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Smart polyaniline nanoparticles with thermal and photothermal sensitivity

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Abstract

Conductive polyaniline nanoparticles (PANI NPs) are synthesized by oxidation of aniline with persulfate in acid media, in the presence of polymeric stabilizers: polyvinilpyrrolidone (PVP), poly(N-isopropylacrylamide) (PNIPAM), and hydroxylpropylcellulose (HPC). It is observed that the size of the nanoparticles obtained depends on the polymeric stabilizer used, suggesting a mechanism where the aggregation of polyaniline molecules is arrested by adsorption of the polymeric stabilizer. Indeed, polymerization in the presence of a mixture of two polymers having different stabilizing capacity (PVP and PNIPAM) allows tuning of the size of the nanoparticles. Stabilization with biocompatible PVP, HPC and PNIPAM allows use of the nanoparticle dispersions in biological applications. The nanoparticles stabilized by thermosensitive polymers (PNIPAM and HPC) aggregate when the temperature exceeds the phase transition (coil to globule) temperature of each stabilizer ($T_{pt} = 32$ °C for PNIPAM or $T_{pt} = 42$ °C for HPC). This result suggests that an extended coil form of the polymeric stabilizer is necessary to avoid aggregation. The dispersions are reversibly restored when the temperature is lowered below Tpt. In that way, the effect could be used to separate the nanoparticles from soluble contaminants. On the other hand, the PANI NPs stabilized with PVP are unaffected by the temperature change. UV-visible spectroscopy measurements show that the nanoparticle dispersion changes their spectra with the pH of the external solution, suggesting that small molecules can easily penetrate the stabilizer shell. Near infrared radiation is absorbed by PANI NPs causing an increase of their temperature which induces the collapse of the thermosensitive polymer shell and aggregation of the NPs. The effect reveals that it is possible to locally heat the nanoparticles, a phenomenon that can be used to destroy tumor cells in cancer therapy or to dissolve protein aggregates of neurodegenerative diseases (e.g. Alzheimer). Moreover, the long range control of aggregation can be used to modulate the nanoparticle residence inside biological tissues.

S Online supplementary data available from stacks.iop.org/NANO/25/495602/mmedia

Keywords: conductive polyaniline nanoparticles, thermosensitive polymers, near infrared radiation, photothermal efect, aggregation

(Some figures may appear in colour only in the online journal)

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1. Introduction

Polyaniline is the most widely studied conducting polymer [1]. It is an electro-active polymer of great interest thanks to its outstanding physical and chemical properties which make it suitable for various applications in optics, bioelectronics, biosensors, diagnostics and therapeutic devices. Unfortunately, PANI as other conducting polymers, are insoluble in most common solvents and, thus, very difficult to process [2].

Polyaniline is only soluble in few solvents (N-methylpyrrolidone, sulfuric or formic acid). To overcome such problems is possible the chemical functionalization of substitute groups on which are linked to the polyaniline backbone [3] within loss the conductive properties, or through the preparation of stable dispersion of polymer nanoparticles which can be coated with different substrate [4, 5].

Polyaniline nanoparticles (PANI NPs) have been taken advantage for different applications, such as photothermal tumor therapy [6, 7] electrorheological fluids [8], gas sensors [9], electrochemical sensors [10], nanocomposite actuators [11], etc PANI NPs can be produced by different methods [12]. Usually, the particles are maintained dispersed using a polymeric stabilizer adsorbed onto the nanoparticle surface. The stabilizer is soluble in the dispersing solvent and the polymer chains are extended in it. The volume occupied by the chains in solution prevents that the nanoparticles approaching each other, and the attractive dispersion interactions are too weak to induce particle aggregation. If the stabilizer polymer chains responsive to change of external medium, then they could change from coil (extended) to globule (folded) state, the stabilizing effect fails to act, and the particles are aggregated. That phase transition could be induced by change of solvent properties or temperature. One of thermosensitive polymers used as stabilizer is poly(N-isopropylacrylamide) (PNIPAM) which has a coil to globule transition at ca. 32 °C [13, 14, 15]. Cruz-Silva *et al* synthesized deprotonated PANI nanoparticles in neutral media using enzymatic oxidation of aniline and PNIPAM as stabilizer [16]. Below 32 °C, the polyaniline nanoparticles dispersion is stable while above the transition, the nanoparticles are aggregated. The enzymatic method requires special synthetic conditions and the established method for aniline polymerization is the chemical oxidative polymerization in acid media [17]. On the other hand, Stejskal and coworkers described a simpler method of PANI NPs synthesis, using ammonium persulfate as oxidant and hydrophilic polymers (e.g. polyvinylpyrrolidone, PVP) as stabilizer [18, 19, 20]. The method produced nanoparticles in its conductive protonated state.

Additionally, PANI could be applied in biologic systems because it has a broad absorption band with a maximum at ca. 800 nm in the NIR range. This characteristic coincides with the low light absorption capacity of living tissue between 700 and 1200 nm. Therefore, light in this region could penetrate several centimeters inside tissue and to be absorbed by a suitable susceptor, such as polyaniline.

In this work, we present the synthesis of PANI NPs produced by aniline oxidative polymerization with ammonium persulfate in the presence of a stabilizer. Polyvinylpyrrolidone (PVP), Poly-N-isopropylacrylamide (PNIPAM) and Hydroxypropylcellulose (HPC) are used as stabilizers. Further, HPC [21], and PNIPAM [22] are biocompatible and thermoresponsive. The smart nanoparticles based on those polymeric stabilizers could have potential biomedical applications such as drug delivery and hyperthermia for cancer treatment. While PNIPAM has a globule-coil transition at ca. 32 °C, HPC has it at 42 °C [23]. Additionally, we show that it is possible to tune the size and thermosensitivity of the nanoparticles by synthesizing the particles in the presence of a mixture of thermosensitive (PNIPAM) and non thermosensitive (PVP) polymeric stabilizers. Combining the NIR absorption of PANI and the thermosensitivity of the polymeric stabilizers, it is possible to induce the aggregation of PANI NPs dispersions using NIR light.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP, (Fluka, type K90, Mw = 360 000), Hydroxypropylcellulose (HPC, Aldrich Mw ~ 370 000), Poly(N-isopropyl acrylamide) (SP2, Mw ~ 300 000), are used without further purification. All other reagents are of analytical quality.

2.2. Synthesis of PANI NPs

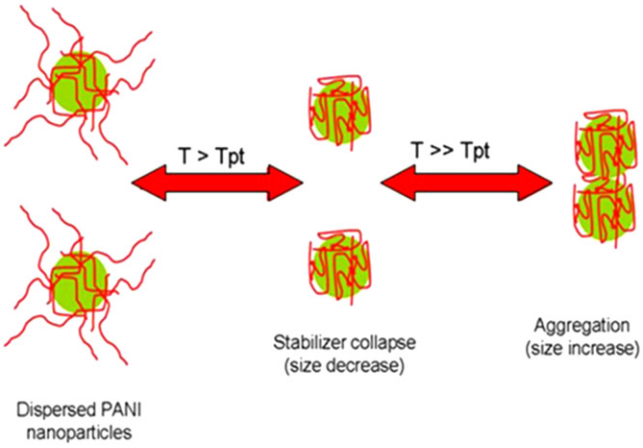
The PANI nanoparticles are produced by precipitation polymerization using hydrophilic polymers as stabilizers. A 0.2 M solution of aniline hydrochloride (Aldrich) was oxidized with 0.25 M ammonium peroxydisulfate (APS, Cicarelli) in the presence of a stabilizer, 2 w w^{-1}% (PVP, HPC or PNIPAM). The polymerization of aniline was started at 20 °C by adding an aqueous solution of APS. The mixture was briefly stirred and left at rest to polymerize for 30 min. In the case of HPC, the polymerization was carried out at 0 °C, to maintain the stability of the polymer.

2.3. Characterization of dispersion

The colloidal dispersion of nanoparticles was diluted 60 times with 1 M HCl, and the particle diameter and shape size were determined by Dynamic Light Scattering (DLS). Measurements were performed in a Malvern 4700 DLS. The measurements were made at scattering angle of 90° at different temperatures.

PANI NPs samples were imaged with a high-resolution scanning electron microscope (SEM) equipped with a field emission gun (FEI) Strata DB 235 at 5 kV acceleration voltages.

The stability of the dispersion was studied at different temperatures and followed by photography. Next, thermal effect on NPs dispersion with different stabilizers was performed by heating in water baths. Turbidimetric technique is used for detection of aggregation.



Scheme 1. Effect of temperature increase on aggregation of thermosensitive NPs.

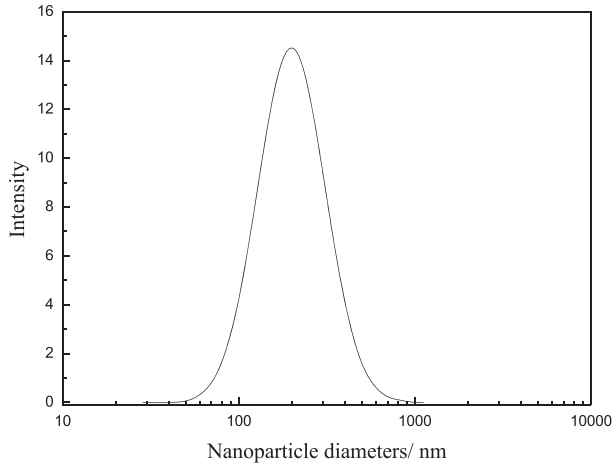
Table 1. Size of PANI NPs stabilized by different polymeric stabilizers at 25 °C.

Polymeric stabilizer	Dh/nm
PVP	220 (+/−10)
PNIPAM	460 (+/−10)
HPC	350 (+/−10)

stabilizer, monomodal dispersions so were observed (supporting information).

The mean hydrodynamic diameters (Dh) of the different PANI nanoparticles, determined by DLS, are shown in table 1.

Since the parameters controlling the kinetics of polyaniline polymerization [24], are the same for all the reactions, it is likely that the variation on the mean size of NPS depends



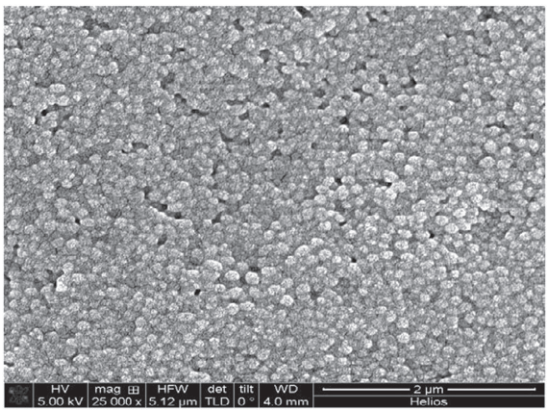


Figure 1. Dynamic light scattering plot of a PANI NPs dispersion using PVP as polymeric stabilizer (left) and SEM micrographs of PANI NPs deposited on Si.

The optical properties of the dispersion were studied at pH 1 and 10 by UV–vis spectroscopy. A Hewlett-Packard-8453 diode array UV-visible spectrophotometer and quartz cells (Helma) were used for the measurement.

Finally, to test the photothermally induced effect, the PANI NPs were irradiated by a near infrared laser (scheme 1. Supporting information) at 780 nm and 100 mW power, while the temperature of system is measured with thermocouple.

3. Results and discussion

3.1. Morphology of PANI NPs synthesized

Polyaniline nanoparticle dispersions were produced by aniline oxidative polymerization with ammonium persulfate in the presence of different stabilizers. The figure 1 shows the plot of DLS and image of scanning electron micrographs for PANI NPs stabilized with PVP. Monomodal dispersion and spherical particles were observed. To PNIPAM and HPC used as

on the stabilizer nature. The polyaniline chains aggregate in solution to form particles and the polymeric stabilizer adsorb on the particle surface. Due to the hydrophilic nature of the stabilizer the shell of extended polymer around the particle excludes the shell of other particles, inhibiting aggregation. In that way, stable dispersions of polyaniline nanoparticles can be prepared. In the absence of the polymeric stabilizer, the nanoparticles aggregate into micrometric sized particles which precipitate from the solution. As it can be seen, each polymeric stabilizer has different interaction with polyaniline and/or different unfolding into the solution. That effect explains the different mean sizes of nanoparticles are described in table 1.

The fact that the same procedure produces smaller nanoparticle sizes for PVP than PNIPAM suggests that the former is more effective as polymeric stabilizer. It is known that the pyrrolidone group can strongly interact with polyaniline chains by hydrogen bonding [25]. The PVP monomer units could have a behavior similar to N-methylpyrrolidone, with strong adsorption, acting as good polymer stabilizer of PANI nanoparticles [26].

Table 2. Hydrodynamic diameter (Dh) determinate by DLS for PANI NPs stabilized by PVP, PNIPAM and both in different concentrations ratio at 25 °C.

Stabilizer	Dh/nm
100% PVP	220 (+/−10)
75% PVP/25%PNIPAM	291 (+/−10)
50% PVP/50%PNIPAM	371 (+/−10)
25% PVP/75%PNIPAM	447 (+/−10)
100% PNIPAM	462 (+/−10)

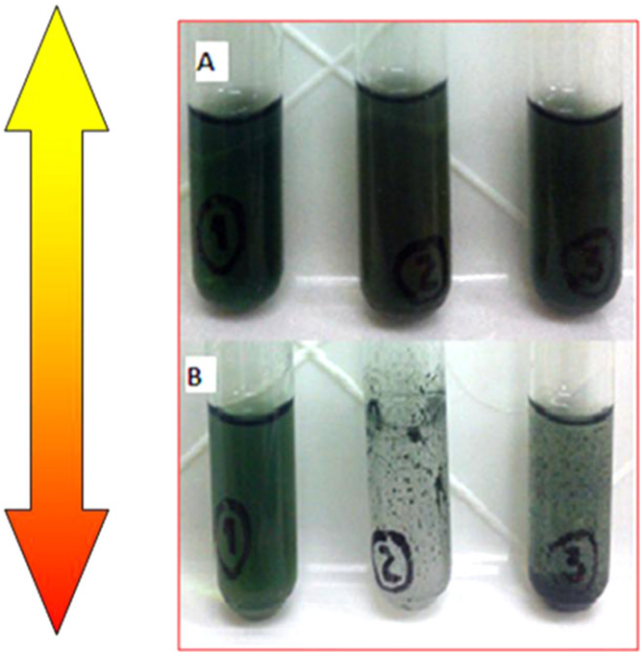


Figure 2. PANI nanoparticles dispersions with different polymeric stabilizers: PVP (left), PNIPAM (center) and HPC (right) photographed at (A) 25 °C and (B) 50 °C.

3.2. Mixed stabilizer effect on the size of PANI NPs

Since the stabilizing effect seems to occur by adsorption of the hydrophilic polymer on the growing nanoparticle, it should be possible to use mixtures of two stabilizers to prepare nanoparticle dispersions. PANI NPs were synthesized with different ratios of PNIPAM and PVP stabilizers, at the same total concentration. The mean sizes of the PANI NPs, measured by DLS, are described in table 2. It can be seen that the hydrodynamic diameter of NPs increase with the relative amount of PNIPAM stabilizer in the mixture.

The results suggest that the polymeric stabilizer's nature determines the final NPs size. In that way, it is possible to adjust the size of the PANI NPs by changing the ratio of PVP/PNIPAM present during polymerization.

3.3. Effect of temperature on PANI NPs dispersions

The thermal stability of PANI NPs dispersions was qualitatively studied monitoring the appearance of the dispersions at 25 °C and 50 °C by photography. In figure 2, it can be seen the PANI NPs dispersions with different stabilizers at 25 °C

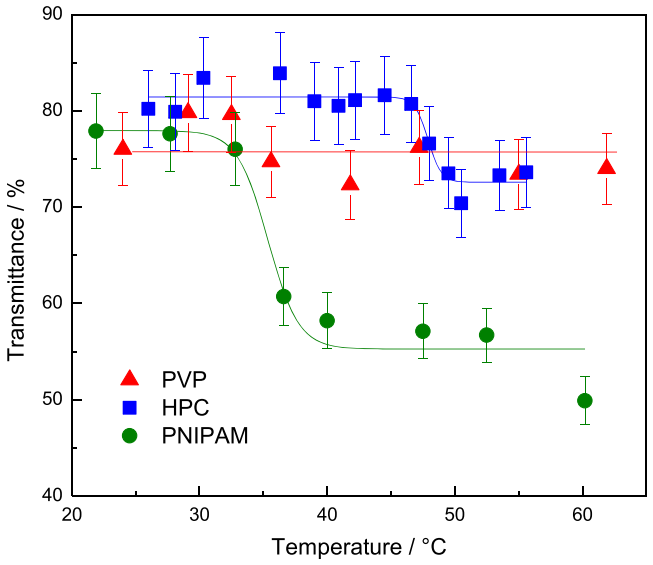


Figure 3. Transmittance versus temperature of system for PANI NPs dispersion with different stabilizer.

(A) and 50 °C (B). In the left tube, NPs stabilized with PVP do not show a noticeable change with temperature. While, the dispersions with PNIPAM (center) and HPC (right) show aggregation when the temperature is increased to 50 °C, which is above the phase transition of both stabilizers used (PNIPAM (32 °C) and HPC (42 °C)).

It is noteworthy that the aggregation is completely reversible when the dispersion is restored by cooling the solution at temperature below 20 °C with mild agitation. This process was repeated several times without observing apparent changes in the stability of the dispersion.

A quantitative measurement of the effect is performed using turbidimetry. The light transmission of PANI NPs dispersions, with different polymeric stabilizers, was measured at varying temperatures. In figure 3 shows the transmission as a function of temperature. As it can be seen, transmittance decreases suddenly at temperatures above 32 °C (PANI-PNIPAM) and 45 °C (PANI-HPC). In the case of PNIPAM the transmittance decreases ca. 45% upon heating above 32 °C, while for HPC decreases ca. 20%. In both cases, the temperature effect is observed near the phase transition temperature of the thermosensitive polymer. On the other hand, no change of transmission is observed with PANI NPS stabilized with PVP. For that, PANI NPs sensitive to variation of temperature can be obtained when thermosensitive stabilizer are used.

Another way to study the effect of temperature on nanoparticle dispersion involves determining the mean size of the PANI NPs, using dynamic light scattering. The nanoparticle dispersions are stabilized with a thermosensitive polymer, at temperatures below and above the phase transition. For thermosensitive NPs, PANI NPs stabilized with PNIPAM, it can be seen in figure 4 the variation of hydrodynamic diameter of NPs (Dh) in function of temperature. The diameter decreases from 460 nm to 350 nm when the

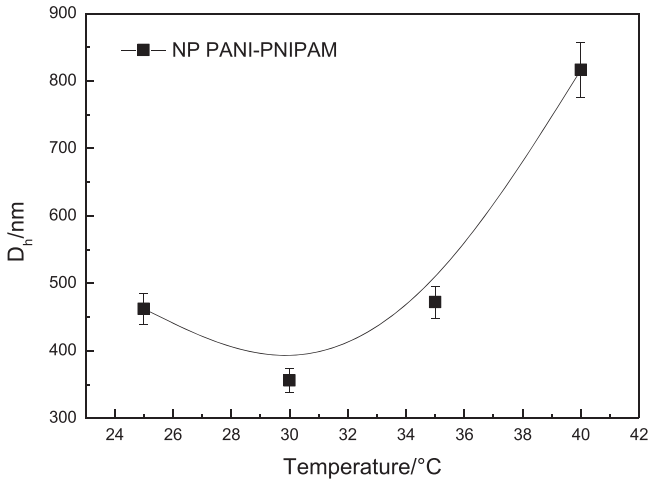


Figure 4. Effect of temperature on the hydrodynamic diameter of PANI nanoparticles stabilized with a thermoresponsive polymer (PNIPAM), measured by DLS.

temperature change from 25 to 30 °C, and above the phase transition (32 °C) the size increase again until 800 nm.

This result confirms the behavior observed qualitatively in figure 2 and figure 3 and the agglomeration process can be described according to scheme 1. The formations of colloidal particles are produced by the polymerization of aniline in a medium containing the stabilizer, a suitable water-soluble polymer. It has been proposed that an aniline oligomer adsorbs at the stabilizer chains and produces a PANI nucleus. By the auto-acceleration mechanism, the formation of new oligomers and polymerization proceeds in the close vicinity, and the PANI particle grows. Occasionally, other stabilizer chains become entrapped in the growing particle, producing a particle shell that prevents the particles from aggregating [20].

If a polymer is capable of passing through a reversible phase transition within a certain environmental conditions, it is called a smart polymer or a stimuli-responsive macromolecule (artificial or natural). The transitions are triggered by small shifts in the local environment, are fast and reversible, i.e., the system returns to its initial state when the trigger is removed [27]. Thermosensitive polymers chains used in this work are hydrated and have an expanded structure, at room temperature. When the temperature of environment exceeds the phase transitions temperature, the alkyl groups, as isopropyl in case of PNIPAM, tend to expel the water due to increased motion; and the polymer chains adopt a globular structure. This process induces the collapse of polymeric chains stabilizers and subsequent aggregation and precipitation of PANI NPs.

PANI NPs dispersion stabilized by smart polymers observed by DLS indicates that PNIPAM and HPC act as stabilizer and not lose the thermosensitivity. While system temperature increase, the size of each isolated particle decreases due to the adsorbed polymer going from coil to globule. At higher temperature, the collapse of the polymeric stabilizer decreases its ability to inhibit aggregation and the nanoparticles get closer together. The dispersion forces between particles induce the formation of larger aggregates.

3.4. Electronic properties of PANI NPs analyzed by UV–visible Spectroscopy

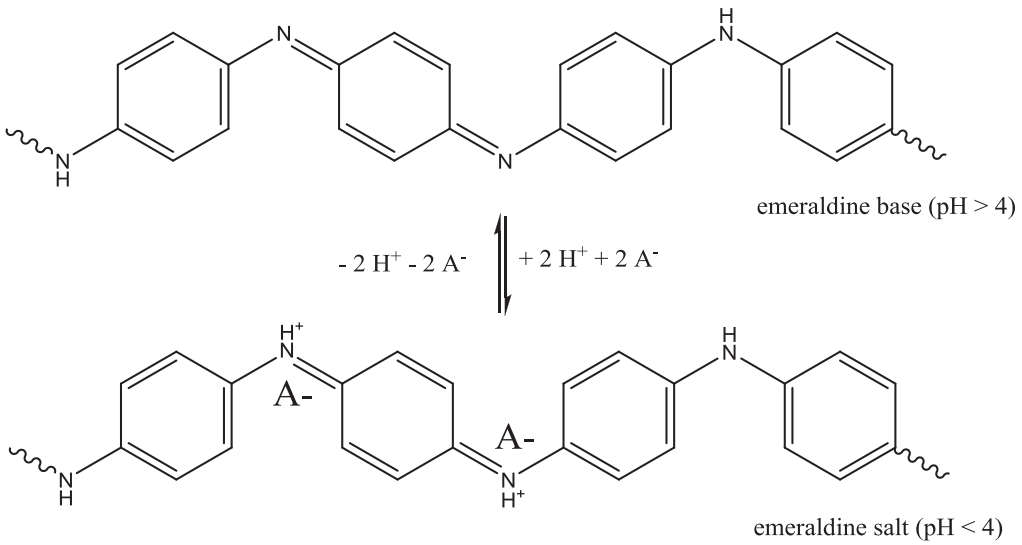
Polyaniline (emeraldine form) presents two protonation states: emeraldine salt and emeraldine base, as it is shown in the scheme 2.

These states can be interconverted between them by means of protonation/deprotonation reactions and we can study the interconversion using ultraviolet/visible (UV-visible) optical absorption spectroscopy [28]. The emeraldine base form (blue) can be easily doped with acid to obtain protonated emeraldine (green) which is electrically conductive. The method presented here should produce nanoparticles in emeraldine oxidized and protonated conductive state (green). To test that, the UV-visible spectra at different pH were recorded for PANI stabilized with PVP. In figure 5, it can be observed the spectral changes and color of solutions, with pH variation which it is agree with those results reported previously for polyaniline films in the emeraldine state [29].

UV–visible spectra of aqueous PANI contain absorption peaks in the (i) 300–340 nm region and in the (ii) 550–800 nm region. The doped PANI NPs in the dispersion at pH 1 show the characteristic absorption bands at 320–340 nm wavelengths in region (i) shifted to red perhaps due to microenvironment effect, and at 740–800 nm wavelengths in region (ii), which are due to the π-π* transition of benzoid rings and the formation of polaron, respectively. Also it shows an additional band at 400–420 nm due to the formation of a doping level owing to 'exciton' transition, caused by interband charge transfer from the benzenoide to the quinoide moieties of the protonated PANI (polaron/bipolaron transition). Deprotonation of PANI by changing pH to 10 produces a gradual blue shift of the absorption bands, and especially in the region (ii) from 800 nm as far as the 550 nm, for the excitation of nitrogen of the quinoide segments present in the violet pernigraniline base form (pH 10). The bands shifting is a reversible process, for that the polymeric chain are accessible to the external solution ions. In addition, the conductive broad band of PANI shifted to red increase the absorption capacity of near infrared radiation (>800 nm). That property is relevant to the application of the PANI NPs in tumoral photothermical therapy, since the pH inside the tumoral cell is lower than in the extracellular media [6, 30]. Changes of pH do not seem to alter the dispersability of the PANI NPs.

3.5. Purification of PANI NPs

As the polyaniline nanoparticles are produced by in-situ polymerization, the dispersion contains both unreacted chemicals (aniline, ammonium persulfate) and secondary products (4-aminodiphenylamine, benzidine, olygomers), which are known to be produced during aniline oxidation [31], and are highly toxic [32, 33]. Therefore, those low molecular weight impurities have to be removed before use in biological applications. This is usually done by dialysis, which is a slow procedure. Besides its potential application as thermoresponsive nanomaterials, the reversible thermosensitivity drives to collapse of stabilizer allows to purify the



Scheme 2. Emeraldine protonation states.

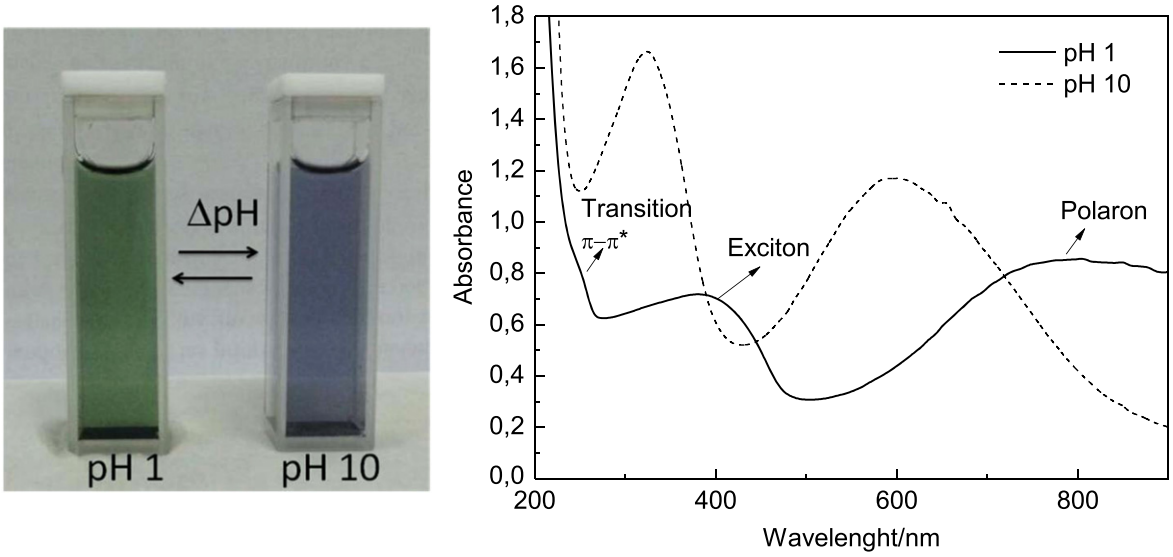


Figure 5. Photography of PANI NPs and UV-Vis spectra of PANI NPs stabilized with PVP at pH 1 and 10, taken at room temperature.

nanoparticles by expulsion of impurities through collapse, supernatant removal and dispersion in clean solution.

3.6. Photothermal effect by near Infrared Radiation absorption

Photothermal effect is a phenomenon associated with absorption of electromagnetic radiation which is non-radiatively released as heat to the irradiated system. In biomedicine, the photothermal effect is used as a laser treatment, mainly at infrared radiation, where laser light is absorbed and the absorbed energy is converted to thermal energy (heat) inside the tissue. The phenomenon is the basis for treatments of blood vessel lesions, laser resurfacing, hair removal and laser surgery.

To test the absorption capacity of infrared radiation by PANI NPs dispersion and subsequent conversion to heat, the dispersion with PNIPAM/PVP (50:50 w w^{-1}) as stabilizer is irradiated with NIR laser at 780 nm and 100 mW power while the temperature of system is measured with an IR thermometer or a thermocouple. It is known that the tumor cell has a metabolic regime with higher temperature and lower pH than normal or healthy cells [34]. Therefore, the experiences are carried out at pH 4 in order to simulate the internal condition pH of tumor cell. Figure 6(A) shows the transmittance measured of NPs dispersions during irradiation time. The PANI NPs dispersion with PNIPAM/PVP (50:50 w w^{-1}) as stabilizer is responsive the absorption of NIR radiation after 6 min (400 sec) of laser application. The decreasing of transmittance confirm that the condition of pH is optima to induce the collapse of NPs dispersion by heating, since that its conductive absorption band coincide with wavelength of emission laser, as it can be seen in the insert of figure 6(A).

Upon irradiation with a NIR laser, the NPs heats up and the dispersion aggregates, as seen by the decrease of

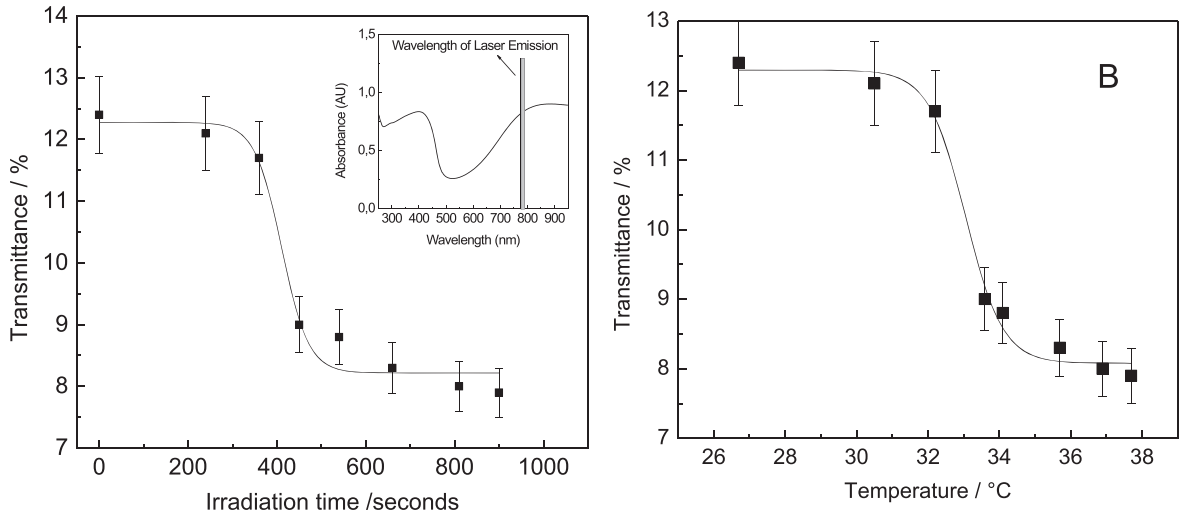


Figure 6. Turbidimetric measurements of a PANI NPs-PNIPAM/PVP (50:50 w w^{-1}) dispersion at pH 4, during irradiation with a NIR (780 nm) laser (100 mW) (A) plot of transmittance as a function of he irradiation time (UV-visible spectral of PANI NPs dispersion is inserted), (B) plot of transmittance versus particles temperatures.

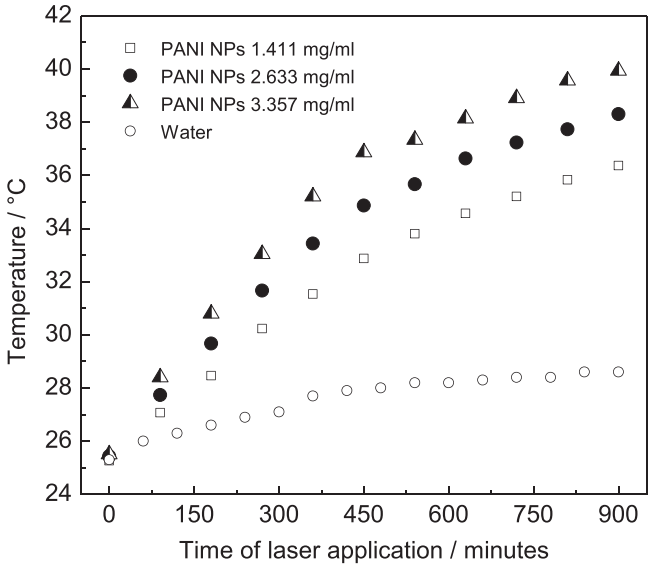


Figure 7. Temperature variation of PANI NPs dispersions with 50% PVP/PNIPAM as stabilizer, as a function of irradiation time with NIR laser (780 nm, 100 mW).

transmittance. On the other hand, when the transmittance is plotted as a function of the nanoparticle temperatures (figure 6(B)), it can be seen that the aggregation occurs at a temperature close to the coil to globule transition of the polymeric stabilizer (PNIPAM).

Indeed, the energy of the laser light absorbed by the PANI NPs is being transferred to the solvent, as it can be seen by the measurement of the dispersion temperature using a thermocouple (figure 7). By irradiation NIR, the temperature of aqueous medium (without PANI NPs) increases only 3 °C after 10 min (600 sec) of laser application, while in presence of PANI NPs the temperature increase 9.5 °C with 1.41 mg ml^{-1} PANI NPs until 13 °C with 3.36 mg ml^{-1} PANI NPs, at same application time. The temperature change scales up with the concentration of nanoparticles indicating that the nanoparticles absorb strongly the NIR light.

The temperature change is enough to induce cell death of tumoral cells because those cells have a diminished functionality of the DNS repair systems, correlated with its increased growth rate. Indeed, it has been shown that excellent photothermal therapy efficacy is achieved *in-vivo* upon intratumoral injection of PANI NPs followed by near-infrared light exposure [35]. The results suggested that PANI NPs could be considered as an effective photothermal agent and pave the way to future cancer therapeutics. On the other hand, *in-vitro* studies on photothermal therapy by irradiation with NIR laser (780 nm, 100 mW) has been performed to LM2 cell line using a PANI NP concentration of 1.04 mg l^{-1}. PANI NPs incorporated (with 200 nm of size). *In-vitro* results showed clear photothermal effect and cell death by apoptosis [36]. Since the experimental conditions (figure 7) are similar to in-vivo experiences, we considered that cell death takes place by apoptosis and not by laser ablation.

On one side, small nanoparticles can be aggregated locally by use of a laser producing a tumor cell damage analogous to the protein plaques occurring in neurological diseases (e.g. Alzheimer) [37]. On the other hand, induced aggregation block the exocytosis of nanoparticles from the cell, as it has been shown to occur by pH effects [38]. In that way, the reversible formed aggregates could be heated up photothermally, inducing tumor cell death.

Moreover, it has been shown that gold nanoparticles having a PNIPAM based shell become hydrophobic at temperatures above the transition temperature, increasing the internalization of the nanoparticles into the cell [39]. A similar increase of internalization can be achieved using the nanoparticles described in this paper, driven either by a temperature increase of the surrounding media or photothermal heating by light irradiation.

4. Conclusions

A simple route for synthesizing polyaniline colloidal particles with smart behavior is described. By using PNIPAM and HPC as polymeric stabilizers, temperature-dependent colloidal stability can be imparted to the polyaniline colloids. Their size depends strongly of the stabilizer nature used. Besides, nanoparticles with intermediate size can be obtained by using a mixture of PVP and PNIPAM as co-stabilizers. Above the coil to globule transition temperature of the polymeric stabilizer, the nanoparticles aggregate. By UV-visible spectroscopy, it can be seen that the PANI NPs form stable suspensions at different pH values. The spectroscopic features of the synthesized polyaniline nanoparticles are in agreement with those of polyaniline films. The thermosensitive colloids could be used in biomedical applications such as drug delivery and hyperthermia for cancer treatment. Additionally, the reversible aggregation, drove by temperature, can be used to eliminate soluble contaminants from the nanoparticle dispersions. The PANI NPs dispersions absorb NIR radiation, which is converted into heat and induces the aggregation of dispersion stabilized with thermosensitive polymers (e.g. PNIPAM).

Vitae

Silvestre Bongiovanni Abel holds a B.Sc in Chemistry (UNRC, 2013) and is presently pursuing a PhD in Chemistry at National University of Rio Cuarto in the subjects of advanced materials based on synergic nanocomposites made of conductive and thermo-sensitivity polymers. He holds a PhD fellowship from the National Science Council of Argentina (CONICET).

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References

[1] Bhadra S 2010 *Polyaniline: Preparation, Properties, Processing and Applications* (Germany: Lambert Academic)
[2] Dispenza C, Leone M, Presti C L, Librizzi F, Spadaro G and Vetri V 2006 *J. Non-Cryst. Solids* **352** 3835–40
[3] Acevedo D F, Rivarola C R, Miras M C and Barbero C A 2011 *Electrochim. Acta* **56** 3468–73
[4] Morrin A, Ngamna O, O'Malley E, Kent N, Moulton S E, Wallace G G, Smyth M R and Killard A J 2008 *Electrochim. Acta* **53** 5092–9
[5] Chen F and Liu P 2011 *ACS Applied Materials & Interfaces* **3** 2694–702
[6] Yang J *et al* 2011 *Angewandte Chemie Inter. Edn* **50** 441–4
[7] Barbero C A *et al* 2010 *Mol. Cryst. Liq. Cryst.* **521** 214–28
[8] Yin J, Xia X, Xiang L and Zhao X 2011 *Smart Mater. Struct.* **20** 015002
[9] Virji S, Huang J, Kaner R B and Weiller B H 2004 *Nano Lett.* **4** 491–6
[10] Ambrosi A, Morrin A, Smyth M R and Killard A J 2008 *Analytica Chimica Acta* **609** 37–43
[11] Molina M A, Rivarola C R, Miras M C, Lescano D and Barbero C A 2011 *Nanotechnology* **22** 245504
[12] Pecher J and Mecking S 2010 *Chemical Reviews* **110** 6260–79
[13] Ono Y and Shikata T 2007 *J. Phys. Chem.* B **111** 1511–3
[14] Molina M A, Rivarola C R and Barbero C A 2012 *Polymer* **53** 445–53
[15] Rivarola C R, Biasutti M A and Barbero C A 2009 *Polymer* **50** 3145–52
[16] Cruz-Silva R, Arizmendi L, Del-Angel M and Romero-Garcia J 2006 *Langmuir* **23** 8–12
[17] Fedorova S and Stejskal J 2002 *Langmuir* **18** 5630–2
[18] Stejskal J, Kratochvíl P and Helmstedt M 1996 *Langmuir* **12** 3389–92
[19] Riede A, Helmstedt M, Riede V and Stejskal J 1998 *Langmuir* **14** 6767–71
[20] Stejskal J and Sapurina I 2005 *Pure Appl. Chem.* **77** 12
[21] Gaharwar A K, Wong J E, Müller-Schulte D, Bahadur D and Richtering W 2009 *J. Nanosci. Nanotechnol.* **9** 5355–61
[22] Meenach S A, Anderson A A, Suthar M, Anderson K W and Hilt J Z 2009 *J. Biomed. Mater. Research Part* A **91A** 903–9
[23] Winnik F M, Tamai N, Yonezawa J, Nishimura Y and Yamazaki I 1992 *The Journal of Physical Chemistry* **96** 1967–72
[24] Cavallo P C, Muñoz D J, Miras M C, Barbero C and Acevedo D F 2014 *J. Appl. Polym. Sci.* **131** 39409
[25] Stockton W B and Rubner M F 1997 *Macromolecules* **30** 2717–25
[26] Ponzio E A, Echevarria R, Morales G M and Barbero C 2001 *Polymer International* **50** 1180–5
[27] Galaev I and Mattiasson B 2007 *Smart polymers: Applications in Biotechnology and Biomedicine* 2nd Edn (Boca Raton FL: CRC Press)
[28] De Albuquerque J E, Mattoso L H C, Faria R M, Masters J G and MacDiarmid A G 2004 *Synth. Met.* **146** 1–10
[29] Huang W S and MacDiarmid A G 1993 *Polymer* **34** 1833–45
[30] Yslas E I, Ibarra L E, Peralta D O, Barbero C A, Rivarola V A and Bertuzzi M L 2012 *Chemosphere* **87** 1374–80

[31] Planes G A, Rodriguez J L, Miras M C, Garcia G, Pastor E and Barbero C A 2010 *Phys. Chem. Chem. Phys.* **12** 10584–93
[32] Baynes R E, Monteiro-Riviere N A, Qiao G L and Riviere J E 1997 *Toxicol. Letters* **93** 159–69
[33] Khan Firoze M, Kaphalia B, Boor P and Ansari G A S 1993 *Arch. Environ. Contam. Toxicol.* **24** 368–74
[34] Yang J *et al* 2011 *Angew. Chem.* **123** 461–4
[35] Ibarra L E, Yslas E I, Molina M A, Rivarola C R, Romanini S, Barbero C A, Rivarola V A and Bertuzzi M L 2013 *Laser Phys.* **23** 066004
[36] Molina M A, Rivarola C R, Yslas E I, Rivarola V and Barbero C A 2010 *Biocell.* **34** A46
[37] Barrio J R, Satyamurthy N, Huang S-C, Petrič A, Small G W and Kepe V 2009 *Acc. Chem. Res.* **42** 842–50
[38] Nam J, Won N, Jin H, Chung H and Kim S 2009 *J. Am. Chem. Soc.* **131** 13639–45
[39] Salmaso S, Caliceti P, Amendola V, Meneghetti M, Pall Magnusson J, Pasparakisc G and Alexander C 2009 *J. Mater. Chem.* **19** 1608–15