



Anionic 11-mercaptoundecanoic acid capped ZnO nanoparticles



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ABSTRACT

The anionic zinc oxide nanoparticles have been prepared at room temperature by a precipitation method using $ZnCl_2$ and NaOH and surface modification with 11-mercaptoundecanoic acid (MUA). Atomic force microscopy (AFM) was used for definition of morphology and size of prepared nanoparticles which was proved by measurements of particle size distribution using Zetasizer. Successful coating with MUA as surfactant was acknowledged by X-ray photoelectron spectroscopy and ATR FT-IR spectroscopy.

The isoelectric point (IEP) of ZnO–MUA nanoparticles was obtained by measurements of zeta potential and FT-IR dependence on pH; the obtained value was approximately 3.58. The value of exchanged protons was 2.88 which indicates a positive binding cooperativity of modified nanoparticles.

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1. Introduction

In the present time, an attachment of nanoparticles to the various biomaterials represents a rich emerging area. The nanoparticles conjugates with biomolecules have found applications in imaging and diagnostic [1], delivery [2], the control of protein activity with an external field or understanding a local structure in protein folding [3,4]. NP–biomolecule complexes are interesting also for many other fields, i.e. material science, physics and energy, the design of devices such as nanosensors [5] and biofuel cells [6]. The nanoparticle interactions with biological materials are often mediated through adsorption onto the NPs surface or covalent attachment. The formation of nano-biocomplexes can be accomplished by the surface modification of nanoparticles, as well. Some studies have reported the surface functionalization of nanoparticles and their interaction with biomolecule and possible application of constructed complexes, i.e. study of protein binding by mercaptoundecanoic acid [7] or thioctic acid [8] stabilized gold nanoparticles or dendrimer modified magnetite nanoparticles [9], study of albumin quenching by capped CdS nanoparticles [10], quantum dots with bounded arginine cross-linked via mercaptoundecanoic acid for two-photon imaging of live

cancer cells [11], delivery of nucleic acid by functionalized nanoparticles [12,13].

ZnO in nanometre scale is not attractive only for its high surface area, good biocompatibility, chemical stability and low toxicity, but it also shows unique properties, i.e. antibacterial, catalytic, optic, biomimetic and high electron communication features which make it great for potential applications in biosensing [14,15], biolabeling [16] or drug delivery [17,18]. There are also literature reports about zinc oxide nanoparticles as active element in photodynamic and radiation therapies [19,20] or in a drug delivery system of different anticancer drugs, such as daunorubicin [21] and doxorubicin [22].

The conjugates of ZnO nanoparticles with different biomolecules also offer promising means with broad range possibility of application. Unfortunately, ZnO nanoparticles are characterized by large surface and high surface energy which usually caused their aggregation. The surface functionalization can prevent the formation of agglomerates and leads to provide the side group on surface which can be further conjugated with biomolecules. Many studies have been done toward the functionalization of NPs surface through natural or artificial compounds – chitosan [17], starch [23], synthetic polymers [24], organic compound or inorganic materials, i.e. mercaptopropionic acid [25,26], thioglycolid acid [27–29], and silanization agents [30,31].

The pure zinc oxide nanoparticles with its high isoelectric point of about 8.7–10.3 [32,33] is able adsorption of proteins with low IEPs through electrostatic interaction. The introduction of function

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groups on the nanoparticles surface can increase their interaction with bio-moieties. However, the surface modification usually does not affect the charge of nanoparticles thus significantly, therefore ZnO NPs can interact only with a limited number of biomolecules based on their IEP.

In this paper we describe a preparation of ZnO nanoparticles capped by 11-mercaptoundecanoic acid (MUA) which was chosen as one of the most used thiol acid for nanoparticle surface functionalization, low cost, nontoxic and the ability to construct biocompatible nanoparticles [34,35]. The 11-mercaptoundecanoic acid in synthesis procedure was used to prepare the ZnO nanoparticles which will be able to the better interaction with biomolecules. The linking of zinc oxide nanoparticle with biomolecule could be provide via carboxyl group (COO^-) of MUA which was incorporate to the nanoparticles surface via interaction of hydrosulfide group (HS^-) with Zn^{2+} . The prepared ZnO NPs capped by 11-mercaptoundecanoic acid were characterized by isoelectric point approximately 3.58. The low IEP indicates the ability of prepared nanoparticles to interact with various biomolecules in broad range of pH.

2. Materials and methods

2.1. Synthesis

Zinc chloride ($\text{ZnCl}_2 \geq 98\%$) was purchased from Centralchem (Slovakia), sodium hydroxide ($\text{NaOH} \geq 98\%$) and 11-mercaptoundecanoic acid MUA ($\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$, 95%) were obtained from Sigma (USA) and they were of analytical grade. Water was purified by a Millipore Synergy system (Merck, Germany).

Zinc oxide nanoparticles (ZnO NPs) modified by 11-mercaptoundecanoic acid (MUA) were prepared using a precipitation method. To the solution of 0.1 M 11-mercaptoundecanoic acid (54.59 g, 2.5 ml) was drop by drop added 0.2 M NaOH and stirred while the powder of 11-mercaptoundecanoic acid was dissolved. Subsequently, 0.2 M ZnCl_2 solution (0.06885 g, 2.5 ml) was slowly added into alkaline mixture of thiol acid and reacted at room temperature ($25^\circ\text{C} \pm 1$) for 3 h during the continuous stirring. By this procedure a milky white solution was obtained.

After continuous stirring, the precipitate was collected through centrifugation (Eppendorf 5804R centrifuge; 6 min, 25°C) at 100 rpm and subsequently after the removing the settled particles, the suspension was centrifugated at 15,000 rpm. By this procedure the eventual aggregates were removed from the sample. The resulting fraction was washed in ultrapure Millipore water several times and allowed to evaporate at room temperature in order to obtain ZnO–MUA nanoparticles in white powder form.

2.2. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed with XPS instrument (SPECS) equipped with PHOIBOS 100 SCD and non-monochromatic $\text{MgK}\alpha$ X-ray source. The survey surface spectrum was measured at 70 eV transition energy and core spectra at 20 eV at room temperature. All spectra were acquired at a basic pressure 2×10^{-8} mbar with $\text{MgK}\alpha$ excitation at 15 kV (250 W).

The data was analyzed by SpecsLab2 CasaXPS software (Casa Software Ltd).

2.3. Atomic force microscopy (AFM)

Samples for AFM were prepared by spreading on the surface of freshly cleaved mica and then left to adsorb for 5 min. Images of MUA modified ZnO nanoparticles were collected using an Innova

AFM system (Veeco Instruments) in tapping mode. The AFM tips used for the measurement were commercial antimony-doped silicon cantilevers (NCHV, Veeco Instruments) with their nominal tip radius of approximately 10 nm and a resonance frequency 301–331 kHz.

The data was analyzed with NanoScope Analysis (1.20) to obtain particle sizes and morphology.

2.4. Particle size distribution and zeta potential

Malvern Zetasizer Nano ZS (4 mW, 633 nm laser) equipped with MPT-2 autotitrator was used for measure of particle size, polydispersity index (PDI) and zeta potential dependence on pH.

The average particle size of 11-mercaptoundecanoic acid capped zinc oxide nanoparticles was determined by measurements of size distribution at pH 6.98. The 0.01 M HCl, 0.01 M NaOH and 0.1 M NaOH as titration solutions were used to determinate the zeta potential. For all experiments we used suspension prepared by dispersing of 1 mg ZnO–MUA nanoparticles in 1 ml of ultrapure water by ultrasonic agitation at room temperature ($25^\circ\text{C} \pm 1$).

2.5. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR)

Infrared ATR spectra were recorded on a Nicolet 8700 Fourier transform infrared spectrometer (Thermo Scientific) equipped with Smart OMNI-Sampler (diamond crystal), deuterated triglyceride sulfate (DTGS) detector and a KBr beamsplitter. All spectra were collected for 64 scans at a resolution of 4 cm^{-1} in range of $4000\text{--}400\text{ cm}^{-1}$ with a 150 cm^{-1} aperture. Spectra referenced to the air or to distilled water served as a background spectrum previously recorded on the crystal without the nanoparticles.

FT-IR spectroscopy was also used for IR titration of sample zinc oxide nanoparticles modified by 11-mercaptoundecanoic acid. Solutions in the pH range of 1.15–11.00 were prepared by dissolving the sample in distilled water and concentrated HCl and aqueous NaOH were used for the titration. The pH values were measured using the SENSOREX glass electrode before and after the spectra were recorded.

From the obtained data the isoelectric point (IEP) and numbers of exchanged protons (n) of coated nanoparticles was determined using a fitted curve of the dependence of absorbance changes on the pH measured at 1695 cm^{-1} . The obtained data were analyzed using the following formula:

$$A_{\text{obs}} = 10^n(\text{pK} - \text{pH}) \quad (1)$$

where A_{obs} is the observed absorbance at 1695 cm^{-1} for ZnO–MUA nanoparticles, n is the number of protons involved in the transition, and pK is the midpoint of the transition.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy (XPS)

The chemical composition of ZnO nanoparticles modified by 11-mercaptoundecanoic acid was confirmed by X-ray photoelectron spectroscopy (XPS).

The survey spectrum in Fig. 1 reveals the presence of Zn, O, C and S elements without any other contaminant species. The Zn 2p core level XPS spectrum in Fig. 1b is symmetric and centered at 1025.5 eV which is attributed to the Zn $2p_{3/2}$ of Zn(II) [36]. The oxygen peak in significant amounts at 535.5 eV confirms the formation of oxidized zinc nanoparticles. The binding energy at 287.5 eV can be ascribed to the carbon atoms in the $-\text{COO}(\text{H})$ moieties are due to carboxyl groups of thiol acid bounded on ZnO surface. The signals at

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