Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Fabrication of phosphonic acid films on nitinol nanoparticles by dynamic covalent assembly

Rosalynn Quiñones^{a,*}, Samantha Garretson^a, Grayce Behnke^a, Jonathan W. Fagan^b, Karl T. Mueller^{b,c}, Sushant Agarwal^d, Rakesh K. Gupta^d

^a Department of Chemistry, Marshall University, Huntington, WV 25755, United States

^b Department of Chemistry, Pennsylvania State University, State College, PA 16802, United States

^c Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, United States

^d Department of Chemical & Biomedical Engineering, West Virginia University, Morgantown, WV 26506, United States

ARTICLE INFO

Keywords: Self-assembly films Nitinol Phosphonic acid Nanoparticles Zeta potential Solid-state nuclear magnetic resonance

ABSTRACT

Nitinol (NiTi) nanoparticles are a valuable metal alloy due to many unique properties that allow for medical applications. NiTi nanoparticles have the potential to form nanofluids, which can advance the thermal conductivity of fluids by controlling the surface functionalization through chemical attachment of organic acids to the surface to form self-assembled alkylphosphonate films. In this study, phosphonic functional head groups such as 16-phosphonohexadecanoic acid, octadecylphosphonic acid, and 12-aminododecylphosphonic acid were used to form an ordered and strongly chemically bounded film on the NiTi nanopowder. The surface of the NiTi nanoparticles was modified in order to tailor the chemical and physical properties to the desired application. The modified NiTi nanoparticles were characterized using infrared spectroscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy and ³¹P solid-state nuclear magnetic resonance. The interfacial bonding was identified by spectroscopic data suggesting the phosphonic head group adsorbs in a mixed bidentate/monodentate binding motif on the NiTi nanoparticles. Dynamic light scattering and scanning electron microscopy-energy dispersive X-ray spectroscopy revealed the particle sizes. Differential scanning calorimetry was used to examine the phase transitions. Zeta potential determination as a function of pH was examined to investigate the surface properties of charged nanoparticles. The influence of environmental stability of the surface modifications was also assessed.

1. Introduction

Nanoparticles are particles with a diameter of < 100 nm that possess properties that differ from the properties of the bulk material of the same composition [1]. Due to their decreased volume-to-surface area, nanoparticles experience an increase in quantum effects and kinetic energy [2] when compared to the bulk material. Nitinol, discovered by William J. Buehler and Frederick Wang in 1959 for Goodyear Aerospace Corp., is a metal alloy of equal atomic percentages of nickel and titanium [2–4]. Originally, it was designed to produce a missile nose cone resistant to heat and fatigue. Nitinol (NiTi) is best known for its superelasticity, shape-memory, and corrosion resistance, making it an ideal component for aerospace and biomedical tools. NiTi is capable of undergoing a controlled distortion and is then able to return to the original morphology at a slightly higher temperature [5]. The transformation temperature or pressure is the line between martensite and austenite forms, in which the martensite form is more flexible at low temperatures. This process is reversible, so that the product can be used repeatedly with little fatigue [6].

When NiTi shifts between the austenite and martensite forms, nanoparticles of this material also experience a change in electrical and thermal conductivity, which may allow NiTi to act as a chemical sensor in the form of a smart nanofluid [1,7]. In terms of medical applications, the shape memory and flexibility of NiTi metal has been exploited to create a less invasive heart stent [6]. NiTi nanoparticles have been shown to exhibit bioactive properties, leading to the belief that NiTi nanoparticles could be used to assist in cellular adhesion to biomaterials, such as bone implants and prosthetics, and have also been tested to target cancer cells for apoptosis [7–9]. Furthermore, Ni-based electrodes have received increased attention because of their excellent electrochemical properties and applications in rechargeable Ni-based alkaline batteries [10]. However, most of these alloy electrodes are difficult to operate due to the oxidation of the electrode and complications controlling the size of the particles during fabrication. These

* Corresponding author.

E-mail address: quinonesr@marshall.edu (R. Quiñones).

http://dx.doi.org/10.1016/j.tsf.2017.09.048 Received 9 January 2017; Received in revised form 13 September 2017; Accepted 24 September 2017 Available online 25 September 2017

0040-6090/ \odot 2017 Elsevier B.V. All rights reserved.





CrossMark

issues can be resolved using surface modification to provide a practical, robust electrode and a material with long-term stability. Adding a coating to the nanoparticles can also alter the charge, functionality, and reactivity of the surface, and improve the dispersity of the nanoparticles [11–13].

Coatings are chemically adsorbed onto the surfaces of nanoparticles via the formation of self-assembled monolayers (SAMs), which often include head groups such as thiols, [14,15] silanes, [16] or phosphonates [17,18]. The head group chemically binds to the substrate and a protective layer is thereby formed over the surface of the nanopowder [19,20]. SAMs are formed spontaneously by chemisorption, yielding robust, well-defined structures on substrates. SAMs are particularly useful when they contain modifiable head and tail groups; these bifunctional SAMs provide an effective and inexpensive method for tailoring the surface properties of the nanoparticles [21,22].

The formation of SAMs provides a common means to modify the surfaces of conductors and semiconductors [23]. The occurrence of oxidation and reduction reactions on the nanoparticle exterior can be limited using SAMs, [17] and the type of headgroup used in the production of the monolayer is vital to the stability of the surface [24]. Phosphonic acids are ideal for the production of SAMs on the surface of NiTi nanoparticles due to the low acid dissociation constant, making them safe for use within the human body [6]. Phosphonic acids are also prone to binding to metals due to their ability to have as many as three covalent bonds on the surface of the nanoparticles [25,26]. The phosphonate head group may increase the nanoparticle stability when paired with an electronegative terminating group, such as a carboxylic acid group, as noted in the literature [27,28].

In this study, phosphonic acids, including 16-phosphonohexadecanoic acid, octadecylphosphonic acid, and 12-aminododecylphosphonic acid, were used to form thin films on NiTi nanoparticles. These modifications were characterized using X-ray photoelectron spectroscopy (XPS) and a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDS). Along with the images collected using SEM, dynamic light scattering (DLS) and zeta potential were used to confirm the sizes of the NiTi nanoparticles and the surface charge. Attenuated total reflectance infrared spectroscopy (ATR-IR) identified the presence and ordering of the alkyl groups within the bonded acids on the surface of the NiTi nanoparticles. Differential scanning calorimetry (DSC) was used to analyze the martensite to austenite transitions and the phosphonic acid desorption. Furthermore, solid-state nuclear magnetic resonance (SS-NMR) was used to analyze the attachment of the phosphorous on the surface of the NiTi.

2. Experimental section

2.1. Materials and methods

Octadecylphosphonic acid (ODPA, 97.0% purity) and 12-aminododecylphosphonic acid hydrochloride (12-NH₂PA, 95.0% purity) were purchased from Alfa Aesar. 16-phosphonohexadecanoic acid (COOH-PA, 97% purity) was purchased from Aldrich. NiTi nanoparticles (99.9% purity, 60–80 nm in diameter, Ni/Ti 50/50 atomic percent) were purchased from SkySpring Nanomaterials Incorporated. The manufacturer reported average particle sizes between 60 and 80 nm with a Brunauer-Emmett-Teller surface area of $15 \text{ m}^2/\text{g}$. Tetrahydrofuran (THF, Optima grade), methanol (ACS grade), acetone, sodium hydroxide (NaOH), lithium hydroxide (LiOH), and plain cell culture medium: Dulbecco's Modified Eagle Medium (DMEM) were purchased from Fisher. Hexane (Tech grade) was purchased from Preiser Scientific, and ethanol (190 proof) was purchased from Pharmo-Aaper. All chemicals were used without further purification.

2.2. Formation of the monolayers

SAMs were formed on the surface of the nanoparticles by sonicating

0.35 g of NiTi nanopowder in 30 mL of THF at a frequency of 40 kHz for 15 min at 33 \pm 3 °C. An organic acid solution, formed by sonicating 15 mM of the organic acids (either ODPA, COOH-PA or 12-NH₂PA) in 6 mL of THF for 5 min, was prepared. The well-dispersed nanopowder was added to the organic acid solution and then the nanoparticle/organic acid solution was sonicated without heat for 30 min. The sample was left to stir under a fume hood overnight. Since a physically adsorbed layer can be formed, the modified particles were rinsed and sonicated again in 10 mL of THF for 15 min at 33 \pm 3 °C and then centrifuged to remove weakly bound molecules from the NiTi surface [26]. The modified nanoparticles were recovered using a vacuum centrifuge (< 20 mbar, 1400 rpm for 10 min) and the particles were again left under a fume hood overnight to dry.

2.3. Environmental stability

Various stability tests were performed and then samples were analyzed by ATR-IR spectroscopy. The stability tests performed include rinsing the nanoparticles with water and humidity testing with the passage of time. Solvent tests utilized the aforementioned procedure to make samples, but substituted THF for deionized water; a basic, mixed alkaline solution containing both 30 mM KOH and 10 mM LiOH in deionized (DI) water (net hydroxide concentration of 40 mM), which was chosen to mimic a base fluid for a nanofluids; and DMEM, which was used in order to mimic a body fluid. To investigate the durability of samples over time, ATR-IR was performed on samples immediately after rinsing and sonication and then again one year after preparation. To examine the effect of humidity on NiTi, individual samples were tested after sitting under 0%, 30%, 60%, and 90% relative humidity for one month. The ATR-IR spectra of the samples after humidity testing were compared to the spectra of the initially modified NiTi samples.

2.4. Characterization of the films

2.4.1. ATR-IR

ATR – IR was performed using a Thermo Scientific Nicolet iS50 FT-IR and was used to analyze the alkyl chain ordering and bonding motif of the molecules to the surface. The unmodified NiTi nanoparticles were used to collect a background spectrum for analysis purposes. Typically, 512 scans were collected.

2.4.2. SS-NMR

Solid state NMR spectra were acquired with a Bruker Avance 300 console and 7 T Bruker magnet. Samples were packed into 4 mm zirconia rotors. A Bruker double resonance Magic-angle-spinning (MAS) probe was tuned to a ¹H frequency of 300.405 MHz and a ³¹P frequency of 121.606 MHz. MAS with rotor frequencies of 10 kHz was employed. The ³¹P direct-polarization pulse sequence used a 3.5 µsec 90° pulse on the ³¹P channel and 30 kHz of proton decoupling during acquisition. The FID was Fourier transformed with 16 Hz of line broadening after zero filling to a total of 32 k points. The ³¹P spectra were referenced externally utilizing measurement of the resonance frequency of an aqueous solution of 85% phosphoric acid (set to 0.0 ppm).

2.4.3. XPS

XPS measurements were performed with a PHI 5000 VersaProbe ESCA Microprobe system (ULVAC-PHI) using a focused Al K-Alpha Xray source at 1486 eV energy and 25 W with an X-ray spot size of 100 μ m. The take-off angle of the photoelectron was set at 45°. An analyzer pass energy of 117.4 eV was used for a survey scan, and highresolution scans for nickel, titanium, oxygen, phosphorus, carbon, and nitrogen elements were carried out at an analyzer pass energy of 23.5 eV. The XPS spectra were referenced to the C1s peak at a binding energy of 284.8 eV.

2.4.4. SEM/EDS

SEM/EDS was performed using a JEOL JSM-7600F field emission SEM. The EDS was collected with an Oxford INCA EDS system and data was analyzed using the Oxford Aztec Energy Analyzer software. The chamber of the SEM was held under high vacuum conditions. The accelerating voltage for the EDS ranged from 3 to 10 kV. Samples were prepared individually in pin stubs and sputtered with a 10-nm thin coating of gold/palladium. SEM/EDS was used to analyze the surface composition of the nanoparticles and obtain information about particle size and elemental composition. The size distribution of the nanoparticles was calculated from the size measurements of > 50 nanoparticles.

2.4.5. Dynamic light scattering (DLS) and zeta potential measurements

A Brookhaven ZetaPlus Potential Analyzer (90Plus PALS) was used to perform DLS and zeta potential measurements of the unmodified and modified NiTi nanoparticles. The measurements were performed at 25 °C in water and THF. For DLS, at least three measurements were made for each sample and the collected values were averaged. For zeta potential, 10 measurements were made for each sample and the collected values were averaged. The Zeta Potential Analyzer was employed to determine the direction of particles under the influence of an electric field, allowing the estimation of the zeta potential of the NiTi suspensions under water and THF. In order to analyze the dependence of each suspension on pH, the zeta potential of unmodified and modified NiTi nanoparticles was measured at consecutive pH values from 2 to 12 in 2.0 mL samples in deionized water. The dispersions were manually stirred for proper particle and ion distribution.

2.4.6. Differential scanning calorimetry (DSC)

DSC experiments were conducted with a TA Instruments Q100 instrument calibrated for temperature by means of an indium standard. The DSC was employed to determine the phase transformation temperatures by using a 10 °C/min heating/cooling rate in a temperature range of -60 to 140 °C. Thermograms were run on samples of -20 mg of NiTi nanoparticles in sealed aluminum pans under a purging atmosphere of helium. Values of peaks' positions and transition temperatures were determined using TA Universal Analysis software that accompanies the DSC instrument.

3. Results and discussion

Various phosphonic acid functionalized thin films were formed through chemical bonding of ODPA, COOH-PA, and 12-NH₂PA onto the NiTi nanoparticles.

3.1. Attenuated total reflectance infrared spectroscopy (ATR-IR)

ATR-IR spectroscopy was used to confirm the presence of the organic modifiers on the surface of the nanoparticles and to determine the manner by which the SAMs were bonded to the surface. The NiTi nanoparticles were modified via surface chemical adsorption of three organic acids with phosphonic functional groups (ODPA, COOH-PA, and 12-NH₂PA). This treatment led to the formation of self-assembled monolayers on the surface of the nanoparticles, which were rinsed and sonicated to verify that the attachments were both stable and stronglybound. Modified samples were then characterized using infrared spectroscopy; the spectra of the unmodified NiTi nanoparticles contained no peaks indicative of the presence of organic materials.

In the IR spectra of the modified substrates, the C–H stretches of the methylene group are used as the reference peaks for SAM organization [6,29]. The C–H stretch has two common vibrations: a symmetric stretch corresponding to a peak at ~2850 cm⁻¹ and an asymmetric stretch corresponding to a peak at ~2918 cm⁻¹. These two energies are shifted depending on the alkyl chain conformation. In this study, the values of $\bar{\nu}_{CH2}$ after rinsing and sonication were $\bar{\nu}_{CH2}$ asym/ $\bar{\nu}_{CH2}$



Fig. 1. Infrared spectra of NiTi nanoparticles modified with (A) ODPA, (B) COOH-PA, and (C) 12-NH₂PA are displayed. The spectral regions correspond to the CH region and measurements occurred after rinsing and sonication.

 $_{\rm sym} = 2916 \ {\rm cm}^{-1}/2850 \ {\rm cm}^{-1}$, 2916 ${\rm cm}^{-1}/2847 \ {\rm cm}^{-1}$, and 2916 ${\rm cm}^{-1}/2848 \ {\rm cm}^{-1}$ for nanoparticles modified with ODPA, COOH-PA, and 12-NH₂PA, respectively (Fig. 1). These results indicate that the attachment of organic acids forms strongly-bound and ordered monolayers on the surface of NiTi. Due to the low surface area of the NiTi nanopowder, the formation of an organized film may be more difficult



Fig. 2. Infrared spectra of NiTi nanoparticles modified with (A) ODPA, (B) COOH-PA, and (C) 12-NH₂PA are displayed. The spectral regions correspond to the PO region. Black lines are the acid control samples.

[30-32].

The spectra acquired following sonication also indicate the manner in which the molecules are bound to the surface of the nanoparticles [26]. Sonication, which removes weakly bound or physically-adsorbed material, ensures the remaining material is strongly bound to the surface. The nature of the interaction between the molecules and the surface can be determined from the shifts and broadening of $\bar{\nu}_{P=O}$, $\bar{\nu}_{P=O}$, and $\bar{\nu}_{POH}$, indicating a change in head group bonding. Specifically, the PO region of the ODPA solid shows $\bar{\nu}_{P=O} = 1227 \text{ cm}^{-1}$ and 1217 cm^{-1} , $\bar{\nu}_{P-O} = 1076 \text{ cm}^{-1}$ and 1005 cm^{-1} , and $\bar{\nu}_{POH} = 957 \text{ cm}^{-1}$, 948 cm⁻¹, and 933 cm⁻¹. The PO region of the bound ODPA displayed peaks that were similar to those of the unbound ODPA $\bar{\nu}_{P=O} = 1227 \text{ cm}^{-1}$ and 1217 cm^{-1} , $\bar{\nu}_{P-O} = 1060 \text{ cm}^{-1}$ and 1005 cm^{-1} , and 932 cm^{-1} (Fig. 2A).

Solid COOH-PA shows $\bar{\nu}_{P=O} = 1229 \text{ cm}^{-1}$ and 1214 cm^{-1} , $\bar{\nu}_{P-O} = 1077 \text{ cm}^{-1}$ and 1009 cm^{-1} , and $\bar{\nu}_{POH} = 951 \text{ cm}^{-1}$, while bound COOH-PA stretches occurred at $\bar{\nu}_{P=O} = 1229 \text{ cm}^{-1}$, $\bar{\nu}_{P-O} = 1077 \text{ cm}^{-1}$ and 1010 cm^{-1} , and $\bar{\nu}_{POH} = 970 \text{ cm}^{-1}$ and 935 cm^{-1} (Fig. 2B). Similarly, solid 12-NH₂PA shows $\bar{\nu}_{P=O} = 1232 \text{ cm}^{-1}$ and 1217 cm^{-1} , $\bar{\nu}_{P-O} = 1077 \text{ cm}^{-1}$, 1015 cm^{-1} , and 1006 cm^{-1} , and $\bar{\nu}_{POH} = 952 \text{ cm}^{-1}$ and 934 cm^{-1} , and bound shows $\bar{\nu}_{P=O} = 1164 \text{ cm}^{-1}$, $\bar{\nu}_{P-O} = 1153 \text{ cm}^{-1}$ and 1064 cm^{-1} , and $\bar{\nu}_{POH} = 926 \text{ cm}^{-1}$ (Fig. 2C). For all the ODPA and COOH-PA modifications of phosphonic acid on NiTi, the presence of P=O, P-O, and POH vibrations in the IR spectra mostly indicate the presence of monodentate attachment to the surface of the nanoparticles [6,33–35]. For the 12-NH₂PA modifications, the shifts for POH and P–O vibrations are likely due to a mixed bidentate–monodentate motif of the phosphonate head group on the NiTi nanoparticles.

3.1.1. Environmental stability analysis

Since NiTi can be utilized for nanofluids and biomedical purposes. the ability to remain stable in a variety of environments is vital for the longevity of the nanoparticles. In the body or in a solution, NiTi would constantly be exposed to oxidative and aqueous surroundings, so the allov must be modified in order to withstand these conditions for extended periods of time. In SAMs, different head groups have different affinities for metal oxides. Terminated functional groups, hydrogen bonding of the organic molecule, and van der Waals interactions between the chains also affect the bonding to the surface [6,26]. Durability of SAMs can be monitored through a variety of techniques. The stability of the phosphonate films on the NiTi surfaces was also investigated by IR spectroscopy. For one of the stability tests, nanoparticles were left for one year under atmospheric conditions and analyzed by ATR-IR before and after. The SAMs remained in trans/ gauche conformation $(2917/2847 \text{ cm}^{-1})$ after one year. There was no change in the location or relative intensity of the peaks. Furthermore, samples were prepared by the aforementioned method, but substituting THF with a basic solution made with NaOH and LiOH to make a total of 40 mM hydroxide concentration, a plain cell culture medium solution (DMEM), or DI water. Based on the ATR-IR data, the peaks in the modified NiTi remained ordered but with less intense peaks in the CH region for the other solvents and solutions when compared to the peak intensities of the samples made using THF. Humidity testing was also performed to simulate the water that NiTi would be exposed to as a nanofluid or a biomedical tool. ATR-IR was used to examine nanoparticles stored for a month at 0%, 30%, 60%, and 90% relative humidity. Modification of the nanoparticles resulted in no shift in peak position in the ATR-IR spectra and little change in peak intensity at all tested increments of humidity (2916/2847 cm⁻¹). Based on this data, it can be concluded that the coated NiTi nanoparticles remain stable in various solvents, with the passage of time, and over a large range of humidities when modified with phosphonic acid films.

3.2. Solid-state nuclear magnetic resonance (SS-NMR)

3.2.1. ³¹P SS- NMR

In order to better characterize the grafting of the phosphonic acids at the surface of NiTi, ³¹P solid-state NMR experiments were carried out. In Fig. 3, the ³¹P MAS-NMR spectra of the modified nanopowders are compared to the spectra of the pure phosphonic acids (control



Fig. 3. Solid-state 31 P CP-MAS NMR spectra of (A) ODPA, (B) COOH-PA, and (C) 12-NH₂PA modifications and bulk controls.

samples). The ³¹P MAS-NMR spectrum of NiTi nanoparticles modified with ODPA shows a much broader peak (or overlapping set of peaks) with a maximum intensity at 25.9 ppm compared to the single peak observed for the phosphonic acid control, which can be found at 30.9 ppm (Fig. 3A). In previous ³¹P CP-MAS-NMR studies, phosphonic acids were reacted with silica gel surfaces; analogous changes in ³¹P chemical shifts by -5 ± 1 ppm were observed compared to the chemical shift of the pure phosphonic acids [36]. However, there is a report stating that when peaks are resolved for a variety of bonding moieties, the least shifted of the peaks is associated with a physisorbed film on the surface [37]. This possibility was disregarded as a major contributor to a broader line, as the NiTi nanoparticle samples modified with phosphonic acid were rinsed and sonicated before extensive characterization. Similar chemical shift variations are observed for ODPA on NiTi as in the treated silica samples, from the previously mentioned study, and therefore the NMR results indicate covalently bonded monodentate phosphonic acid groups. The significant broadening of the peak can be attributed to ODPA and NiTi interactions due to a low surface area that can lead to a disordered interface with a wide distribution of chemical environments around the phosphonate groups [31,37,38].

³¹P MAS-NMR spectra of the NiTi modified nanoparticles with COOH-PA are compared to the spectra of the SS ³¹P spectra of the bulk COOH-PA control sample in Fig. 3B. The COOH-PA ³¹P chemical shift changes from a single peak at 31.4 ppm to an upfield peak at 28.4 ppm with a shoulder around 22.8 ppm upon adsorption on the NiTi nanoparticles. The observation of an upfield ³¹P chemical shift when phosphonic acids are bound to metal oxides has been previously reported [26,39,40], and again the lack of resonances for the pure ligands in this spectrum indicates that the functionalized NiTi samples have been rinsed well and that none of the free ligand remains [37]. As the ligand interacts more strongly with the surface, the change in chemical shift relative to the crystalline ligand increases [37]. A lower chemical shift (by about 2 ppm) was observed, indicating a much weaker interaction with the nanoparticle interface, with the possibility of a mixed bidentate/monodentate binding mode due to the shoulder at the right of the peak with a larger shift. This bonding mode was previously observed on anatase TiO2 (101) surfaces modified with phosphonic acid [41]. Previously, NiTi foils were modified with phosphonic acid SAMs, and the predominant bonding seemed to be monodentate with the possibility of hydrogen bonding among the molecules and the surface [6].

The spectra of the NiTi modified using 12-NH₂PA show peaks at 26.2 ppm with a shoulder around 23.3 ppm, while the 12-NH₂PA control show one peak at 30.3 ppm (Fig. 3C). For the peak at 26.2 ppm, a change in chemical shift from the control sample of about 4 ppm was observed, which is again indicative of a change in surface bonds and bonding sites [40,42]. However, this peak is not shifted as strongly as the main peaks observed from bonding of the other acids. The signals at 26.2 ppm from the modified NiTi particles could, in part, correspond to two different moieties condensed with each other through a P–O–P bond as well as bound to the NiTi surface [38]. In general, analysis of unresolved peaks cannot be used to fully determine the bonding mode. But these data do show that each sample contains a range of local bonding environments, most likely due to one or more bonds to the NiTi nanoparticle surface.

3.3. X-ray photoelectron spectroscopy (XPS)

While observation of the PO region in the ATR-IR spectra suggests that the SAMs are chemically bound to the surface, the bonding type (mono- or bi- dentate) is indeterminable by ATR-IR spectroscopy. Therefore, XPS was used to further analyze the bonding motif and the linkage of the phosphonic acid modification on NiTi nanoparticles. Compositional survey scans (Ni2s, Ni2p, Ni3s, Ni3p, Ti2p, O1s, C1s, P2s, P_{2p} , N_{1s}) were acquired using a pass energy of 117.4 eV and high-resolution spectra (Ni_{2p}, Ti_{2p}, O_{1s} , C_{1s} , P_{2p}) were acquired for the phosphonic acid samples using a pass energy of 23.5 eV. The representative survey spectrum of the NiTi nanoparticles, presented in Fig. 4A, exhibits intense Ti_{2p} and O_{1s} peaks with smaller Ni_{2p} and Ni_{1s} peaks, characteristic of titanium and nickel atoms, of which NiTi nanoparticles are comprised. For the titanium analysis in the high resolution spectra, a peak at 458.4 eV was observed and assigned to titanium oxide as a passivation layer at the top of the NiTi nanoparticles [10]. Another peak was observed at 464.2 eV, which is assigned to $Ti_{2p1/2}$. For nickel analysis, a peak at 856.0 eV was assigned to Ni_{2p3/2} for Ni(OH)₂. Another peak centered at 852.5 eV was assigned to $Ni_{2p3/2}$, and is related to nickel metal [33]. According to the XPS profile data, oxygen is present in the surface layer. The oxygen content from the vaporized



Fig. 4. XPS survey spectra of (A) NiTi nanoparticles unmodified (control), (B) ODPA on NiTi, (C) COOH-PA on NiTi, and (D) 12-NH₂PA on NiTi nanoparticles.

solvent at NiTi's surface may result in the formation of a titanium oxide layer [43,44]. Oxygen content at the top layer is a very attractive feature for surface modifications since oxygen can be used as an anchor for the SAMs formation [45]. The oxygen was detected by the O_{1s} at 529.9 eV and is assigned to the oxygen bound to titanium oxide and/or nickel oxide [46]. Another peak at 531.2 eV was assigned to nickel hydroxide and/or titanium hydroxide [46]. The presence of oxygen close to the surface is also noteworthy, suggesting that the topmost layer of NiTi is some type of oxide rather than pure NiTi. Carbon was found in the XPS analysis and this is likely caused by the surface contamination due to air exposure of the sample.

When the nanopowder was modified with ODPA, COOH-PA, and 12-NH₂PA, new peaks were observed (Fig. 4B–D). XPS survey scans of the ODPA on the NiTi sample clearly indicate a significant increase in carbon concentration, concurrent with the appearance of P_{2s} and P_{2p} peaks at 191.6 eV and 133.5 eV, respectively, compared to that of unmodified NiTi. Phosphonic acid modifications were identified through the high-resolution scan P_{2p} binding energy (E_b) of 133.6 eV, which is assigned to the phosphorus bound to oxygen atoms (Fig. 5A–C). Another peak at 133.6 eV was observed, and it may be attributed to phosphorus bonded to carbon, oxygen, and titanium (P–O–Ti) [33]. The low quality of the spectra is mainly due to an extremely low concentration of phosphorus in the modified sample. The measured element-element ratio for titanium, nickel, and oxygen decrease after

phosphonic acid adsorption, (Table 1) with the appearance of the "P" and "N" peaks (Figs. 4 and 5).

Deconvolution of the O_{1s} spectrum of NiTi showed a peak at 530.2 eV corresponding to oxygen atoms in the form of oxides [33]. Another peak is found at 533.2 eV, which appears after the deposition of ODPA (Fig. 5D). This peak can be attributed to the bonds P–OH or C–OH, which could suggest partially hydrolyzed phosphonic ester groups [33,34,47]. As previously mentioned, different types of covalent bonding configurations have been postulated for the phosphonate films. Here, we propose that NiTi nanoparticles have a more favorable monodentate motif than bidentate due to the appearance of P-OH in the FT-IR and XPS data. Another peak at 531.7 eV was detected in the XPS analysis. This peak can be attributed to P=O or P–O–Ti. This result points to the possibility of some degree of bi/monodentate binding motif of the phosphonic acid on the NiTi nanoparticles surface [41].

The high resolution of the C_{1s} spectrum of the phosphonic acid modification of NiTi is dominated by the C–C/C–H peak at 284.9 eV (red dashed line in Fig. 5E), which shows a dramatic increase compared to the control sample and indicates a significant increase in carbon concentration due to the addition of the SAMs backbone alkyl chain. This is suggested by the % atomic concentration in Table 1 and can be seen directly from Fig. 4 by comparing the relative peak intensity between the C_{1s} peak and the Ti_{2p} peak within each spectrum. A second peak at 286.5 eV was assigned to the carbon bound to the phosphorus



Fig. 5. High resolution XPS lines (A–C) P_{2p} of (A) ODPA on NiTi, (B) COOH-PA on NiTi, and (C) 12-NH₂PA on NiTi nanoparticles; (D) O_{1s} of ODPA on NiTi and (E) C_{1s} of COOH-PA on NiTi after renormalization, and (F) N_{1s} of 12-NH₂PA on NiTi nanoparticles. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Table 1
XPS determined % atomic concentrations of control NiTi nanoparticles and SAMs on NiTi

	% Ti	% Ni	% O	% C	% P	% N	% Cl
Control	13.5	2.2	44.8	39.6	0.0	0.0	0.0
ODPA	9.1	1.8	29.6	57.2	2.3	0.0	0.0
COOH-PA	8.3	1.9	30.0	56.8	3.0	0.0	0.0
$12-NH_2PA$	7.6	2.5	30.6	51.7	3.1	3.1	1.3

and to the carbon bound to the oxygen (C–P and C–O). Peak fitting also suggests a very weak peak at 288.7 eV from the COOH-PA modification on NiTi nanoparticles, which could be assigned to the carboxylic group (green dashed line in Fig. 5E).

Furthermore, when the samples were modified using 12-NH₂PA, an N_{1s} signal at 400 eV was obtained due the addition of a nitrogen atom. The curve fitted N_{1s} regions of the high-resolution XPS spectrum presented two peaks at 399.9 eV and 401.6 eV (Fig. 5F). These energies correspond to the presence of a neutral amine group (NH₂) and a protonated amine group (NH₃⁺), respectively [48]. In addition, XPS spectra show all of the fitted spectra for each element (Ni, Ti, O, and C) for the NiTi control and modifications.

Due to a greater ratio of titanium-to-nickel (Ti/Ni) in the bulk material (6.2) than in the modifications (average of 3.0), it can be concluded that the surface of the nanoparticles is enriched with titanium. Since the nanoparticles are synthesized using high temperature, this may cause the surface to be covered predominantly by a TiO₂ layer as observed by the XPS spectra, which would cause an increase of titanium when compared to nickel [33,49]. Furthermore, the carbon-to-phosphorus (C/P) ratio calculated from the relative intensity of the elements obtained at a grazing angle incidence C/P = 24.9 for ODPA ($C_{18}H_{39}O_3P$), 18.9 for COOH-PA ($C_{16}H_{33}O_5P$), and 116.7 for 12-NH₂PA ($C_{12}H_{29}CINO_3P$), is consistent with the molecules bonded on the surface creating a thin film. These values approach the theoretical values with

the deviation attributed to the hydrocarbon contamination noted above. The agreement between the stoichiometric compositions and the measured C/P ratios indicate that the films are uniform and homogeneous.

3.4. Scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDS)

SEM/EDS assisted in the visualization of the NiTi nanoparticles and identified the elemental composition of the modified NiTi nanoparticles. The SEM images (Fig. 6A and B) indicate that both unmodified and modified materials are composed of uniform spherical nanoparticles with typical particle diameters < 100 nm. However, a distribution of sizes occurred. There was no visible change in the morphology of the nanoparticles after the modifications of SAMs when compared to the unmodified NiTi nanoparticles (Fig. 6). The diameter of the modified nanoparticles is slightly larger than the diameter of the unmodified nanoparticles. These measurements are summarized in Table 2. The particle agglomeration from the modified particles is likely due to an increase of interaction between the particles and the charge on the surface as observed using zeta potential analysis, specifically in the case of the carboxylic and amino terminated phosphonic acid film modifications (see below) [50]. It has been previously stated that when nanoparticles are modified with long, closely packed, alkyl chain films, the agglomerated particles are difficult to break, causing the appearance of an increase in particle size, as observed in the SEM and DLS analysis [51].

EDS elemental analysis obtained in conjunction with the SEM images revealed the presence of nickel, titanium, carbon, oxygen, and phosphorus atoms in all examined sections of NiTi modified with ODPA, COOH-PA, 12-NH₂PA, whereas the unmodified sample revealed nickel, titanium, oxygen and carbon atoms. The nitrogen peak for the 12-NH₂PA modification cannot be observed in the EDS spectrum since

Fig. 6. SEM images of (A) NiTi control and (B) NiTi modified using 12-NH₂PA films, and (C) EDS phosphorus elemental mapping pattern for 12-NH₂PA.



B. 12-NH, PA





Table 2

Summary of SEM particle size data of all the modifications on the NiTi surface.

Average particle size (nm)	Particle distribution (\pm nm)
72.7	44.2
81.8	33.7
85.6	38.5
81.1	36.4
	Average particle size (nm) 72.7 81.8 85.6 81.1

the energy range is low, and it is difficult for the instrument to detect. However, EDS mapping images provide a visual evidence that P is uniformly distributed on the NiTi surface and showing spatial distribution of the P element in the films [26,52,53]. Here, SEM mapping shows that 12-NH₂PA is bound onto the NiTi nanoparticles, partially covering the surface. While there is no visible order, the particles are well dispersed and are not aggregated (Fig. 6C).

3.5. Dynamic light scattering (DLS) and zeta potential measurements

DLS was used to measure the particle sizes of the unmodified and modified nanoparticles in water and THF. The SEM measurements indicate that the particles are significantly smaller (73 to 86 nm) than the results from DLS (189 to 243 nm). This discrepancy is most likely due to the different methods and mathematical models used. One reason is due to the Brownian particle displacement of the particles in solution for the DLS measurements [51,54]. Another explanation for this difference is that DLS measures the hydrodynamic diameter, which is the diameter of the particle and ligands, ions, or molecules that are associated with the surface and travel along with the particle in colloidal solution, increasing the average particle size [55]. On the solid surfaces, the counter ion effects and/or electrostatic interactions between the oppositely charged ions are limited compared to DLS analysis.

Zeta potential is correlated to the surface charge of the particle and the nature and composition of the surrounding medium in which the particle is dispersed [56]. It should be noted that the composition and the properties of the surface of the particles are important parameters in determining the zeta potential. After surface modification with phosphonic acids, zeta potential values showed significant variation. The zeta potential decreased from - 25.2 mV for NiTi without phosphorus content to - 52.4 mV for NiTi nanoparticles modified with ODPA (see Table 3). The phosphonic acid modifications were negatively charged, imparting a negative charge to the dispersed nanoparticles as previously reported [57,58]. This negative charge led to electrostatic repulsion between molecules, stabilizing the nanoparticles. The contributions from the acid-base and electrostatic interactions between the hydroxyl groups on the surface of NiTi particles and the phosphorus atom promote the adsorption onto the NiTi nanoparticles. Consequently, the higher absolute value of the zeta potential means an

Table 3

Hydrodynamic particle sizes and zeta potential values of NiTi suspensions with different solvents and phosphonic acids, obtained by DLS directly after dispersing.

Modifications	W	Jater		THF
_	Particle size (nm)	Zeta potential (mV)	Particle size (nm)	Zeta potential (mV)
NiTi control	206.7 ± 1.1	-21.3 ± 1.4	224.3 ± 5.0	-25.2 ± 2.8
COOH-PA	212.3 ± 7.7	-35.6 ± 0.4	215.8 ± 4.4	-29.6 ± 2.1
ODPA	189.0 ± 1.5	-29.0 ± 0.5	217.5 ± 2.6	-52.4 ± 1.4
12-NH ₂ PA	209.9 ± 5.9	-19.76 ± 0.5	227.6 ± 2.7	-10.0 \pm 3.6



Fig. 7. pH dependence of the zeta potentials of surface functionalized NiTi films and unmodified NiTi nanoparticles.

increased stability of the suspended particles against coagulation [58,59]. Here, COOH-PA is found to be more effective in reducing aggregation when compared to ODPA, which preserves a better stability of the nanoparticles. This result may be because COOH-PA is more negative due to the ionization of the –COOH functional groups.

The surface charges of unmodified and modified NiTi nanoparticles were assessed by zeta potential measurements over various pH ranges (Fig. 7), providing further support of the conclusions reached from the DLS data. Solid oxides in aqueous suspension are generally electrically charged as may be observed most directly in electrophoresis experiments [60]. The isoelectric point (IEP) represents the pH value at which the zeta potential value is equal to zero [61]. It can be seen that unmodified NiTi nanoparticles do not reach their isoelectric point within the pH range in the experiments performed here (Fig. 7). The zeta potential of the unmodified NiTi nanoparticles remained practically constant in the studied pH range, which is expected for particles that have structures with negative charges. The negative charge, for unmodified NiTi nanoparticles, is probably caused by oxygen content at the surface layer and hydroxyl groups that are adhered to the surface [61]. At pH 4, the NiTi modified with 12-NH₂PA reached the isoelectric point which correlates with the previously described IEPs of titanium (4–6), from literature reports [27,60]. A lack of particle surface charges leads to the absence of inter-particle repulsive forces, causing the colloidal system to be the least stable at the IEP [62]. The samples modified with 12-NH₂PA contain a large amount of positively charged groups due to the amino phosphonic acid surface and therefore can only have a positive charge when the pH is lower than 4.0. The NiTi modified with ODPA and COOH-PA are negatively charged in the pH range studied as observed in Fig. 7. However, NiTi modified with ODPA is not very soluble in aqueous solution and would not exhibit many negative surface charges by zeta potential measurements. In neutral solution, 12-NH₂PA, ODPA and COOH-PA are slightly negatively charged, neutral, and negatively charged, respectively. The protonation of 12-NH₂PA creates some positive charges at the surface of the nanoparticles, but the results still show a negative value in this study [11,63]. As for ODPA on NiTi, the negative charges were insufficient to improve its dispersity, possibly due to the hydrophobicity and highly ordered structure of the long alkyl chain lengths [64-66]. Furthermore, there is a tendency for strong and ordered formation of the longer C18 chain (ODPA) compared to the shorter C12 and C16 chains. As previously reported, the zeta potential becomes more negative as the alkyl chain length increases [67]. For the COOH-PA modification, a higher negative charge is expected due to the addition of the carbonyl-terminated group [68].

the stability of the modified surface using zeta potential. As shown in Table 3, these observations suggest that the interactions between the phosphonic acid and the surface metal in water and THF are relatively significant. While the zeta potential was solvent dependent for the surface modified samples, the zeta potential of unmodified NiTi was not solvent dependent. The selection of various solvent polarities could increase and improve the adsorption capacity of NiTi nanoparticles. Furthermore, the surface charge is also dependent on the solvent viscosity. Water evaporates more slowly than other solvents, which allows the nanoparticles to remain in solution and prevents the formation of films, making it a promising solvent for nanofluid and cell adhesion applications [69]. Usually, viscosity increases as particle size decreases. as shown in Table 3 [69.70]. It has been shown that surface chemical composition, surface polarity, and swelling behavior all affect the zeta potential, leading to the conclusion that the observed variations may be due to differences in the solvents used [71].

3.6. Differential scanning calorimetry (DSC)

DSC analysis was conducted using a heating/cooling rate of 10 °C/ min. Starting at room temperature, it was initially heated to 140 °C and then cycled to a low temperature of -60 °C before ramping up again to 140 °C. Masses of the samples analyzed were approximately 20 mg. Fig. 8 shows the DSC peaks corresponding to the martensite to austenite transformations upon heating and the reverse austenite to martensite phase transition upon cooling. Such a DSC curve is typical for indicating a direct austenite to martensite transformation. During the first heating cycle, a broad endothermic peak was observed in the temperature range of 60-70 °C, which was attributed to the transformation to austenite phase (Fig. 8A). During the cooling cycle, a broad exothermic peak was observed between the temperatures of 50-60 °C, which is attributed to transformation to martensite phase (Fig. 8B). It has been previously reported that when a material has a low and broad DSC peak, it is known to be near the cold-worked defect, which blocks the phase transition [72]. In the second heating cycle, the martensite to austenite transformation temperature decreases, showing a pronounced downward shift from 68.3 °C in Fig. 8A to 43.2 °C in Fig. 8C. These shifts in transformation temperatures may be caused by the increase in deformation substructure, as well as an increase in dislocation tangling [73,74]. During the heating and cooling cycles in the intermediate temperature range, a rhombohedral phase was not observed.

The DSC curves of the NiTi surface modified with phosphonic acid (Fig. 8) yielded a stronger endothermic peak at higher temperatures compared to the unmodified NiTi nanoparticles. This first transition is attributed to the solid to liquid state transition of the phosphonic acid (91-98 °C). It was noted when comparing 12-NH₂PA (C₁₂) to ODPA (C_{18}) that the melting point and melting enthalpy increase with the phosphonic acid chain length [75]. Previously, work on alkylphosphonate salts had proposed that the transition temperatures are independent of the chain length, but the enthalpies increase linearly with chain length in this study [76]. There has not been much reported on phosphonic acids chemically bounded on metal oxide surfaces and the effect of the chain length on the adsorption/desorption process due to thermal and phase transitions using DSC. Melting point demonstrates the crystallinity of the nanostructure and it is proportional to the order/ trans conformation, which also implies a much denser coverage of the sample [76,77]. Here, ODPA modifications have been proven to be more ordered, using SS-NMR and XPS analysis, when compared to 12-NH₂PA and COOH-PA. For the martensite/austenite transformation in the modified samples, phase transformation was not observed in the DSC analysis. Therefore, the temperatures and the type of phase transformation could not be determined.

For the second transition in the first heating cycle, in the case of ODPA and 12-NH₂PA modifications, the DSC data shows that the nanoparticles were stable up to 129 °C. Here, an endothermic peak is observed that can be attributed to the desorption of the film (Fig. 8A)



Fig. 8. DSC heating and cooling curves of (A) 1st heating cycle(B)1st cooling cycle, and (C) 2nd heating cycle for NiTi control and NiTi modified using phosphonic acid films.

[78]. ODPA on NiTi has a high peak temperature at 131.2 °C that is not observed for either the COOH-PA or 12-NH₂PA modifications on NiTi nanoparticles. This indicates that the ODPA molecules are bound more strongly to the surface and are cleaved only at higher temperatures due to a higher coverage than the other two modifications [75,78]. There is a clear indication that the electrostatic forces of ODPA dominate over the weaker van der Waals interactions between chains lengths that were observed in the lower transition peak [76]. Here, it is observed that 12-NH₂PA on NiTi showed a smaller and broader phase transition at 86.6 °C when compared to the COOH-PA and ODPA modifications as observed in Fig. 8C. Broadening of the transitions may be caused by poor bulk crystallization of the 12-NH₂PA/NiTi nanoparticles, more disordered alkyl chains on the surface, and fairly large particle size distribution, which can affect the alkyl chain packing [75]. When the samples were cooled to low temperature, the transition temperature of the crystallization of the liquid to solid state shifted to a lower temperature. This may be due to the effect of the austenite/martensite transformation in the presence of the phosphonic acid recrystallization.

In the second cooling-heating cycle, a single transition peak for COOH-PA and two transition peaks for 12-NH₂PA and ODPA were observed. The first transition temperature is attributed to the martensite/austenite transformation of NiTi showing a shift toward lower temperature compared to the NiTi unmodified (Fig. 8A and C). The liquid to solid transition was not observed for COOH-PA, but it was observed for ODPA and 12-NH₂PA with a lower temperature shift compared to the first heating cycle. This decrease of temperature between the first and second heating cycles suggest that heat treatment disrupted the order of the films and a more gauche conformation is now present in the samples, as seen in Fig. 8C [75,79]. In the literature, it has been observed that alkylthiolates on copper nanoclusters, as well as alkylphosphonate salts, were able to almost completely revert to their original conformation even after several heating-cooling cycles, but the transitions appear to deteriorate [76,77]. A similar phenomenon was observed for ODPA and 12-NH₂PA samples, showing some "film memory". However, the COOH-PA modification does not exhibit that property, implying that the films decomposed at these temperatures.

From the DSC experiments it can be concluded that various surface treatments have a significant effect on the thermal transition behavior of NiTi nanoparticles. In addition, surface film conformation and its stability are affected by repeated heating and cooling cycles.

4. Conclusions

In this study, NiTi nanoparticles were modified by the attachment of phosphonic head groups with three different organic tails (methyl, carboxylic, and amine-terminated functional groups) by self-assembly. Using ATR-IR spectroscopy and XPS data, the alkylphosphonic acid molecules were found to attach and form strong uniform covalent bonds on the surface of the NiTi nanoparticles that indicated durability through a variety of stability testing for up to one year.

The upfield resonances of the ³¹P SS-NMR spectra lead to the determination of additional bonding (i.e. monodentate or mixed mono/bidentate motif) or intermolecular surface interactions. SEM and DLS were used to demonstrate the increase in particle size following the surface modification. Based on the analysis of the zeta potential, it was concluded that throughout the studied pH range, the zeta potential values decrease after the addition of an anionic functional group, such as a carboxylic acid, and increase in the presence of the cationic amino groups, which are positively charged.

In general, our study is an important step to a better understanding of the interaction between phosphonic acids and NiTi as observed by DSC on a macroscopic level as well as the stability of the adsorbed phosphonic acid molecules on the surface, both of which could be useful in the creation of nanofluids with excellent colloidal stability. Furthermore, the outcome of the study can serve as a model to precisely control and characterize surface modifications and formulate an ideal functionalized nanocoating for biomedical or industrial applications with future studies focusing on further analysis of novel binding motifs.

Acknowledgment

This work was partially supported by a grant from NASA WV Space Grant Consortium (NASA Grant #NNX15AI01H) and internal funding from Marshall University. KTM and JWF acknowledge the support of the National Science Foundation (Grant CHE 1411687). We would like to thank Dr. Weiqiang Ding and Marcela Redigolo from West Virginia University (WVU) Shared Research Facilities for the use of the XPS and SEM/EDS, respectively. SA and RKG acknowledge George B. and Carolyn A. Berry fund for partially supporting this work.

References

- E.L.C.A. Torres Castro, U. Oriz Mendez, M. Jose Yacaman, Advances in developing TiNi nanoparticles, Mater. Sci. Eng. 438-440 (2006) 411–413.
- [2] V.G. Sujat Sen, Christopher J. Pelliccione, Jie Wang, Dean J. Miller, Elena V. Timofeeva, Surface modification approach to TiO₂ nanofluids with high particle concentration, low viscosity, and electrochemical activity, ACS Appl. Mater. Interfaces 7 (2015) 20538–20547.
- [3] X.G. Peng, L. Manna, W.D. Yang, J. Wickham, E. Scher, A. Kadavanich, A.P. Alivisatos, Shape control of CdSe nanocrystals, Nature 404 (2000) 59–61.
- [4] Q. Shen, D. Arae, T. Toyoda, Photosensitization of nanostructured TiO₂ with CdSe quantum dots: effects of microstructure and electron transport in TiO₂ substrates, J. Photochem. Photobiol., A 164 (2004) 75–80.
- [5] W.J.G. Buehler, J. V., R.C. Wiley, Effect of low-temperature phase changes on the mechanical properties of alloys near composition TiNi, J. Appl. Phys. 34 (1963) 1475.
- [6] R. Quiñones, E.S. Gawalt, Study of the formation of self-assembled monolayers on nitinol, Langmuir 23 (2007) 10123–10130.
- [7] A.N. Sarah Strau, Stephan Barcikowski, Dietmar Kracht, Jorn W. Kuhbier, Christine Radtke, Kerstin Reimers, Peter M. Vogt, Adhesion, vitality and osteogenic differentiation capacity of adipose derived stem cells seeded on nitinol nanoparticle coatings, PLoS One 8 (2013) e53309.
- [8] N.G. Donghui Wang, Jinhua Li, Yuqin Qiao, Hongqin Zhu, Xuanyong Liu, Selective tumor cell inhibition effect of Ni – Ti layered double hydroxides thin films driven by the reversed pH gradients of tumor cells, ACS Appl. Mater. Interfaces 7 (2015) 7043–7054.
- [9] S. Barcikowski, A. Hahn, Merlin Guggenheim, Kerstin Reimers, A. Ostendorf, Biocompatibility of nanoactuators: stem cell growth on laser-generated nickel-titanium shape memory alloy nanoparticles, J. Nanopart. Res. 12 (2010) 1733–1742.
- [10] Y. Yu, Q. Yang, X. Li, M. Guo, J. Hu, A bimetallic Ni-Ti nanoparticle modified indium tin oxide electrode fabricated by the ion implantation method for studying the direct electrocatalytic oxidation of methanol, Green Chem. 18 (2016) 2827–2833.
- [11] T. Jesionowski, Influence of aminosilane surface modification and dyes adsorption on zeta potential of spherical silica particles formed in emulsion system, Colloids Surf. A Physicochem. Eng. Asp. 222 (2003) 87–94.
- [12] T. Ye, E.A. McArthur, E. Borguet, Mechanism of UV photoreactivity of alkylsiloxane self-assembled monolayers, J. Phys. Chem. B 109 (2005) 9927–9938.
- [13] Y.-H. La, Y.J. Jung, H.J. Kim, T.-H. Kang, K. Ihm, K.-J. Kim, B. Kim, J.W. Park, Sub-100-nm pattern formation through selective chemical transformation of self-assembled monolayers by soft X-ray irradiation, Langmuir 19 (2003) 4390–4395.

- [14] S. Reese, M.A. Fox, Self-assembled monolayers on gold of thiols incorporating
- conjugated terminal groups, J. Phys. Chem. B 102 (1998) 9820–9824.
 [15] F. Sinapi, A. Naji, J. Delhalle, Z. Mekhalif, Assessment by XPS and electrochemical techniques of two molecular organosilane films prepared on stainless-steel surfaces, Surf. Interface Anal. 36 (2004) 1484–1490.
- [16] A.S. Duwez, U. Jonas, H. Klein, Influence of molecular arrangement in self-assembled monolayers on adhesion forces measured by chemical force microscopy, ChemPhysChem 4 (2003) 1107–1111.
- [17] R. Quiñones, A. Raman, E.S. Gawalt, Functionalization of nickel oxide using alkylphosphonic acid self-assembled monolayers, Thin Solid Films 516 (2008) 8774–8781.
- [18] A. Raman, M. Dubey, I. Gouzman, E.S. Gawalt, Formation of self-assembled monolayers of alkylphosphonic acid on the native oxide surface of SS316L, Langmuir 22 (2006) 6469–6472.
- [19] R.J. Jouet, A.D. Warren, D.M. Rosenberg, V.J. Bellitto, K. Park, M.R. Zachariah, Surface passivation of bare aluminum nanoparticles using perfluoroalkyl carboxylic acids, Chem. Mater. 17 (2005) 2987–2996.
- [20] V.L. Colvin, A.N. Goldstein, A.P. Alivisatos, Semiconductor nanocrystals covalently bound to metal surfaces with self-assembled monolayers, J. Am. Chem. Soc. 114 (1992) 5221–5230.
- [21] A. Gole, S.R. Sainkar, M. Sastry, Electrostatically controlled organization of carboxylic acid derivatized colloidal silver particles on amine-terminated self-assembled monolayers, Chem. Mater. 12 (2000) 1234–1239.
- [22] R.G. Nuzzo, D.L. Allara, Adsorption of bifunctional organic disulfides on gold surfaces, J. Am. Chem. Soc. 105 (1983) 4481–4483.
- [23] M. Dubey, I. Gouzman, S.L. Bernasek, J. Schwartz, Characterization of self-assembled organic films using differential charging in X-ray photoelectron spectroscopy, Langmuir 22 (2006) 4649–4653.
- [24] D.P. Anna Cattani-Scholz, Manish Dubey, Stefan Neppl, Bert Nickel, Peter Feulner, Jeffrey Schwartz, Gerhard Abstreiter, Marc Tornow, Organophosphonate-based PNA functionalization of silicon nanowires for label-free DNA detection, ACS Nano 2 (2008) 1653–1660.
- [25] A. Mahapatro, T.D.M. Negrón, A. Nguyen, Spectroscopic evaluations of interfacial oxidative stability of phosphonic nanocoatings on magnesium, J. Spectrosc. 2015 (2015) 8.
- [26] R. Quiñones, K. Rodriguez, R.J. Iuliucci, Investigation of phosphonic acid surface modifications on zinc oxide nanoparticles under ambient conditions, Thin Solid Films 565 (2014) 155–164.
- [27] A. Raman, R. Quiñones, L. Barriger, R. Eastman, A. Parsi, E.S. Gawalt, Understanding organic film behavior on alloy and metal oxides, Langmuir 26 (2010) 1747–1754.
- [28] S. Szillies, P. Thissen, D. Tabatabai, F. Feil, W. Fürbeth, N. Fink, G. Grundmeier, Formation and stability of organic acid monolayers on magnesium alloy AZ31: the role of alkyl chain length and head group chemistry, Appl. Surf. Sci. 283 (2013) 339–347.
- [29] G.M. Whitesides, P.E. Laibinis, Wet chemical approaches to the characterization of organic surfaces: self-assembled monolayers, wetting, and the physical-organic chemistry of the solid-liquid interface, Langmuir 6 (1990) 87–96.
- [30] S. Pawsey, M. McCormick, S. De Paul, R. Graf, Y.S. Lee, L. Reven, H.W. Spiess, ¹H Fast MAS NMR studies of hydrogen-bonding interactions in self-assembled monolayers, J. Am. Chem. Soc. 125 (2003) 4174–4184.
- [31] S. Pawsey, K. Yach, L. Reven, Self-assembly of carboxyalkylphosphonic acids on metal oxide powders, Langmuir 18 (2002) 5205–5212.
- [32] W. Gao, L. Dickinson, C. Grozinger, F.G. Morin, L. Reven, Order-disorder transitions in self-assembled monolayers: a ¹³C solid-state NMR study, Langmuir 13 (1997) 115–118.
- [33] I. Milošev, M. Metikoš-Huković, Ž. Petrović, Influence of preparation methods on the properties of self-assembled films of octadecylphosphonate on Nitinol: XPS and EIS studies, Mater. Sci. Eng. C 32 (2012) 2604–2616.
- [34] J. Rechmann, A. Sarfraz, A.C. Götzinger, E. Dirksen, T.J.J. Müller, A. Erbe, Surface functionalization of oxide-covered zinc and iron with phosphonated phenylethynyl phenothiazine, Langmuir 31 (2015) 7306–7316.
- [35] S. Hannah, J. Cardona, D.A. Lamprou, P. Šutta, P. Baran, A. Al Ruzaiqi, K. Johnston, H. Gleskova, Interplay between vacuum-grown monolayers of alkylphosphonic acids and the performance of organic transistors based on dinaphtho[2,3-b:2',3'-f] thieno[3,2-b]thiophene, ACS Appl. Mater. Interfaces 8 (2016) 25405–25414.
- [36] I. Lukes, M. Borbaruah, L.D. Quin, Direct reaction of phosphorus acids with hydroxy of a silanol and on the silica gel surface, J. Am. Chem. Soc. 116 (1994) 1737–1741.
- [37] S.K. Davidowski, G.P. Holland, Solid-state NMR characterization of mixed phosphonic acid ligand binding and organization on silica nanoparticles, Langmuir 32 (2016) 3253–3261.
- [38] D. Aiello, N. Folliet, G. Laurent, F. Testa, C. Gervais, F. Babonneau, T. Azaïs, Solid state NMR characterization of phenylphosphonic acid encapsulated in SBA-15 and aminopropyl-modified SBA-15, Microporous Mesoporous Mater. 166 (2013) 109–116.
- [39] P. Fiurasek, L. Reven, Phosphonic and sulfonic acid-functionalized gold nanoparticles: a solid-state NMR study, Langmuir 23 (2007) 2857–2866.
- [40] G.P. Holland, R. Sharma, J.O. Agola, S. Amin, V.C. Solomon, P. Singh, D.A. Buttry, J.L. Yarger, NMR characterization of phosphonic acid capped SnO₂ nanoparticles, Chem. Mater. 19 (2007) 2519–2526.
- [41] M. Wagstaffe, A.G. Thomas, M.J. Jackman, M. Torres-Molina, K.L. Syres, K. Handrup, An experimental investigation of the adsorption of a phosphonic acid on the anatase TiO₂(101) surface, J. Phys. Chem. C 120 (2016) 1693–1700.
- [42] W.O. Yah, A. Takahara, Y.M. Lvov, Selective modification of halloysite lumen with octadecylphosphonic acid: new inorganic tubular micelle, J. Am. Chem. Soc. 134 (2011) 1853–1859.

- [43] G.B. Kauffman, I. Mayo, The story of nitinol: the serendipitous discovery of the memory metal and its applications, Chem. Educ. 2 (2) (1997) 1–21.
- [44] B.D. Jaydeep Adhikary, Sourav Chatterjee, Sandeep Kumar Dash, Sourav Chattopadhyay, Somenath Roy, Jeng-Wei Chen, Tanmay Chattopadhyay, Ag/CuO nanoparticles prepared from a novel trinuclear compound [Cu(Imdz)₄(Ag (CN)₂)₂] (Imdz = imidazole) by a pyrolysis display excellent antimicrobial activity, J. Mol. Struct. 1113 (2016) 9–17.
- [45] S.Y. Lin, T.K. Tsai, C.M. Lin, C.H. Chen, Y.C. Chan, H.W. Chen, Structures of selfassembled monolayers of n-alkanoic acids on gold surfaces modified by underpotential deposition of silver and copper: odd-even effect, Langmuir 18 (2002) 5473–5478.
- [46] S. Devillers, B. Barthélémy, J. Delhalle, Z. Mekhalif, Induction heating Vs conventional heating for the hydrothermal treatment of nitinol and its subsequent 2-(methacryloyloxy)ethyl 2-(trimethylammonio)ethyl phosphate coating by surfaceinitiated atom transfer radical polymerization, ACS Appl. Mater. Interfaces 3 (2011) 4059–4066.
- [47] Ž. Petrović, J. Katić, M. Metikoš-Huković, H. Dadafarin, S. Omanovic, Modification of a nitinol surface by phosphonate self-assembled monolayers, J. Electrochem. Soc. 158 (2011) F159–F165.
- [48] T.A. Al-Khaldi, S.B. Lyon, The effect of interfacial chemistry on coating adhesion and performance: a mechanistic study using aminobutylphosphonic acid, Prog. Org. Coat. 75 (2012) 449–455.
- [49] A. Maho, F. Kanoufi, C. Combellas, J. Delhalle, Z. Mekhalif, Electrochemical investigation of nitinol/tantalum hybrid surfaces modified by alkylphosphonic selfassembled monolayers, Electrochim. Acta 116 (2014) 78–88.
- [50] S. Betancur, J.C. Carmona, N.N. Nassar, C.A. Franco, F.B. Cortés, Role of particle size and surface acidity of silica gel nanoparticles in inhibition of formation damage by asphaltene in oil reservoirs, Ind. Eng. Chem. Res. 55 (2016) 6122–6132.
- [51] B. Feichtenschlager, S. Pabisch, H. Peterlik, G. Kickelbick, Nanoparticle assemblies as probes for self-assembled monolayer characterization: correlation between surface functionalization and agglomeration behavior. Lanemuir 28 (2012) 741–750.
- [52] M. Nosuhi, A. Nezamzadeh-Ejhieh, High catalytic activity of Fe(II)-clinoptilolite nanoparticales for indirect voltammetric determination of dichromate: experimental design by response surface methodology (RSM), Electrochim. Acta 223 (2017) 47–62.
- [53] Y. Chaikin, T.A. Bendikov, H. Cohen, A. Vaskevich, I. Rubinstein, Phosphonatestabilized silver nanoparticles: one-step synthesis and monolayer assembly, J. Mater. Chem. C 1 (2013) 3573–3583.
- [54] X.Y. Ling, D.N. Reinhoudt, J. Huskens, Ferrocenyl-functionalized silica nanoparticles: preparation, characterization, and molecular recognition at interfaces, Langmuir 22 (2006) 8777–8783.
- [55] P.B. Kasva Anuradha, Sunkara Sakunthala Madhavendra, Macromolecular arabinogalactan polysaccharide mediated synthesis of silver nanoparticles, characterization and evaluation, Macromol. Res. 24 (2015) 152–162.
- [56] A. Sizovs, X. Song, M.N. Waxham, Y. Jia, F. Feng, J. Chen, A.C. Wicker, J. Xu, Y. Yu, J. Wang, Precisely tunable engineering of sub-30 nm monodisperse oligonucleotide nanoparticles, J. Am. Chem. Soc. 136 (2014) 234–240.
- [57] C. Schmitt Pauly, A.-C. Genix, J.G. Alauzun, G. Guerrero, M.-S. Appavou, J. Pérez, J. Oberdisse, P.H. Mutin, Simultaneous phase transfer and surface modification of TiO₂ nanoparticles using alkylphosphonic acids: optimization and structure of the organosols, Langmuir 31 (2015) 10966–10974.
- [58] C. Oueiny, S. Berlioz, L. Patout, F.X. Perrin, Aqueous dispersion of multiwall carbon nanotubes with phosphonic acid derivatives, Colloids Surf. A Physicochem. Eng. Asp. 493 (2016) 41–51.
- [59] A. Mikolajczyk, A. Gajewicz, B. Rasulev, N. Schaeublin, E. Maurer-Gardner, S. Hussain, J. Leszczynski, T. Puzyn, Zeta potential for metal oxide nanoparticles: a predictive model developed by a nano-quantitative structure-property relationship approach, Chem. Mater. 27 (2015) 2400–2407.

- [60] G.A. Parks, The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems, Chem. Rev. 65 (1965) 177–198.
- [61] K.P. Lopes, L.S. Cavalcante, A.Z. Simões, R.F. Gonçalves, M.T. Escote, J.A. Varela, E. Longo, E.R. Leite, NiTiO₃ nanoparticles encapsulated with SiO₂ prepared by sol–gel method, J. Sol-Gel Sci. Technol. 45 (2008) 151–155.
- [62] S. Clement, W. Deng, K. Drozdowicz-Tomsia, D. Liu, C. Zachreson, E.M. Goldys, Bright, water-soluble CeF₃ photo-, cathodo-, and X-ray luminescent nanoparticles, J. Nanopart. Res. 17 (2015) 7.
- [63] G. Wu, J. Wang, X. Chen, Y. Wang, Impact of self-assembled monolayer films with specific chemical group on bFGF adsorption and endothelial cell growth on gold surface, J. Biomed. Mater. Res. A 102 (2014) 3439–3445.
- [64] P. Zhang, Y.-P. Chen, J.-S. Guo, Y. Shen, J.-X. Yang, F. Fang, C. Li, X. Gao, G.-X. Wang, Adsorption behavior of tightly bound extracellular polymeric substances on model organic surfaces under different pH and cations with surface plasmon resonance, Water Res. 57 (2014) 31–39.
- [65] J.-J. Shyue, M.R. De Guire, T. Nakanishi, Y. Masuda, K. Koumoto, C.N. Sukenik, Acid – base properties and zeta potentials of self-assembled monolayers obtained via in situ transformations, Langmuir 20 (2004) 8693–8698.
- [66] C.S. Pauly, A.-C. Genix, J.G. Alauzun, M. Sztucki, J. Oberdisse, P. Hubert Mutin, Surface modification of alumina-coated silica nanoparticles in aqueous sols with phosphonic acids and impact on nanoparticle interactions, Phys. Chem. Chem. Phys. 17 (2015) 19173–19182.
- [67] M.R. Ivanov, A.J. Haes, Anionic functionalized gold nanoparticle continuous full filling separations: importance of sample concentration, Anal. Chem. 84 (2012) 1320–1326.
- [68] I. Ostolska, M. Wiśniewska, Application of the zeta potential measurements to explanation of colloidal Cr₂O₃ stability mechanism in the presence of the ionic polyamino acids, Colloid Polym. Sci. 292 (2014) 2453–2464.
- [69] M. Borlaf, M.T. Colomer, F. Cabello, R. Serna, R. Moreno, Electrophoretic deposition of TiO₂/Er³⁺ nanoparticulate sols, J. Phys. Chem. B 117 (2013) 1556–1562.
- [70] L. Fedele, L. Colla, S. Bobbo, Viscosity and thermal conductivity measurements of water-based nanofluids containing titanium oxide nanoparticles, Int. J. Refrig. 35 (2012) 1359–1366.
- [71] A. Raman, E.S. Gawalt, Self-assembled monolayers of alkanoic acids on the native oxide surface of SS316L by solution deposition, Langmuir 23 (2007) 2284–2288.
- [72] A. Nespoli, E. Villa, L. Bergo, A. Rizzacasa, F. Passaretti, DSC and three-point bending test for the study of the thermo-mechanical history of NiTi and NiTi-based orthodontic archwires, J. Therm. Anal. Calorim. 120 (2015) 1129–1138.
- [73] A.R. Pelton, G.H. Huang, P. Moine, R. Sinclair, Effects of thermal cycling on microstructure and properties in Nitinol, Mater. Sci. Eng., A 532 (2012) 130–138.
- [74] M. Chakif, A. Essaid, E. Gurevich, A. Ostendorf, O. Prymak, M. Epple, Generation of NiTi nanoparticles by femtosecond laser ablation in liquid, J. Mater. Eng. Perform. 23 (2014) 2482–2486.
- [75] A. Badia, L. Cuccia, L. Demers, F. Morin, R.B. Lennox, Structure and dynamics in alkanethiolate monolayers self-assembled on gold nanoparticles: a DSC, FT-IR, and deuterium NMR study, J. Am. Chem. Soc. 119 (1997) 2682–2692.
- [76] W. Gao, L. Dickinson, F.G. Morin, L. Reven, Phase transitions in lamellar alkylphosphonate salts, Chem. Mater. 9 (1997) 3113–3120.
- [77] T.P. Ang, T.S.A. Wee, W.S. Chin, Three-dimensional self-assembled monolayer (3D SAM) of n-alkanethiols on copper nanoclusters, J. Phys. Chem. B 108 (2004) 11001–11010.
- [78] G. Kataby, T. Prozorov, Y. Koltypin, H. Cohen, C.N. Sukenik, A. Ulman, A. Gedanken, Self-assembled monolayer coatings on amorphous iron and iron oxide nanoparticles: thermal stability and chemical reactivity studies, Langmuir 13 (1997) 6151–6158.
- [79] M.A. Osman, M. Ernst, B.H. Meier, U.W. Suter, Structure and molecular dynamics of alkane monolayers self-assembled on mica platelets, J. Phys. Chem. B 106 (2002) 653–662.