FULL PAPER

Photochemical Switching of the Phase-Transition Temperatures of p-NIPAM-Pt Nanoparticles Thermosensitive Polymer Composites Associated with Electrodes: Functional Electrodes for Switchable Electrocatalysis**

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Abstract: The thermosensitive poly(N-isopropylacrylamide) (p-NIPAM) is electropolymerized onto Au surfaces. The incorporation of the photoisomerizable *N*-carboxyethyl nitrospiropyran compound into p-NIPAM allows the reversible photochemical control of the gel-to-solid phase-transition temperatures of the polymer. Whereas the gelto-solid phase-transition temperature of the nitrospiropyran-modified p-NIPAM is 33 ± 2 °C, the phase-transi-

tion temperature of the nitromerocyanine-functionalized p-NIPAM matrix corresponds to 38 ± 1 °C. Upon the incorporation of Pt nanoparticles (NPs) into the photochemically controlled p-NIPAM, a hybrid photoswitchable

Keywords: electrocatalysis • isomerization • phase transitions • Pt nanoparticles • thermosensitive polymers electrocatalytic matrix is formed. At a fixed temperature corresponding to $38 \,^{\circ}$ C, the effective electrocatalytic reduction of H₂O₂, or the oxidation of ascorbic acid, proceeded in the presence of the nitromerocyanine-functionalized p-NIPAM, yet these electrocatalytic transformations were inhibited in the presence of the nitrospiropyran-modified p-NIPAM.

Introduction

Signal-triggered phase transitions of polymers have attracted substantial research efforts aimed to develop polymer materials with new catalytic^[1] and electronic^[2] properties, and to design polymers for controlled drug delivery and release,^[3] separation matrices,^[4] and sensor systems.^[5] Electrical,^[6] magnetic,^[7] photoresponsive,^[8] and thermosensitive polymers^[9] have been synthesized, and applied for switchable bioelectrocatalysis,^[10] controlled surface wettability,^[11] surface patterning,^[12] and controlled release of substrates.^[13] Also, different chemical or pH stimuli have been used to induce phase transitions in polymer matrices.^[14] Among the different signal-responsive polymers, the thermosensitive poly(N-isopropylacrylamide) (p-NIPAM) have attracted substantial research efforts. This polymer undergoes a gelto-solid transition at 32 ± 1 °C, and this phenomenon has been theoretically addressed.^[15] Also, the effects of pH,^[16] added salt,^[17] organic solvents,^[18] and copolymer units^[19] on

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[**] p-NIPAM = poly(N-isopropylacrylamide)

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the phase-transition temperature have been examined. Different applications of the thermosensitive p-NIPAM matrices have been suggested, including controlled drug delivery,^[20] controlled biocatalysis,^[21] separation,^[22] biological applications, such as delivery of cells,^[23] culturing of cells,^[24] bacteria-induced changes of the polymer structures,^[25] and their use as nanothermometers.^[26] Also, the incorporation of coadditives into p-NIPAM has been found to affect the phase-transition temperatures of the polymer matrices. For example, the copolymerization of photoisomerizable units has been found to affect the transition temperature.^[27] Also, the binding of ions, such as Cu2+, Ag+, or Hg2+, to p-NIPAM affected differently the phase-transition temperature of the polymers, and different metal ion-p-NIPAM thermometers have been reported.^[28] Furthermore, it has been demonstrated that the binding of metal ions to p-NIPAM controls the charge transport through the matrices, and upon the reduction of the ions to metal nanoclusters, switchable electrocatalysis has been reported.^[28] Herein we report on the incorporation of nitrospiropyran photoisomerizable units into the p-NIPAM matrix. Nitrospiropyrans represent a broad class of photoisomerizable (photochromic) materials.^[29] Nitrospiropyran undergoes, upon UV irradiation, isomerization to the zwitterionic merocyanine derivative. The irradiation of the zwitterionic merocyanine state with visible light regenerates the nitrospiropyran state. We found that the different photoisomer states (that are noncovalently associated with the polymer) control the phasetransition temperatures of the polymer, and they enable the photoswitching of the phases at a fixed temperature. We then incorporated Pt nanoparticles (NPs) into the photoactive, thermosensitive polymer and demonstrated photo-



switchable electrocatalysis with the photoisomer–p-NIPAM– Pt NPs hybrid matrix.

Results and Discussion

p-NIPAM was electropolymerized onto Au electrodes under crosslinking conditions in the presence of *N*-isopropylacrylamide, with Na₂S₂O₈ as an initiator. The mechanism of the electrochemically induced polymerization of the *N*-isopropylacrylamide under these conditions has been previously discussed.^[30] The thickness of the p-NIPAM film was estimated by AFM measurements to be 10 ± 1 nm. *N*-carboxyethyl nitrospiropyran (**1a**) was incorporated into the p-NIPAM film by five "breathing-in" cycles, in which the photoisomerizable substrate was taken up by soaking the film in the **1a** solution at 22 °C (at this stage the polymer is in the gel state) and elevating the temperature to 40 °C to form the solid polymer state. By the repeated uptake of **1a** by p-NIPAM, the film was saturated with the photoisomer, Figure 1. The breathing-in mechanism involves the primary exposure of



Figure 1. A) Faradaic impedance spectra (at 20 °C, in the form of Nyquist plots) corresponding to $[Fe(CN)_6]^{3-/4-}$ (2 mM) and following the breathing-in process of nitrospiropyran photoisomerizable units into the p-NIPAM matrix. Number of breathing-in cycles: a) 0, b) 1, c) 2, d) 3, e) 4, f) 5. Inset: The dependence of the interfacial electron-transfer resistances on the number of breathing-in cycles. Data were recorded in an aqueous NaNO₃ solution (0.2 M, pH 9.5) in the frequency range corresponding to 10 kHz to 100 mHz, at a potential of E=0.185 V versus SCE and by using an alternate perturbation potential of $\Delta E=10$ mV. B) Mass changes, detected by QCM, corresponding to the breathing-in of nitrospiropyran photoisomerizable units into the p-NIPAM matrix.

the expanded polymer matrix to the molecular dopant that diffuses into the film, followed by the thermal collapse of the matrix to the shrunken solid state.

Although **1a** is noncovalently linked to the polymer, the crosslinking of the polymer and the entanglement of **1a** in the matrix lead to a stable composite without noticeable leakage of the photoisomer during a period of time corresponding to 24 h. The saturation of the film with **1a** was followed by Faradaic impedance spectroscopy, with $[Fe(CN)_6]^{3-/4-}$ as a redox couple (Figure 1A), and by quartz-crystal microbalance (QCM) (Figure 1B). Evidently, both the impedance and QCM measurements indicated that the saturation of the composite with **1a** occurred after five breathing-in cycles and corresponded to a maximal loading of 2 µg cm⁻². Impedance spectroscopy was also proven as an effective method to follow the thermal phase transitions of the p-NIPAM film, and these were characterized in the presence of photoisomers **1a** or **1b**.

Figure 2A and Figure 2B show the Nyquist plots corresponding to p-NIPAM films that include **1a** or **1b**, respectively, at variable temperatures. Figure 2C, curve (a), depicts the interfacial electron-transfer resistances of the p-NIPAM film that includes the nitrospiropyran photoisomer 1a, at variable temperatures. An increase in the interfacial electron resistance that reflects the gel-to-solid transition is observed at 33 ± 2 °C. Figure 2C, curve (b), depicts the interfacial electron-transfer resistances corresponding to the p-NIPAM film that includes the nitromerocyanine photoisomer state (1b) at variable temperatures. A clear shift in the phase-transition temperature is observed, and the gel-tosolid transition temperature is estimated to be 38 ± 1 °C. These results suggest that at 36°C, the 1a-containing p-NIPAM matrix exists mostly in the solid form, whereas the 1b-containing p-NIPAM is mostly in the gel form. These results indicate that the gel-to-solid phase transitions of the p-NIPAM matrix can be photomodulated by the photoisomer state of the additive. The slightly higher gel-to-solid phase transition of the 1b-p-NIPAM matrix as compared to the 1a-p-NIPAM system may be attributed to H bonds or dipole interactions between 1b and the acrylamide groups of p-NIPAM that perturb the temperature-induced collapse of the amide groups. That is, the normal collapse of the p-NIPAM gel to the solid state involves the elimination of water from the matrix and the formation of inter H bonds among the acrylamide units.

In the presence of the hydrophilic merocyanine dopant, the confinement of the water in the matrix is enhanced, thus a higher temperature to induce the collapse of the film is required. Indeed, Figure 2D shows that the interfacial electron-transfer resistance of p-NIPAM can be cycled, at 36 °C, between high and low values upon the reversible photoisomerization of the additive between the states **1a** and **1b**, respectively. The increase in the interfacial electron-transfer resistances of the p-NIPAM-modified electrode upon the gel-to-solid phase transition may be explained by the relative permeabilities of the $[Fe(CN)_6]^{3-/4-}$ redox couple through the polymer film. Whereas the redox couple pene-



Figure 2. A) Faradaic impedance spectra corresponding to $[Fe(CN)_6]^{3-/4-}$ (2 mM) on the **1a**–p-NIPAM-modified electrode at variable temperatures: a) 20°C, b) 26°C, c) 28°C, d) 30°C, e) 32°C, f) 34°C, g) 36°C, and h) 40°C. B) Faradaic impedance spectra under the same conditions as in (A) for the **1b**–p-NIPAM-modified electrode, at: a) 20°C, b) 22°C, c) 24°C, d) 26°C, e) 28°C, f) 34°C, g) 36°C, h) 38°C, i) 40°C, j) 44°C. C) Interfacial electron-transfer resistances measured at different temperatures for: a) the **1a**–p-NIPAM-modified electrode and b) the **1b**–p-NIPAM-modified electrode. D) Cyclic changes in the interfacial electron-transfer resistances upon the photochemically induced transition between: a) the **1a**–p-NIPAM-modified electrode, and b) the **1b**–p-NIPAM-modified electrode at T=36°C. Data were recorded in an aqueous NaNO₃ solution (0.2 M, pH 9.5) containing [Fe(CN)₆]^{3-/4-} (2 mM).

trates the gel form of the film, the solid form of the p-NIPAM film blocks the penetration of the labels, thus increasing the interfacial electron-transfer resistances. Also, control experiments revealed that irradiation of a p-NIPAM-modified electrode at either $\lambda = 365$ nm or at $\lambda >$ 475 nm, in the absence of **1a**, did not lead to any differences in the gel-to-solid phase transitions (phase-transition temperature, 32 ± 1 °C). These results indicate that the photostimulated control of the phase-transition temperatures of p-NIPAM, indeed, originates from the photoisomerizable additive.

Realizing that the photoisomerizable component embedded in the p-NIPAM matrix photostimulates a change in the transition temperature of the polymer, we implemented the system to develop photoswitchable electrocatalytic transformations. In contrast to previous studies that photoswitched an electrocatalytic process by photostimulated binding or dissociation of metallic nanoparticles to, or from, the electrode surface,^[31] the present approach attempts to use the different phases of the polymer film to switch the electrocatalytic functions of the modified electrode. Toward this goal, we used the breathing-in process to incorporate Pt NPs into the p-NIPAM film. Accordingly, we have applied five breathing-in cycles to saturate the film with the Pt NPs, while monitoring the gravimetric loading of the film with the NPs by using QCM (see the Supporting Information,

FULL PAPER

Figure S1). After five cycles, the film was saturated with the Pt NPs, and the loading corresponded to about $2.5 \,\mu g \, cm^{-2}$. The gel-to-solid transition of the p-NIPAM containing the photoisomerizable units and the Pt NPs is depicted in Figure 3A. It should be noted that the phase-transition temperature of the p-NIPAM matrix that included the Pt NPs, but lacked the photoisomerizable component, was not affected upon illumination at $\lambda = 365$ nm or $\lambda > 475$ nm. The photoactive p-NIPAM-Pt NPs matrix was then applied to photostimulate the electrocatalytic reduction of H_2O_2 or the electrocatalytic oxiof ascorbic dation acid (Scheme 1).

Figure 3B depicts the linearsweep voltammograms corresponding to the electrocatalytic reduction of H_2O_2 by the **1a**-p-NIPAM-Pt NPs matrix, curve (a), and by the **1b**-p-NIPAM-Pt NPs composite, curve (b).



Scheme 1. Photostimulated electrocatalytic reduction of H_2O_2 or oxidation of ascorbic acid on a photoisomer–p-NIPAM–Pt NPs matrix.

Evidently, the electrocatalytic current is up to 70% higher in the presence of the **1b**–p-NIPAM–Pt NPs. Because the **1b**–p-NIPAM–Pt NPs exists (at 38°C) mainly in the gel state, whereas at the same temperature, the **1a**–p-NIPAM– Pt NPs composite exists mainly in the solid phase, the higher currents in the **1b**–p-NIPAM–Pt NPs composite are attributed to the enhanced permeability of the H₂O₂ substrate to the Pt NPs sites in the gel phase of the polymer. By the cyclic photoisomerization (at 38°C) between the **1a**–p-

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Figure 3. A) Interfacial electron-transfer resistances measured at different temperatures for a) the **1a**-p-NIPAM-Pt NPs-modified electrode and b) the **1b**-p-NIPAM-Pt NPs-modified electrode. Data were recorded in an aqueous NaNO₃ solution (0.2 m, pH 9.5) containing $[Fe(CN)_6]^{3-/4-}$ (2 mM). B) Linear sweep voltammograms corresponding to the electrocatalytic H₂O₂ reduction on a) the **1a**-p-NIPAM-Pt NPs-modified electrode and b) the **1b**-p-NIPAM-Pt NPs-modified electrode lack-ing the photoisomerizable units. C) Similar measurements as in (B) for the electrocatalytic oxidation of ascorbic acid. Measurements were recorded in an aqueous NaNO₃ solution (0.2 m, pH 9.5) that included H₂O₂ (36 mM) or ascorbic acid (2.5 mM) at T=38 °C. Scan rate: 10 mV s⁻¹.

NIPAM-Pt NPs and the 1b-p-NIPAM-Pt NPs composites, the electrocatalytic cathodic currents are reversibly switched between low and high values, respectively (Figure 3B, inset, curve (I)). For comparison, the electrocatalytic cathodic currents corresponding to the reduction of H₂O₂ by the p-NIPAM-Pt NPs composite that lacks the photoisomerizable component, under illumination at $\lambda = 365$ nm or at $\lambda >$ 475 nm, are depicted in Figure 3B, inset, curve (II). Under these conditions, lower cathodic currents of a comparably constant value of about 2.5 µA are observed, irrespective of the wavelength of the irradiation. The nonswitchable current value implies that the photoswitchable electrocatalysis originates from the photoisomerization of the coadditive in the 1a and 1b states. In a further control experiment, we probed the possibility that the photoisomers 1a/1b affect the catalytic functions of the Pt NPs. Accordingly, Pt NPs were functionalized with a monolayer of 1-mercaptobutyl nitrospiropyran. The resulting 2a-capped Pt NPs were immobilized on a benzene-dithiol-monolayer-functionalized Au electrode. The electrocatalytic reduction of H_2O_2 by the nitrospiropyran- and the nitromerocyanine-functionalized Pt NPs-modified electrode was then examined (Figure S2 in the Supporting Information). We found that the electrocatalytic activities of the Pt NPs are identical in the two photoisomer states, indicating that the photoisomer states do not affect the catalytic functions of the Pt NPs. These control experiments imply that the photoswitchable electrocatalytic activities of the 1a/1b-p-NIPAM-Pt NPs composite originate from the effect of the photoisomerizable components on the polymer phase, rather than an effect on the catalytic functions of the Pt NPs.

Similar photoswitchable electrocatalytic functions of the photoisomerizable p-NIPAM-Pt NPs were observed upon the electrochemical oxidation of ascorbic acid, Figure 3C. The linear-sweep voltammogram corresponding to the oxidation of ascorbate by the 1a-p-NIPAM-Pt NPs (at 38°) is shown in Figure 3C, curve (a), whereas the voltammogram corresponding to the oxidation of the substrate by the 1b-p-NIPAM-Pt NPs composite (at 38°) is shown in Figure 3C, curve (b). Clearly, the electrocatalyzed oxidation of ascorbic acid by the 1b-p-NIPAM-Pt NPs composite yields about 2.5-fold higher electrocatalytic anodic currents, indicating a superior electrocatalytic function of the 1b-p-NIPAM-Pt NPs composite. Also, the electrocatalytic functions of the photoisomerizable composite are photoswitchable, and upon the photochemical cycling of the polymer between the 1a and 1b-p-NIPAM-Pt NPs states, the electrocatalytic functions of the system are switched between low and high amperometric responses, respectively (Figure 3C, inset, curve (I)). In a control experiment, the photochemical irradiation, at $\lambda = 365$ nm or at $\lambda > 475$ nm, of the p-NIPAM-Pt NPs hybrid that lacked the photoisomerizable units, did not lead to photoswitchable electrocatalytic functions, and resulted (at 38°C) only in low anodic currents (Figure 3C, inset, curve (II)). These low current responses are attributed to the fact that the p-NIPAM-Pt NPs composite reveals, in the absence of the photoisomerizable units, a phase-transition

11240 .

FULL PAPER

temperature corresponding to 32 ± 1 °C. Thus, at 38 °C, the polymer exists mostly in the solid phase; this prohibits the accessibility of ascorbic acid to the Pt NPs catalytic sites. Furthermore, the photoswitchable catalytic functions of the 1a/1b-p-NIPAM-Pt NPs composite are attributed to the effect of the photoisomers on the transition temperatures of the p-NIPAM hybrids. The nitrospiropyran-p-NIPAM-Pt NPs composite exists (at 38°C) mostly in the solid phase, leading to an inefficient electrocatalytic oxidation of ascorbic acid. On the contrary, the merocyanine-p-NIPAM-Pt NPs hybrid exists (at 38°C) mostly in the gel phase, allowing the easy permeation of the ascorbic acid molecules into the matrix and effective oxidation at the catalytic sites. As before, the electrocatalytic oxidation of ascorbic acid by a monolayer of Pt NPs functionalized with the nitrospiropyran or nitromerocyanine components, yet lacking the polymer matrix, revealed no noticeable differences. These results indicate that the electrocatalyzed oxidation of ascorbic acid by the Pt NPs is not affected by the different photoisomer states, and demonstrate that the photoswitchable electrocatalytic functions of the hybrid polymer matrices originate from the effect of the photoisomerizable units on the phasetransition temperatures of the polymer.

Conclusion

In conclusion, the present study has demonstrated that the incorporation of a photoisomerizable unit into the thermosensitive p-NIPAM polymer matrix allows photochemical control of the gel/solid phase transitions of the polymer by means of the photoisomer states of the additive substrate. This allowed the selection of a specific temperature (36 °C), at which the p-NIPAM existed in the gel phase (in the presence of the nitromerocyanine (1b) isomer), which could be photochemically transformed into the solid phase (the nitrospiropyran (1a) isomer). This photoswitchable control of the phase of the thermosensitive p-NIPAM matrices allowed the design of polymer-NPs composites with inherent photoswitchable electrocatalytic properties. The incorporation of Pt NPs into the photoisomerizable p-NIPAM matrix allowed the photoswitchable electrocatalyzed reduction of H_2O_2 or the electrocatalyzed oxidation of ascorbic acid by the lightinduced controlled permeability of the substrates to the Pt NP catalytic sites, and through the transformations between gel and solid phases of the polymer.

Experimental Section

Synthesis of 1a: The material was prepared by a slight modification of a previously reported procedure.^[32] 2,3,3-trimethylindoline (6.4 mL, 40 mmol) and iodopropionic acid (7.8 g, 39 mmol) were heated in a flask for 3 h. The resulting red solid was washed with butanone to yield 1-(β -carboxyethyl)-2,3,3-trimethylindolynium iodide (9 g). The product (2 g, 5.7 mmol) was dissolved in boiling butanone (5 mL) in the presence of piperidine (0.5 mL). The solution was then reacted with a solution of 2-hydroxyl-5-nitrobenzaldehyde (1 g, 6 mmol) in butanone (2 mL). The re-

sulting mixture was heated at 60 °C for 10 min and allowed to react at room temperature overnight. The resulting precipitate was filtered and washed with butanone to yield a yellow powder (1.2 g). ¹H NMR (CDCl₃): δ =1.14 (s, 3H), 1.28 (s, 3H), 2.71 (t, 2H), 3.65 (t, 2H), 5.85 (d, 1H), 5.91 (d, 1H), 6.62–7.18 (m, 5H), 8.05 (m, 2H).

Pt NPs synthesis: Citrate-capped Pt NPs were prepared by heating a PtCl₆⁻ solution (100 mL, 1 mM) to reflux, followed by the addition of an aqueous sodium citrate solution (10 mL, 38.8 mM). After 10 min of boiling, the solution turned from clear to black colored, after which heating was turned off and the solution was stirred for additionally 10 min. Finally, the solution was allowed to cool to room temperature, filtered through a 0.2 µm cellulose acetate filter (Schleicher and Schuell, Keene, NH), and rinsed two times through a 100000 MW cutoff Centricon tube (Millipore Inc., Billerica, MA) with water. For the preparation of mercaptobutyl nitrospiropyran (2a)-capped Pt NPs, N-4-mercaptobutyl nitrospiropyran (1 mm, 1 mL, dissolved in a 1:4 mixture of DMSO:H₂O) was added into the citrate-capped Pt-NPs solution (9 mL). The mixture was kept in the dark for 4 h, and the resulting 2a-capped Pt NPs precipitated. Following a centrifugation at 5000 rpm for 15 min, the precipitated Pt NPs were purified by repeated resuspension and centrifugation in a NaNO3 solution (0.2м).

Modification of the electrodes: Electropolymerization of the p-NIPAM film was performed in an aqueous solution, purged by nitrogen for 30 min, that contained N-isopropylacrylamide (1.0 M), N,N'-methylenebisacrylamide (40 mm), NaNO₃ (0.2 m), and Na₂S₂O₈ (0.01 m), by using 60 repetitive cyclic voltammetry scans, ranging between -0.35 and -1.35 V versus SCE, at a scan rate of 100 mVs⁻¹. Following the electropolymerization process, the electrodes were washed with distilled water to remove residues of the monomers. The breathing-in of N-carboxyethyl nitrospiropyran 1a was performed by soaking the p-NIPAM-modified electrodes in an aqueous solution that contained 1a (2 mm) for 2 h. The breathing-in of Pt NPs was similarly performed. In a control experiment, a Au slide was immersed for 4 h in an ethanolic solution of benzene dithiol (2 mm) and the modified electrode was reacted with the 2a-capped Pt NPs to form a monolayer of the photoisomerizable particles on the Au surface. Instrumentation: Nanopure (Barnstead) ultrapure water was used in the preparation of the different solutions. Au-coated glass plates (Evaporated Coatings, PA, USA) were used as working electrodes. Prior to modification, the Au surface was flame-annealed for 5 min in an n-butane flame and allowed to cool down for 10 min under a stream of N2. Linear-sweep voltammetry experiments were carried out with a PC-controlled (Autolab GPES software) electrochemical analyzer potentiostat/galvanostat (µAutolab, type III). A graphite rod (d=5 mm) was used as a counter electrode, and the reference was a saturated calomel electrode (SCE). A HETO HMT 200 thermostated bath (±0.2 °C), in which the electrochemical cell was installed, was used throughout the experiments. Faradaic impedance measurements were recorded at 0.185 V versus SCE in the frequency range of 10 kHz to 100 mHz with an alternating voltage of ± 10 mV. Prior to each measurement, the cell temperature was equilibrated for 15 min. QCM measurements were performed with a home-built instrument linked to a frequency analyzer (Fluke) by using Au-quartz crystals (AT-cut 10 MHz). Photochemical transformations were carried out with a UV lamp (Upland, USA, P=8 W) at $\lambda = 365$ nm for 25 min and a Xe lamp (Oriel Instruments, USA, model 6255OF, 150 W) in an Oriel Research Housing (model 66002 with a power supply Oriel 68700) at $\lambda >$ 475 nm, for 25 min.

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CHEMISTRY

A EUROPEAN JOURNAL

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11242 -