoparticles from the composite materials back into reaction solution, to large degree, contributes to catalytic activity of prepared nanocomposite materials. This can be summarized that the “free” silver nanoparticles prove a high catalytic activity when compared with the nanoparticles anchored onto the surface of inert carriers. Less efficient catalytic activity of the supported silver NPs can be attributed to lower accessible surface for catalysis in comparable with “free” silver NPs by the parts which the NPs are bounded onto the surface of MMT.





**Fig 4:** The UV-Vis adsorption spectra of the catalytic reduction reaction of 4-nitrophenol in presence of (a) nanoAg@MMT-1 (c) nanoAg@MMT-2 and (e) “free” silver NPs and the plot of absorbance of 4-aminophenol versus time for reaction catalyzed by (b) nanoAg@MMT-1 (d) nanoAg@MMT-2 and (f) “free” silver NPs.

#### 4. Conclusion:

Composite materials containing silver nanoparticles were prepared via simple adsorption method of silver NPs from their aqueous dispersion onto the surface of two types of montorillonite samples. The TEM images revealed a homogeneous distribution of anchored nanoparticles onto the surface of inert carriers without agglomerate formation. The catalytic activity of both types of prepared nanocomposite was examined for the reduction reaction of 4-nitrophenol in the presence of sodium borohydride. Obtained kinetic data were subsequently compared with the value of the rate constant acquired for the mentioned reaction, catalysed by “free” silver NPs prepared in the same way. Even though the highest catalytic activity exhibited “free” silver nanoparticles, the catalytic activity of prepared nanocomposites is not negligible and this materials could potentially be used for catalytic applications in practice.

## 5. Acknowledgements

This work has been supported by the Operational Program Research and Development for Innovations - European Social Fund (CZ.1.05/2.1.00/03.0058), Czech Science Foundation (Project No. GAP304/10/1316), Operational Program Education for Competitiveness--European Social Fund (CZ.1.07/2.3.00/20.0056) and also by internal grant of Palacký University in Olomouc (PřF\_2012\_028).

## 6. References:

- [1] Martínez-Castanón GA, Nino-Martínez N, Martínez-Gutierrez F, Martínez-Mendoza JR; Facundo R. Synthesis and antibacterial activity of silver nanoparticles with different sizes. *J. Nanopart. Res.* 2008; **10**: 1343–8.
- [2] Lu Y, Mei Y, Schrinner M, Ballauf M, Möller MW, Breu J. In situ formation of Ag nanoparticles in spherical polyacrylic acid brushes by UV irradiation. *J. Phys. Chem. C* 2007; **111**:7676–81.
- [3] Lu Y, Mei Y, Ballauf M. Thermosensitive Core-Shell Particles as Carrier Systems for Metallic Nanoparticles. *J. Phys. Chem. B* 2006; **110**: 3930–7.
- [4] Varma RS. Clay and clay-supported reagents in organic synthesis. *Tetrahedron* 2002; **58**:1235–55.
- [5] Praus P, Turicová M, Machovič V, Študentová S, Klementová M. Characterization of silver nanoparticles deposited on montmorillonite. *Appl Clay Sci* 2010; **49**:341–5.
- [6] Myoshi H, Ohno H, Sakai K, Okamura N, Kourai H. Characterization and photochemical and antibacterial properties of highly stable silver nanoparticles prepared on montmorillonite clay in n-hexanol. *J Colloid Interface Sci* 2010; **345**:433–41.
- [7] Darroudi M, Ahmad MB, Shameli K, Abdullah AH; Ibrahim NA. Synthesis and characterization of UV-irradiated silver/montmorillonite nanocomposites. *Solid State Sci.* 2009; **11**:1621–4.
- [8] Leopold N, Lendl B. A new method for fast preparation of highly surface-enhanced raman scattering (SERS) active silver colloids at room temperature by reduction of silver nitrate with hydroxylamine hydrochloride. *Langmuir* 2005; **21**:8546–53.
- [9] Cañamares MV, Garcia-Ramos JV, Gómez-Varga JD, Domingo C, Sanchez-Cortes S. Comparative Study of the Morphology, Aggregation, Adherence to Glass, and Surface-Enhanced Raman Scattering Activity of Silver Nanoparticles Prepared by Chemical Reduction of Ag<sup>+</sup> Using Citrate and Hydroxylamine. *Langmuir* 2005; **21**:8546–53.
- [10] Qin Y, Ji X, Jing J, Liu H, Wu H, Yang W. Size control over spherical silver nanoparticles by ascorbic acid reduction. *Colloids Surf A Physicochem Eng Asp* 2010; **21**:172–6.
- [11] Panáček A, Kvítek L, Pucek R, Kolář M, Večeřová R, Pizúrová N, et al. Silver colloid nanoparticles: Synthesis, characterization and their antibacterial activity. *J. Phys. Chem. B* 2006; **110**:16248–53.