Noble Metal Nanoparticles in Pectin Matrix. Preparation, Film Formation, Property Analysis, and Application in Electrocatalysis

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ABSTRACT: Stable polymeric materials with embedded nano-objects, retaining their specific properties, are indispensable for the development of nanotechnology. Here, a method to obtain Pt, Pd, Au, and Ag nanoparticles (ca. 10 nm, independent of the metal) by the reduction of their ions in pectin, in the absence of additional reducing agents, is described. Specific interactions between the pectin functional groups and nanoparticles were detected, and they depend on the metal. Bundles and protruding nanoparticles are present on the surface of nanoparticles/pectin films. These films, deposited on the electrode surface, exhibit electrochemical response, characteristic for a given metal. Their electrocatalytic activity toward the oxidation of a few exemplary organic molecules was demonstrated. In particular, a synergetic effect of simultaneously prepared Au and Pt nanoparticles in pectin films on glucose electro-oxidation was found.

INTRODUCTION

Nowadays, researchers focus on matrices allowing for the stable immobilization of noble metal nanoparticles (NMNPs) because of their optical, (electro)catalytic, and antibacterial properties.

In the bottom-up approach, NMNPs are prepared by the reduction of metal salts or metalorganic compounds to metal atoms in the presence of a stabilizing agent. Polymers are better stabilizing agents than small ions because their charged functionalities are attached to flexible chains, preventing coalescence of nanoparticles formed within the polymer matrix. If a polymer has functionalities capable of reducing metal ions, an excess of a reductant, which may be difficult to remove, can be eliminated. Biopolymers were applied for the stabilization of nanoparticles 200 years ago. They are produced by living organisms such as plants, trees, and bacteria and decomposed through the enzymatic action of microorganisms without the emission of toxic waste. Pectins are biodegradable, nontoxic, flexible, cheap, and are very popular thickeners or stabilizing agents in the food industry and households. They are present in all primary cells of plants, and the degree of their methylation depends on the source and the way they are extracted. Most importantly, pectins were applied as reductants and stabilizers of NMNPs.

Pectins are structural heteropolysaccharides consisting mainly of D-galacturonic acid units, connected through α-(1→4) glycosidic linkages. Some of the carboxylic groups of the pectin backbones are methyl-esterified, and the degree of their methylation depends on the source. The availability of carboxyl or hydroxyl groups affects their chemistry because nonesterified carboxyl groups may coordinate to the metal ions and reduce them to metals in the absence of other reductants. The pectin route was applied to prepare Au, Ag, Au/Ag, and Pd nanoparticles. As a result, NMNPs/pectin materials or pectin-stabilized NMNPs were prepared.

Prospective medical applications of NMNPs/pectin materials as controlled release of nanoparticles, targeted drug delivery, singlet oxygen generation for photodynamic therapy, theranostics, and antibacterial/healing treatment were reported. Other areas include surface-enhanced Raman spectroscopy (SERS) and catalysis. The studies of the electrocatalytic properties of films formed by these materials were limited to AuNPs/pectin and explored for sensing.

Here, the goal was to synthesize NMNPs/pectin materials, estimate how pectin affects the nanoparticles’ size and their film topography, and detect the interactions of pectin with...
their surface. We also wanted to know whether the electrocatalytic properties of NMNPs embedded in the pectin film are maintained and how efficient is electronic communication between them and the electrode surface.

For this purpose, we demonstrated a simple and effective method of synthesis of selected NMNPs, that is, AuNPs, PtNPs, PdNPs, and AgNPs, from the metal precursor within the pectin matrix in the absence of an additional reductant. It is already known that pure pectin gelation is enhanced by an excess of sucrose, which influences hydrophobic interactions. Such material was used in our synthesis. Moreover, our preliminary experiments demonstrated that only films prepared from such material on a solid support were stable contrary to those prepared from pure pectin or gelled in the presence of Ca2+ cations or/and excess of hydrated protons. Nuclear magnetic resonance (NMR), UV−vis, infrared (IR), and Raman spectroscopies were employed for the characterization of pectin and/or hybrid materials, in particular the interactions of NMNPs with pectin. X-ray photoelectron spectroscopy (XPS) was used to identify their metallic components, whereas scanning transmission electron microscopy (STEM) allowed for the determination of the size of nanoparticles and its distribution. Atomic force microscopy (AFM) was employed to determine the MeNP/pectin film topography. Voltammetry was performed to study electrochemical surface reactions and the electrocatalysis at NMNPs/pectin films.

RESULTS AND DISCUSSION

NMR Spectroscopy. The 13C NMR spectrum of the studied material reveals signals characteristic for the amidated pectin (Figure S1A) (see Supporting Information S1 for more details). Its characterization is based on the ratio of sucrose molecules to rhamnose units of pectin. Its value 1:12 was estimated on the basis of the 1H NMR spectrum (Figure S1B). The NMR spectra of NMNPs/pectin materials are nearly identical.

Synthesis. In a typical run, 0.01−0.1 g of pectin was carefully mixed with 2 mL of water until the traces of pectin disappeared. Then, an aqueous solution (0.001−0.015 M) of a metal precursor or a mixture of Au and Pt precursors (1:1) was quickly injected and stirred for 1 h. The cloudy solution became transparent and changed from yellow to pale yellow (Ag), amber (Pd), dark brown (Pt), or purple (Au) (Figure S2). The time of the color change ranged from 3 min at 90 °C to 20 min at room temperature. After cooling down, a gelled MeNPs/pectin matrix was formed. The concentration of pectin and the metal precursor was optimized to avoid too fast gelation or generation of large metal particles. In some runs, 1 mL of 1 mM NaBH4 aqueous solution was added to compare the efficiency of the reaction with an additional reductant.

UV−Vis Spectroscopy. Plasmon resonance bands at 413 and 547 nm, respectively, characteristic for AgNPs and AuNPs, are identified on the UV−vis spectra of the sol prepared from the Ag or Au precursor (Figure 1). The absorbance recorded with water as a reference is higher than that recorded versus pectin solution because of the significant turbidity of the pectin solution. It almost disappears when NMNPs are formed. The band position is not affected by the type of the reference sample (Figure 1).

An increase of the pectin concentration affects the color (Figure S3) and UV−vis spectra of AuNPs/pectin sol (Figure S4). It changes from purple to pink, and the band maximum is red-shifted by ca. 10 nm, indicating that a lower concentration of pectin promotes the formation of larger nanoparticles, as indicated by the appearance of a new band at longer wavelengths. The apparent negative absorbance (Figure 1a) results from the turbidity of the pectin solution used as a reference sample (see above).

IR and Raman Spectroscopies. The comparison of the IR spectra of the amidated and nonamidated pectin (Figure S5) allows for determining the signals characteristic for the amidated structure and sucrose (see Supporting Information S4 for details). These results indicate that both pectins are almost high methoxy pectins (ca 45% esterified).

No clear difference is observed in the attenuated total reflection−Fourier transform infrared (ATR−FTIR) spectra of AuNPs/pectin, AgNPs/pectin, and pectin (Figure 2).

Liao et al. and Tao et al. reported that carboxylic groups interact with the silver surface covered by the silver oxide layer formed at atmospheric conditions. This is because basic silver oxide interacts with the COOH groups and COO− groups coordinated to the surface. As an effect, the relative intensities of the COOH and COO− bands on the IR spectra change. This effect may be difficult to notice because of the large number of carboxylic groups in the polymeric pectin chain. Here, both the COOH and COO− bands are visible in the spectra of pectin without nanoparticles (Figure 2 curve a). The similarity of the spectra of AgNPs/pectin and pectin without nanoparticles (Figure 2 curves a, b) may indicate that only a small fraction of carboxylic groups interacts with AgNPs.

Figure 1. UV−vis spectra of (a) AgNPs/pectin (upper curve vs water, lower curve vs pectin solution) and (b) AuNPs/pectin sol (upper curve vs pectin solution, lower curve vs water).
Noticeable differences in the region characteristic for the carboxyl groups are seen in the PdNPs/pectin and PtNPs/pectin spectra. In the case of PdNPs/pectin, the width of the COO$^-$ stretching band (ca. 1600 cm$^{-1}$) is larger than that of pectin, and the COO$^-$ band overlaps with the amide I band (1670 cm$^{-1}$). On the PtNPs/pectin spectrum, this band is also very broad. The changes of the COO$^-$ bands induced by PdNPs and PtNPs are accompanied by the increase of the intensity of the OH stretching band (3400 cm$^{-1}$), suggesting that these samples contain more water than pectin, AuNPs/pectin, and AgNPs/pectin. One may conclude that PdNPs and PtNPs interact stronger with the COO$^-$ groups of pectin, increasing its hydration (see Figure S6 for more details).

Also, the Raman spectrum exhibits features characteristic for the pectin chemical character (Figure 3, curve a) (See Supporting Information S4 for more details). Moreover, some features of the spectra are different when nanoparticles are produced (Figure 3, curves b–e).

There are minor differences in the relative intensities of bands between 1000 and 1500 cm$^{-1}$ of the Raman spectra of PdNPs/pectin, PtNPs/pectin, and AuNPs/pectin (Figure 3, curves b–d). This suggests that NMNPs induce changes in the conformation of pectin without changing its chemical structure. These differences are significant for AgNPs/pectin (Figure 3, curve e), and they can be rationalized by the SERS enhancement. The 532 nm excitation line falls in the typical SERS enhancement range for silver nanostructures.

Unlike the spectra of other NMNPs/pectin samples, the Raman spectrum of AgNPs/pectin shows strong bands at 240, 1360, and 1600 cm$^{-1}$ (Figure 3, curve d). These bands are assigned to the Ag–O stretching mode and the symmetric and antisymmetric motions of COO$^-$ groups, respectively, and suggest strong interactions between AgNPs with these functionalities. This interaction was not identified on the basis of the IR spectra. Such inconsistency can be rationalized by a short range of the SERS enhancement. Only modes of functionalities adjacent to the nanoparticle are visible in the spectrum. Therefore, only the COO$^-$ groups directly interacting with AgNPs contribute to the spectrum. On the contrary, all carboxylic groups contribute to the IR spectra, and the local effect is difficult to be distinguished.

**X-ray Photoelectron Spectroscopy.** To identify metallic components and the degree of their reduction in the absence and presence of an additional reductant, NaBH$_4$, XPS spectra of the MeNPs/pectin films prepared in the absence and presence of NaBH$_4$ were recorded and compared. Deconvolution of the high-resolution (HR) XPS spectra of Au 4f, Ag 3d, Pt 4f, and Pd 3d (Figure S7) reveals the chemical character of Au, Ag, Pt, and Pd, respectively (Table S1). The higher efficiency of reduction by NaBH$_4$ is seen as an increase of XPS signals related to the metal states as compared to those obtained in the absence of the reducing agent (Figure S7). This effect is significant for XPS signals related to the metal states in Au 4f, Ag 3d, and Pt 4f (Figure S7a–c). For Pd-based materials (Figure S7d), this effect is smaller, probably because the Pd surface is recovered by oxygen from the air, prior to the XPS measurement, faster than that on Au-, Pt-, and Ag-reduced sample surfaces. On the basis of the comparison of the metal/carbon atomic ratios (Table S1), one may note that the elemental surface contents of Au, Ag, and Pd are larger when NaBH$_4$ was used. This indicates the segregation of these elements at the surface region of samples during reduction. Materials formed with an additional reductant were not further studied because the foam that was formed during the reaction gel formation was stopped. These products did not form a stable film on the flat surface.

**Scanning Transmission Electron Microscopy.** The STEM images of NMNPs/pectin films revealed nanometer-sized objects (Figure 4). AuNPs and PdNPs are globular and evenly distributed throughout the inspected region. A less regular shape of AgNPs and PtNPs may indicate nanoparticle agglomerates. Cracks seen on the STEM images (Figure 4) result from the destruction of the carbon support film on the copper network because of the shrinking of the deposited pectin following dehydration under low pressure. The pectin film is not visible because it is transparent for the electron beam.

A Gaussian-type behavior with maxima at 10.9 ± 5.2, 9.1 ± 4.7, 11.2 ± 4.7, and 9.7 ± 3.2 nm is seen for AuNPs, AgNPs, PtNPs, and PdNPs, respectively (Figure 5). The lowest polydispersity was obtained for PdNPs, whereas the largest one for AuNPs. The average diameter of AgNPs is the smallest, whereas that of PtNPs is the largest. In general, the size and polydispersity of NMNPs are not significantly affected by the type of metal.

**Atomic Force Microscopy.** AFM experiments were performed under atmospheric pressure to avoid dehydration.
and to preserve the topography of the pectin or NMNPs/pectin film. Relatively clear AFM images show rolled-up objects on a flat surface (Figure S8) identified as fragments of the pectin network. The height images of NMNPs/pectin films are much better resolved and quite different (Figure 6).

They clearly show elongated bundles and globular particles identified as encapsulated NPs. Their size and distribution depend on the metal. AuNPs and PtNPs of diameter 5–10 nm are homogeneously distributed (Figure 6a,c). The image of the AuNPs/pectin film (Figure 6a) is slightly blurred, suggesting the effect of viscosity. PtNPs (Figure 6c) cover both the
bundles of pectin and the space in between. AgNPs (Figure 6b) and PdNPs (Figure 6d) are visible and similar in terms of size (diameter of 10–16 nm, estimated from at least 10 objects found at the given AFM image) and distribution. Larger nanoparticle aggregates are randomly distributed and embedded in the pectin network. The estimated size of nanoparticles is similar to that obtained from STEM images.

Maps of the adhesion force between the AFM probe and the AgNPs/pectin (Figure 7) and PdNPs/pectin (Supporting Information Figure S9) samples simultaneously acquired with the AFM height images indicate that the adhesion force between the AFM tip and nanoparticles is much smaller than that indicated by the AFM height images. Some adhesion force images were taken for the selected area marked with a square. Cross-section profiles of the height and adhesion are marked as (c,d). The profiles were taken along the red line shown on the images presented in insets.

**Figure 7.** PFQNM AFM image of (a) height and (b) adhesion for the AgNPs/pectin film deposited on mica. Insets show HR images taken for the selected area marked with a square. Cross-section profiles of the height and adhesion are marked as (c,d). The profiles were taken along the red line shown on the images presented in insets.

**Information** Figure S9) samples simultaneously acquired with the AFM height images indicate that the adhesion force between the tip and nanoparticles is much smaller than that between the tip and pectin or mica. The correlation between the height and adhesion force maps is nicely seen on the low- and high-resolution images (selected area with two nanoparticles in Figure 7a,b) of the AgNPs/pectin film. Moreover, the cross-section profiles (Figure 7c,d) provide information about the size of the selected nanoparticles, as well as about the adhesion force between the AFM tip and nanoparticles. Some nanoparticles protruding from the pectin film are clearly visible. On the other hand, an analogous map of AuNPs/pectin and PtNPs/pectin film (not shown) is not informative because of the smaller size of the nanoparticles and their distribution.

**Electrochemical Properties of the Nanoparticle Pectin Hybrid Film.** To further identify the metallic nanocomponents of hybrid materials and their electrochemical reactivity, cyclic voltammetry (CV) was run with electrodes modified with MeNPs/pectin film in an aqueous electrolyte solution. Characteristic patterns of Pt and Ag electrodes (Figure 8) are visible, indicating that nanoparticles form percolation paths within the pectin film. At high potentials, CV of PtNPs/pectin-modified electrodes exhibits signals characteristic of the formation and reduction of metal oxide(s) are visible. On the voltammogram obtained for the AgNPs/pectin film-modified electrode (Figure 8b), anodic and cathodic peaks with the midpeak potential at ca. 0.35 V, characteristic for the electrode dissolution/electrodeposition of silver, are visible.

To further test the electrochemical activity of the MeNPs/pectin film, CV was performed in a Fe(CN)₆³⁻ solution. Symmetric CV curves (Figure S10) characteristic for the one-electron electrochemical redox reaction are not much different from those obtained with a bare electrode. More importantly, electrode modification with the MeNPs/pectin film reduces the difference between the peak potentials from 0.12 to 0.06–0.07 V. This indicates a faster heterogeneous electron transfer rate. Perhaps, the surface of nanoparticles is not blocked by pectin chains.

As NMNPs deposited on the electrode surface exhibit an electrocatalytic effect toward a wide range of substrates, selected reactions were tested with MeNPs/pectin electrodes. A negative shift of the onset potential indicates a catalytic effect of PtNPs/pectin and AuNPs/pectin on the electro-oxidation of ascorbic acid (AA) (Figure S11a).59,60 The electrocatalytic effect is seen for H₂O₂ electroreduction at AuNPs/pectin electrodes (Figure S11b).

As AuNPs and PtNPs are known catalysts for glucose electro-oxidation, this reaction was tested with AuNPs/pectin and PtNPs/pectin film electrodes. The characteristic pattern for electrocatalytic glucose oxidation at Au and Pt with the onset potentials of ca. −0.4 and −0.8 V at AuNPs/pectin and PtNPs/pectin, respectively, is visible (Figure 9). Interestingly, when a mixture (1:1) of AuNPs/pectin and PtNPs/pectin solutions was used for electrode modification, an almost 10-fold increase of the oxidation current as compared to the PtNPs/pectin-modified electrode was observed without any overpotential loss, indicating the synergistic effect.

The PtNPs/pectin-modified carbon felt electrode was tested for the electro-oxidation of formic acid (FA). Anodic current related to the FA oxidation with the onset potential at −0.2 V
is visible (Figure 10), and it is absent for the unmodified electrode. On the cyclic voltammogram of the PdNPs/pectin-modified electrode recorded in a pure electrolyte, the characteristic signals at low and high potentials are assigned to the hydrogen electrode processes and formation/reduction of palladium oxide.52

**Conclusions**

We have demonstrated that hybrid materials consisting of Au, Pt, Pd, Ag nanoparticles, and pectin can be prepared by mixing a metal precursor with pectin in the absence of an additional reducing agent. The preparation of PtNPs/pectin material has not been previously reported. Both the temperature and reagent proportion affect the size of the encapsulated nanoparticles. The size and distribution of nanoparticles in a film prepared from hybrid materials are almost independent of the metal. Interactions between the pectin carboxylic groups and the nanoparticle surface, conformational changes, and the enhancement of hydration were detected in the hybrid materials, and they may be a driving force for nanoparticle formation.6 Such examples of spectroscopic detection of metal nanoparticle−biopolymer interactions are rare.66−69 The film of the hybrid material deposited on a solid surface is not flat in the nanometer scale, that is, bundles of pectin and protruding nanoparticles are seen. When deposited on carbon electrodes, pectin-encapsulated nanoparticles form percolation paths, undergoing surface electrochemical reactions and accelerating electrochemical redox reactions. These nanoparticles/pectin-modified electrodes exhibit electrocatalytic properties toward several electrocatalytic reactions. In particular, the synergistic effect of AuNPs and PtNPs on the electrocatalytic oxidation of glucose is striking. This indicates that despite the stabilization of nanoparticles, pectin does not block the electron access to nanoparticles because a fraction of the surface is not covered. Even strong interactions between AgNPs and pectin do not block the electrodissolution of silver. This method of preparation of pectin-embedded nanoparticles can be an asset for future applications. These applications may include biocompatible electronic sensors or other electronic devices,70−76 where nanoparticles are embedded in the biopolymer and provide electronic conductivity and/or serve as a scaffold for electrochemical reactions.

**Experimental Section**

**Materials.** Citrus amidated pectin was donated by Pektowin Jasło (now NATUREX), and the reference sample pectin from citrus peel was obtained from Sigma-Aldrich. NaPdCl₄, H₂AuCl₄ × 3H₂O, H₂PtCl₆ × 6H₂O, AgNO₃, glucose, NaOH, NaBH₄, and FA were obtained from Sigma-Aldrich. HCl, HNO₃, and H₂SO₄ were obtained from Chempur (Warsaw, Poland). AA was purchased from Riedel-de Haën. Deuterium oxide 99.9% atom D with (or without) 0.75 st % trimethylsilylpropanoic acid-d₅ (TSP) (Sigma-Aldrich) was used without any further purification. All solutions were prepared with deionized water (18 mΩ cm) from the Elix Millipore or Arium Sartorius water purification system. The glassware and magnetic stirring bars for synthesis were carefully rinsed with aqua regia (3:1 HCl/HNO₃), thoroughly rinsed with deionized water, and dried to avoid any trace of impurities.

XPS substrates: quartz microscope slides, fused, were obtained from Alfa Aesar Johnson Matthey, GmbH. AFM substrates: V1-grade mica discs (Ted Pella, Inc.). The 5 mm NMR glass tubes were purchased from Wilmad. TEM grids Quantifoil R2/2, 300 Cu mesh were used.

**Apparatus, Procedures, and Data Analysis.** NMR spectra were measured on a 7 Tesla Bruker Avance spectrometer equipped with a broadband inverse Bruker probe head. All spectra were measured at 298 K (calibrated on methanol). Chemical shifts were measured in ppm using...
TSP as an internal reference. For typical NMR experiments, 25 mg of pectin was dissolved in 0.75 mL of D_2O in a standard 5 mm NMR sample tube.

Attempts to obtain HR scanning electron microscopy (SEM) images were not successful because of the charging effects of the material surface. Therefore, STEM imaging was performed with a Nova NanoSEM 450 instrument under a high vacuum (pressure 10^{-7} mbar). It was carried out on samples diluted 10,000 times and deposited on a TEM grid. Images were collected with a high acceleration voltage of 30 kV at a working distance optimized to 6.7 mm from the pole piece. Such dilution of the sample was necessary to avoid the destruction of the copper grid. STEM images were obtained using a bright-field contrast mode of the detector (two segments of the planar solid-state p–n junction) attached under the grid holder at a long scan acquisition time (20 μs) of typically 30 s per frame after choosing the inspection region. Images were analyzed with ImageJ software.

They were subjected to the “bandpass filter” procedure with an inner fast Fourier transform filter to remove dark patches much larger than the nanoparticles’ predicted size, and high and low spatial frequencies (blurring the image), as well as to reduce edge artifacts. Then, the images were processed further by the default thresholding method to obtain a binary image and the watershed segmentation approach to separate noncircular objects. Taking into account their size and circularity, nanoparticles were counted by using the “Analyze Particles” tool of ImageJ software. Based on the data obtained (NP areas) by expressing the nanoparticles as circles of an equivalent area, the equivalent diameters were calculated. Such a route was applied to over a dozen images to provide reliable data statistics.

AFM imaging was performed with a Multimode 8 microscope under the control of a Nanoscope V controller (Bruker). The samples were prepared by drop-casting 3.5 μg NMNPs/pectin solution on a mica surface and then drying in air. AFM substrates were mounted on metallic discs using an adhesive tape. Just before the NMNPs/pectin solution deposition, mica was cleaned in Milli-Q water and dried with an Ar stream. Then, the top layer of mica was peeled off using a scalpel to give a clean and atomically flat surface. To record the surface topography and adhesion force between the probe and the sample, PeakForce quantitative nanomechanical mapping (PFQNM) mode was utilized. In this mode, the AFM probe oscillated at a typical frequency of 2 kHz, and the individual force–distance (F–D) curves are collected for each contact of the probe with the sample. The adhesion force between the probe and the sample can be extracted from the collected F–D curves. All experiments were done under ambient conditions at room temperature. Standard ScanAsyst-Air Bruker probes were used. The radius of the probe was evaluated by scanning the TipCheck sample (RS-12M, Bruker) and by SEM imaging. The spring constant of cantilevers was determined using the thermal tuning method.

The AFM photodetector was calibrated on a freshly cleaved mica.

XPS was performed with a PHI 5000 VersaProbe—Scanning ESCA Microprobe (ULVAC-PHI, Japan/USA) instrument at the base pressure below 5 × 10^{-9} mbar. Samples were deposited on a quartz substrate (4.0 × 5.0 mm) and dried at room temperature. The XPS spectra were recorded using monochromatic Al Kα radiation (hν = 1486.6 eV) from an X-ray source operating at 100 μm spot size, 25 W, and 15 kV. Both survey and HR XPS spectra were collected with the analyzer pass energies of 117.4 and 23.5 eV and the energy step sizes of 0.4 and 0.1 eV, respectively. CasaXPS software (v. 2.3.18) was used to evaluate the XPS data. Shirley background subtraction and peak-fitting with Gaussian–Lorentzian-shaped profiles were performed. The binding energy (BE) scale was referenced to the C 1s peak with BE = 285 eV. For quantification, the PHI MultiPak sensitivity factors and the determining transmission function of the spectrometer were used.

UV–vis spectra were recorded with an Evolution 300 UV–vis spectrophotometer, Thermo Scientific.

IR spectra were recorded with a Nicolet iS50 FT-IR spectrophotometer from Thermo Scientific using the smart iTR ATR accessory with a diamond crystal. The penetration depth of the IR beam ranged from 1 to 10 μm, depending on the wavelength. The ATR correction was applied (using the OMNIC software by Thermo Scientific) to take into account the varied penetration depth. The spectral resolution was 4 cm\(^{-1}\), and typically, 256 scans were averaged for a single spectrum. The samples were cast directly on the top of the diamond crystal. The spectra were studied immediately after casting the sample on the crystal and after drying the sample by a cold air stream for 30 min.

Raman spectra were recorded with a DXR Raman spectrometer (Thermo Scientific). The spectra were recorded with dried samples of pectin or NMNPs/pectin. The instrument was operated using the 532 nm excitation line with 50×/NA 0.75 objective. Typically, the spectral resolution was 1 cm\(^{-1}\), the laser power was 1 mW, and the exposure time was 5 s. A total of 15 scans were averaged for a single spectrum. Both IR and Raman spectra were recorded with the dried samples of pectin or MeNPs/pectin material.

CV experiments were performed with an SP-300 potentiostat (BioLogic, USA) at room temperature, 22 ± 2 °C. Glassy carbon (GC) (discs of 0.07 or 0.007 cm\(^2\) (Mineral, Poland), carbon cloth (AvCarb, 1071 HCB, 1 cm\(^2\), or 0.125 cm\(^2\) carbon screen-printed electrodes (CSPE) (Metrohm/DropSens) served as working electrodes. Pt wire and Ag/AgCl served as the counter and reference electrodes, respectively. Current density at the GC electrode was calculated per projected area. Before measurements, the GC electrode was carefully polished with alumina slurry of 1, 0.3, and 0.05 μm grain size (Buhler) on a polishing cloth (Buhler). The remaining alumina particles were removed by polishing on a clean cloth wetted with ethanol. All electrodes were modified by the injection of gel samples from micropipettes for viscous liquids on the electrode surface. A 5 μL sample was deposited on a 0.007 cm\(^2\) GC disc electrode, whereas a 30 μL sample was deposited on a 0.07 cm\(^2\) GC disc electrode, carbon cloth, or screen-printed electrodes. The volume of the sample deposited on the GC disc was adjusted to cover the entire electrode surface. Afterward, the electrodes were dried in air. All electrochemical experiments were carried out, and solutions were purged with argon (99.99% by Multitax) before and during the experiments.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03167.

Details of NMR characterization together with the spectra; photos of NMeNPs/pectin samples; UV–vis
spectra; FTIR and Raman spectra of pectin samples with their description; XPS spectra of NMeNPs/pectin samples with detailed description; AFM of pectin and PdNPs/pectin film; And cyclic voltammograms of the NMeNPs/pectin film-modified electrodes in K3Fe(CN)6, AA, and H2O2 solution (PDF)

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Notes

The authors declare no competing financial interest.

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