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Chameleon Nonwovens by Green Electrospinning

*Elisabeth Giebel, Claudia Mattheis, Seema Agarwal, and Andreas Greiner**

Electrospun ionic nonwovens are obtained by green electrospinning of aqueous dispersions. The resulting nonwovens are termed as chameleon nonwovens since their surface properties can be tailored in a large variety by coating of different functionalities following the protocol of the layer-by-layer process (LBL). The dimensional stability of the electrospun fibers in the chameleon nonwovens is achieved by photo-cross-linking after electrospinning and thereby overcoming the repulsive forces of the ionic moieties in the fibers. Depending on the nature of the ionic moieties different materials are coated by LBL including dyes, antibacterial materials, silver, and gold nanoparticles. Enhanced coating efficiency for coating of metal nanoparticles is observed when the chameleon nonwovens were precoated by a polyelectrolyte.

1. Introduction

Electrospinning is a versatile method for the preparation of nonwovens consisting of long entangled fibers with diameters in the submicrometer range. Numerous variations of the electrospinning process, materials for electrospinning, properties of electrospun fibers, and their applications have been shown in the past decade, which demonstrates the enormous potential of this research field.[1–4] Still, a major challenge of electrospinning is the use of harmful organic solvents. Although, electrospinning using water as solvent is possible but the electrospun fibers of water-soluble polymers disintegrate immediately upon contact to water unless they are stabilized by cross-linking or other chemical modifications of the polymers.[5–8] Due to the constrains of water-soluble polymers in electrospinning the concept of green electrospinning has been developed for water-stable electrospun nonwovens using water as solvent.[9–15] Following this concept a formulation of an aqueous polymer dispersion mixed with a small amount of a water-soluble polymer is used for electrospinning. Polystyrene,[10] poly(styrene-co-n-butyl acrylate),[11] poly(hexamethylene adipate)-poly(ethylene oxide) block copolymers,[12] and waterborne polyurethane dispersions[13] were electrospun following the concept of green electrospinning using different methods for fiber stabilization.[13,14]

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DOI: 10.1002/adfm.201201873

The key step for fiber formation in green electrospinning is the one-dimensional coagulation of dispersion particles. Although highly versatile, dispersions for green electrospinning have to meet some fundamental requirements for successful fiber formation. One of these requirements is the absence of strong repulsive inter-particle forces. The repulsive forces, for example by equivalent surface charges on the particle surfaces, could lead to fast disintegration upon contact with water or even prevent the fiber formation from dispersion. Therefore, the preparation of electrospun nonwovens with chemically linked surface charges by green electrospinning is a real challenge but worth to achieve since it would open access to a large variety of novel functional nonwovens prepared under ambient conditions and thereby would become attractive for applications beyond chemical laboratories. Electrospun nonwovens with chemically attached surfaces charges could be functionalized, for example, by the layer-by-layer process (LBL) as shown schematically in **Figure 1**. LBL is a very well-known method for functionalization of surfaces through the pioneering work of Decher.[16] LBL has been also applied successfully to electrospun nonwovens for surface functionalization. Electrospun fibers were coated with different materials like polyelectrolytes,[17–21] carbon nanotubes,[22] and inorganic nanoparticles.[22,23] The LBL-coated electrospun fibers can be used in, biosensors,[18] chemical and biological protection,[19] drug delivery,[21] catalysis,[23] and drug delivery.[25] In spite of all these interesting concepts the preparation of water-stable electrospun nonwovens from water, which could be used without any further charge coating is not known to the best of our knowledge but could serve as highly versatile materials for the functionalization by LBL.

We have anticipated based on previous experiences with green electrospinning and photo-crosslinking[15] that the use of copolymer dispersions with a well-balanced amount of ionic moieties, stabilized after electrospinning by photo cross-linking, could yield water-stable fibers by green electrospinning with sufficient charges on the fiber surfaces for successful LBL coatings. Particular challenge and advantage of this approach was to electrospin ionic dispersion particles directly from aqueous dispersion and achieve fiber formation in spite of the electrostatic repulsion of the ionic particles. One part of the successful concept was to use a hydrophobic comonomer which gives water stability and lowers the glass transition temperature and thereby facilitates fiber formation by merging of the dispersion particles. Another part of the concept was to use a third comonomer which is photo cross-linkable and thereby provides thermomechanical stability. These new chameleon fibers

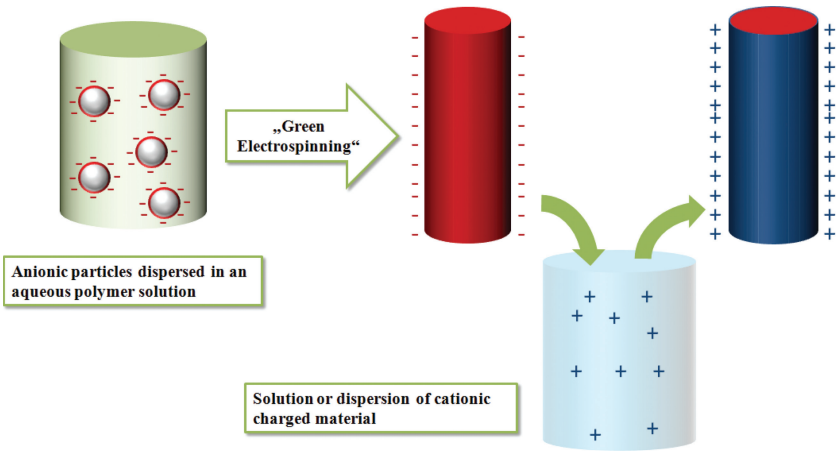


Figure 1. Concept for the preparation of LBL coating of surface charged electrospun fibers obtained by green electrospinning leading to chameleon nonwovens.

could open many new possibilities for post-spinning functionalization. Particular advantage next to the other advantages of green electrospinning (safe and high yield electrospinning) is, that new formulations for electrospinning, which are otherwise very time-consuming, are not required. Following this concept the basis of electrospun nonwovens with distinct charges on the surface can be used to generate a near endless variety of novel functionalizations and thereby new materials with new properties which encouraged us to name the nonwovens obtained by this new concept as chameleon nonwovens. We show how chameleon nonwovens with positive or negative surface charges were prepared and functionalized by LBL-coating with polyelectrolytes, dyes, titanium dioxide nanoparticles, and metal nanoparticles. These examples are just a small selection of possibilities with chameleon nonwovens but should demonstrate the potential of this approach.

2. Results and Discussion

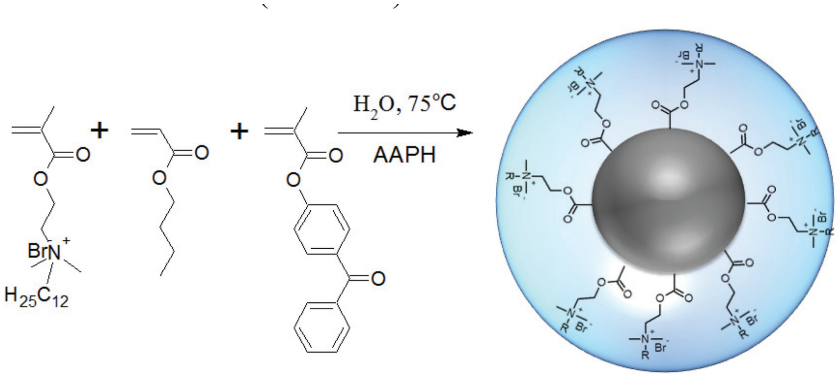
2.1. Preparation of Chameleon Nonwovens

The ionic groups were introduced in the particles by aqueous emulsion polymerization using ionic comonomers. In detail, aqueous acrylate dispersions with cationic surface charges of the particles were prepared by emulsion polymerization of 90 mol% butyl acrylate and 5 mol% of the photo-cross-linker 4-methacryloyl-oxy-benzophenone (MABP) with 5 mol% of 2-methyacryl-oxy-ethyldodecyl dimethyl ammonium bromide (C_{12}-DMAEMA-Br) as polymerizable surfactant in water (**Scheme 1**).

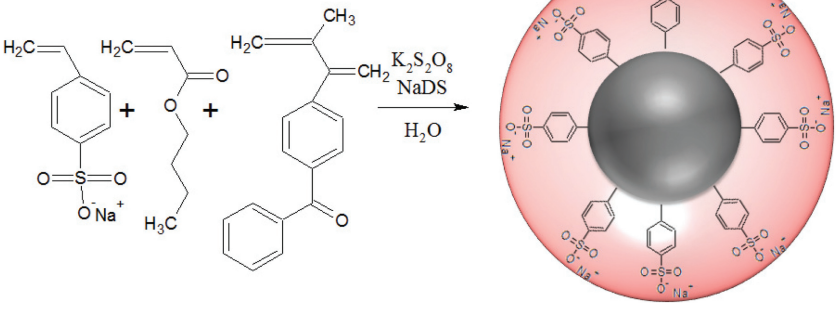
Correspondingly, anionic acrylate dispersions anionic surface charges of the particles were prepared by emulsion polymerization of 90 mol% butyl acrylate, 5 mol% MABP, and 5 mol% sodium styrene sulfonate (SSS) in water. Sodium dodecylsulfate (SDS) was added as supporting surfactant (**Scheme 2**).

Cationic as well as anionic dispersions contained polymer particles with diameters less than 150 nm. The solid content of cationic dispersion was 23 wt% with zeta potential of +37 mV and 24 wt% with zeta potential of –46 mV for the anionic dispersion (**Table 1**).

For the preparation of electrospinning formulations the cationic and anionic dispersion was mixed with a 25 wt% aqueous poly(vinyl alcohol) (PVA) as matrix polymer resulting in a ratio matrix polymer/dispersion (based on solid content) of 1:4. Electrospinning of these formulations under otherwise standard conditions resulted in colorless solid nonwovens with cationically or anionically charged electrospun nonwovens. Electrospun nonwovens formed by a mixture of positively and anionically charged fibers were obtained with a electrospinning set-up similar to previously reported work.[26] The fibers of the nonwovens were stabilized by photo-cross-linking. The matrix polymer PVA was removed by extraction with water at 60 °C. The obtained fibers of the nonwovens, assigned here as *chameleon nonwovens*, were smooth and showed no sign of a particle structure resulting from the dispersion particles (**Figure 2**).



Scheme 1. Preparation of cationic dispersion particles by aqueous emulsion copolymerization of MABP, BA, and C_{12}-(DMAEMA)-Br.



Scheme 2. Preparation of anionic dispersion particles by aqueous emulsion copolymerization of MABP, BA, and the anionic SSS.

Table 1. Properties of the cationic and anionic dispersion.

	Solid content [wt%]	Particle size [nm]	Zeta potential [mV]	T_g [°C]
Cationic dispersion	23	132	37	–41
Anionic dispersion	24	99	–46	–39

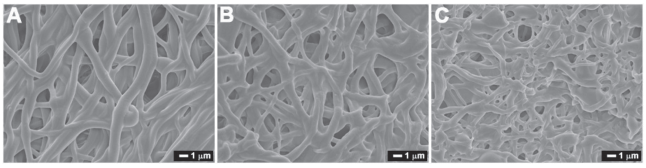


Figure 2. SEM images of electrospun fibers after removal of PVA by aqueous extraction at 60 °C: A) anionic fibers B) cationic fibers C) parallel spun anionic and cationic fibers.

2.2. Coating of Chameleon Nonwovens with Polyelectrolytes by LBL

LBL-coatings of the chameleon nonwovens with polyelectrolytes were done by immersion of the nonwovens in aqueous solutions of the polyanion sodium polyacrylate (SPA) and an antibacterial polycation (polyguanidine) composed of guanidine hydrochloride, diethylene triamine and hexamethylene diamine.[27] Both polyelectrolyte solutions were prepared with a concentration of 0.01 mol/L. The duration of the treatment was 30 min, afterwards the nonwovens were washed in water for 30 min. Multi-layered coatings were obtained by alternating treatment in polyanion sodium polyacrylate and polyguanidine solutions. In the following text a sequence of coating ending with a new layer of polyguanidine is defined as one cycle of LBL coating. Thus the cycle number equals the number of polyguanidine layers.

No visual difference between the nonwovens can be observed before and after water-treatment as exemplarily shown for the coating of anionic nonwovens in **Figure 3**. However, treatment in polyelectrolyte solution led to formation of a film between fibers of the nonwovens at the area of contact, indicating a coating of the fibers with the polyelectrolytes. The cationic fibers showed similar results (not shown here).

The presence of the polyelectrolytes in the nonwovens after different cycles was determined via IR-spectroscopy. The both anionic and cationic surface charged nonwovens consisting mainly of poly(butylacrylate) showed the signal of the acryl ester at 1730 cm^{-1}. The polyguanidine's signal is at 1630 cm^{-1} and the sodium polyacrylate's signal is at 1550 cm^{-1}. As shown in **Figure 4** the intensity of the sodium polyacrylate and polyguanidine signals increased with each cycle. The change of ratio of the polyguanidine's and the sodium polyacrylate's signal to the signal of the nonwovens in correlation to the cycles of treatment are shown in **Figure 5**. The

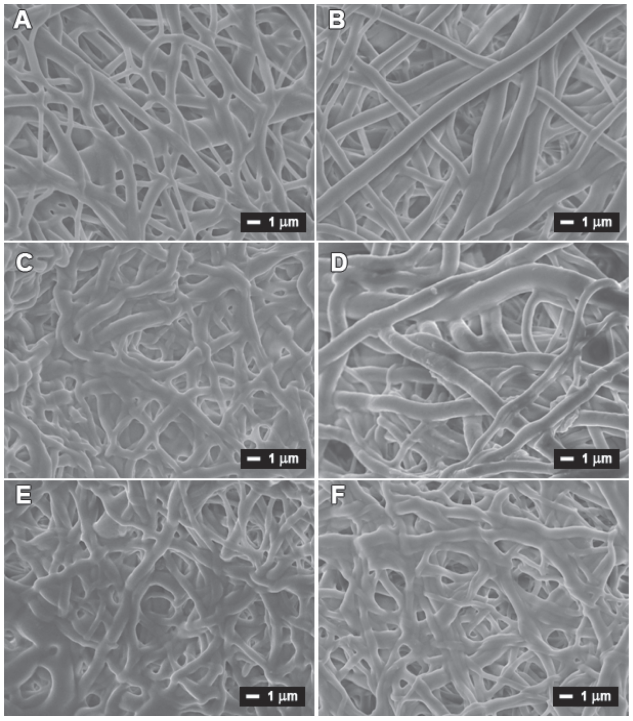


Figure 3. SEM images of the anionic nonwovens A) before water treatment B) after water treatment C) after cycle 1 D) after cycle 2 E) after cycle 3 F) after cycle 4.

adsorption of polyelectrolytes is stronger in case of the cationic nonwovens compared to the anionic nonwovens.

The surface charges of the anionic functionalized nonwovens can be reduced due to protonation of the sodium styrene sulfonate units, while the cationic C_{12}-DMAEMA-Br–units are not influenced by the pH-value.

The nonwonves coated by polyguanide should display antibacterial properties. Indeed, the number of coating cycles directly corresponded with the antibacterial activity of the polyguanidine-coated nonwovens, which was tested against *Escherichia coli* and *Bacillus subtilis* by determination of the reduction of living bacteria compared to the untreated nonwovens (**Figure 6**).

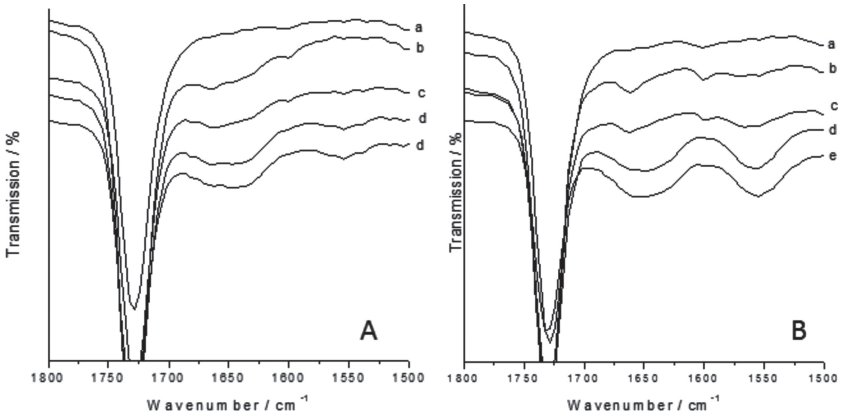


Figure 4. A) Anionic surface charged fibers a) before and after b) cycle 1 c) cycle 2 d) cycle 3 e) cycle 4 B) Cationic surface charged fibers a) before and after b) cycle 1 c) cycle 2) cycle 3 e) cycle 4.

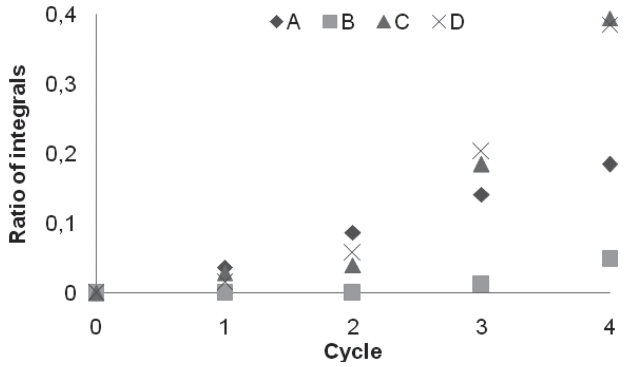


Figure 5. Change of ratio of polyelectrolyte's IR-signal to the IR-signal of the nonwovens in correlation to the cycles of treatment A) polyguanidine to anionic nonwovens B) sodium polyacrylate to anionic nonwoven C) sodium polyacrylate to cationic nonwoven, and D) polyguanidine to cationic nonwovens.

The reduction of living bacteria is smaller in case of the anionic nonwovens, which can be explained by the lower amount of antibacterial polyguanidine adsorbed on the fiber surfaces.

2.3. Coating of Chameleon Nonwovens with Dyes

Many organic dyes are molecules with ionic charges can be selectively coated on chameleon nonwovens. For example the anionic dye fluorescein (**Figure 7**A) coats only the nonwoven with cationic surface charge whereas the cationic dye rhodamine 6G (Figure 7B) coats selectively only the nonwoven with anionic surface charge. In contrast, nonwovens with anionic and cationic surface charges obtained by parallel electrospinning can be coated by both dyes (**Figure 8**).

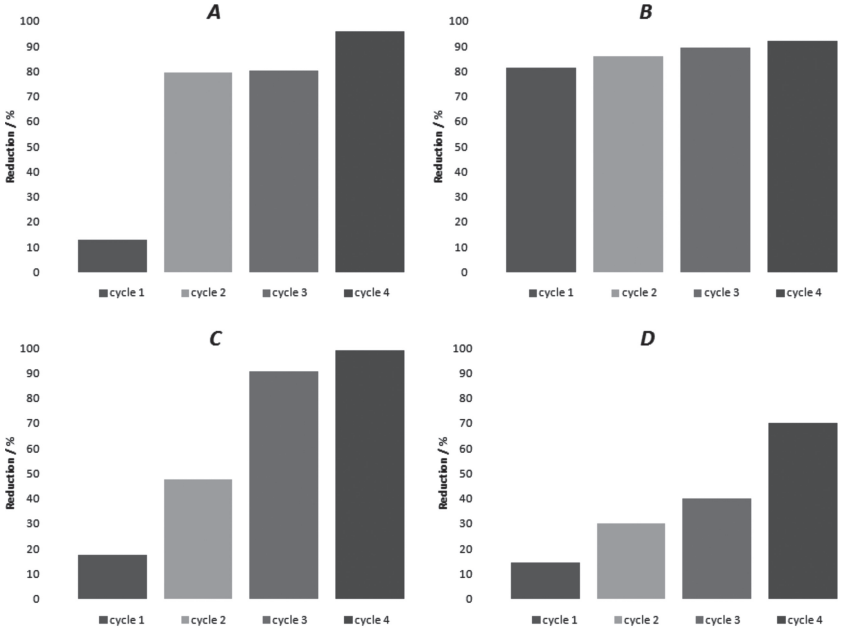


Figure 6. Top row: Reduction of living A) *E. coli* and B) *B. subtilis* on the surface of the coated cationic nonwoven compared to the untreated fibers in correlation to the cycle number; Bottom row: Reduction of living C) *E. coli* and D) *B. subtilis* on the surface of the coated anionic nonwoven compared to the untreated fibers in correlation to the cycle number. Each sample was measured only once.

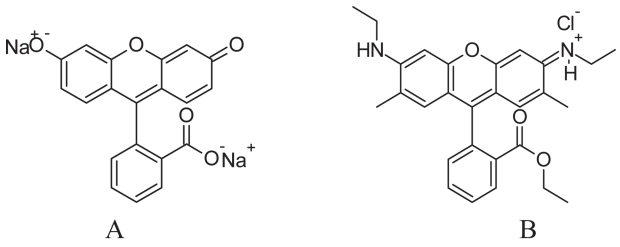


Figure 7. Chemical formula of A) fluorescein which represents an anionic dye and B) rhodamine 6G which represents a cationic dye.

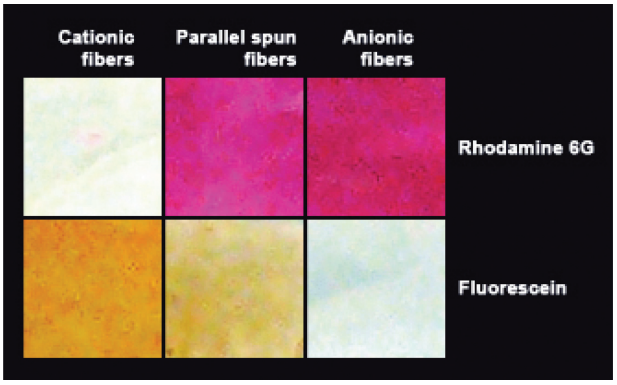


Figure 8. Photographs of cationic, anionic, and cationic anionic mixed (parallel spun fibers) chameleon nonwovens dyed selectively fluorescein and rhodamine 6G.

Consequently, irradiation of the nonwovens with light of 410 nm displayed macroscopically the fluorescence color of the selected. Analysis of the dyed chameleon nonwovens by fluorescence microscope showed selective coating of the charged fibers The sample of parallel spun fibers both fiber types are clearly visible next to each other with different colors (**Figure 9**).

2.4. Coating of Chameleon Nonwovens with Titanium Dioxide

Titanium dioxide is extremely important for photocatalytic reactions[28] as well as for solar cell applications.[29] Due the potential for modulation of the surface charge of titanium dioxide particles dispersed in water by control of the pH-value,[30] they can be utilized nicely for LBL coatings.[22,30] Application of charged titanium dioxide particles on chameleon nonwovens resulted in pH-depending coating of the cationic and anionic nonwovens. After treatment at a pH-value of 2.5 the anionic nonwovens were covered with a layer of titanium dioxide particles, while the cationic fibers were not coated (**Figure 10**A,B). The nonwovens comprised of parallel spun fibers

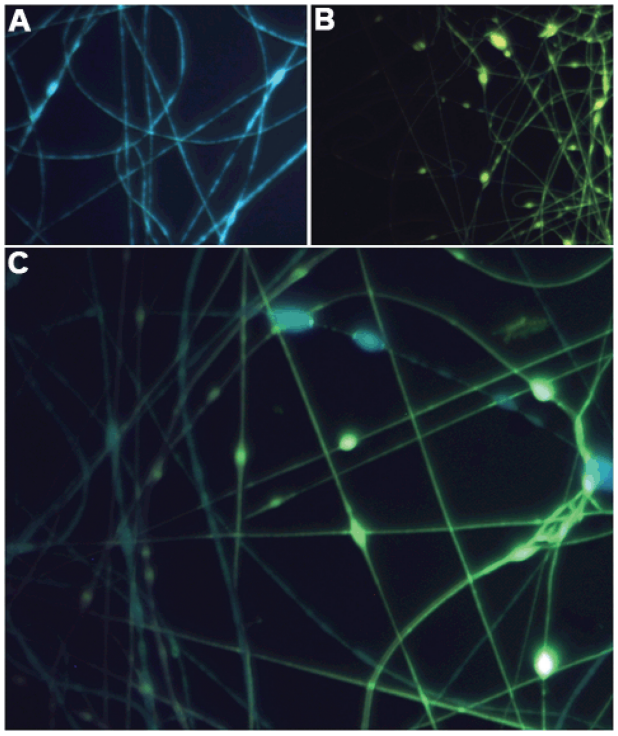


Figure 9. Fluorescence microscope images of A) cationic fibers, B) anionic fibers, and C) parallel spun anionic and cationic fibers after treatment with fluorescein and rhodamine 6G.

showed fibers covered with titanium dioxide particles next to uncovered fibers (Figure 10C). If the nonwovens were treated at pH 11 the cationic fibers were coated with titanium dioxide particles and the anionic fibers were uncoated (Figure 10D,E). The parallel spun sample showed coated fibers next to uncoated ones (Figure 10F).

The photocatalytic activity of the fibers coated with titanium dioxide was demonstrated by photo degradation of methylene blue in aqueous solution. The amount of methylene blue as a function of illumination time was measured by absorption spectroscopy. For accuracy the cationic fibers were used as substrates. As shown in **Figure 11** the nonwoven without titanium dioxide as a reference showed a slight degradation of the dye, while the sample with the titanium dioxide coated nonwoven showed a nearly complete degradation of methylene blue.

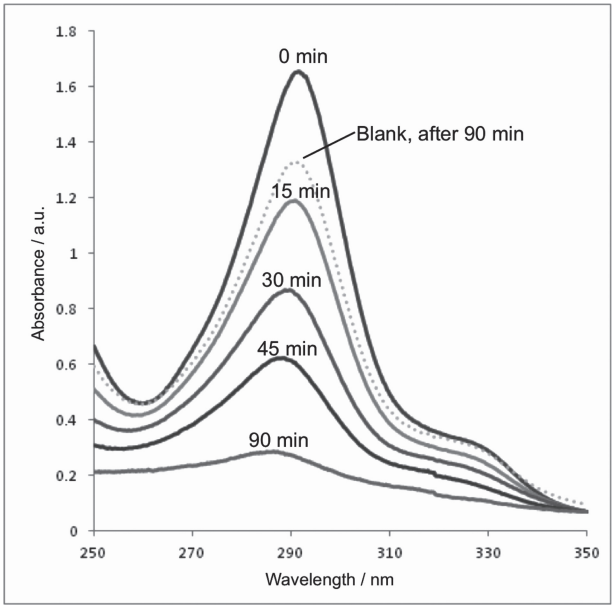


Figure 11. Absorption spectra of the methylene blue solution as function of time with immersed nonwovens coated with and without titanium dioxide particles.

2.5. Coating of Chameleon Nonwovens by Metal Nanoparticles

Metal nanoparticles play an important role for the preparation of functional materials. Silver nanoparticles are standard materials for antibacterial applications[32] and gold nanoparticles are of important for sensor and catalytic applications.[33] The surface charges of the *chameleon nonwovens* could be utilized for the immobilization of silver or gold salts. Subsequent reduction should result in corresponding metal nanoparticles on the surface of the *chameleon nonwovens*.

Prior to decoration with metal nanoparticles the *chameleon nonwovens* were coated with poly(ethyleneimine) (PEI) or sodium polyacrylate (SPA). PEI was selected as a polycation, because of its ability to bound metal ions by forming a complex with the free electron pairs of the nitrogen. Before treating the cationically modified *chameleon nonwovens* with an $AgNO_3$ solution, the counterion bromide had to be exchanged by hydroxide anions by treatment with NaOH solution. Without this treatment, the precipitation of AgBr will cover the fibers with particles independently of any electrostatic interactions. After the ion exchange, the fibers were treated with $AgNO_3$

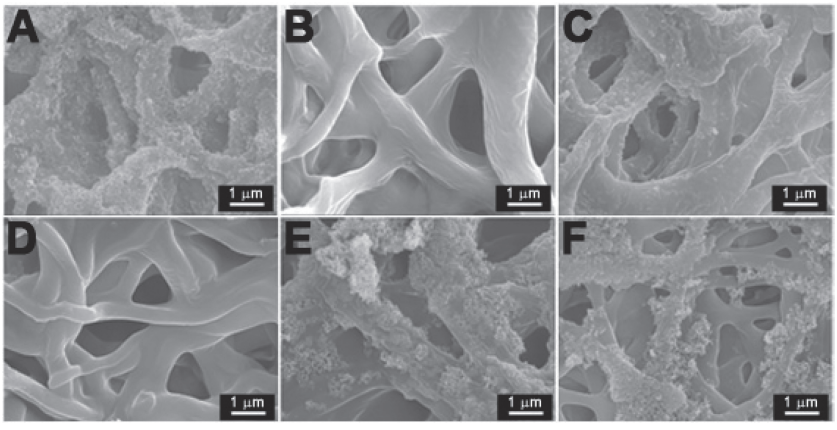


Figure 10. SEM images of A) anionic fibers, B) cationic fibers, and C) parallel spun anionic and cationic fibers after treatment with a TiO_2 dispersion at pH 2.5, and D) anionic fibers, E) cationic fibers, and F) parallel spun anionic and cationic fibers after treatment with a TiO_2 dispersion at pH 11.

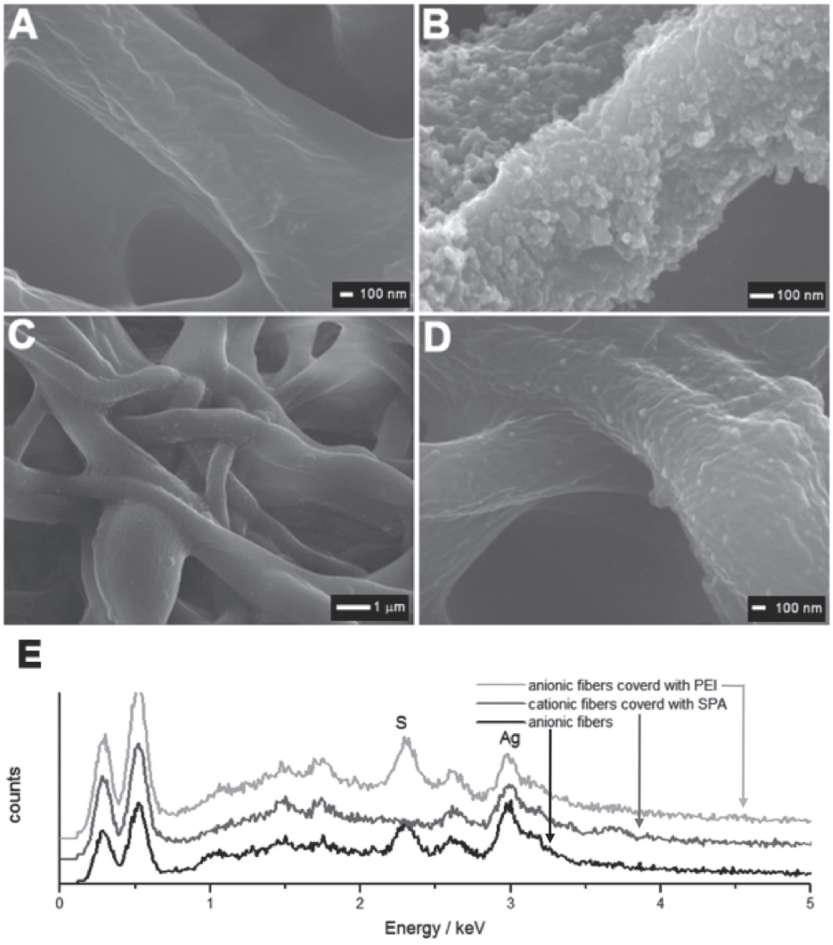


Figure 12. SEM images of fibers after treatment in $AgNO_3$–solution and reduction with $NaBH_4$ A) cationic fiber, B) cationic fiber coated with SPA, C) anionic fiber, D) anionic fiber coated with PEI, and E) EDX spectra of fibers

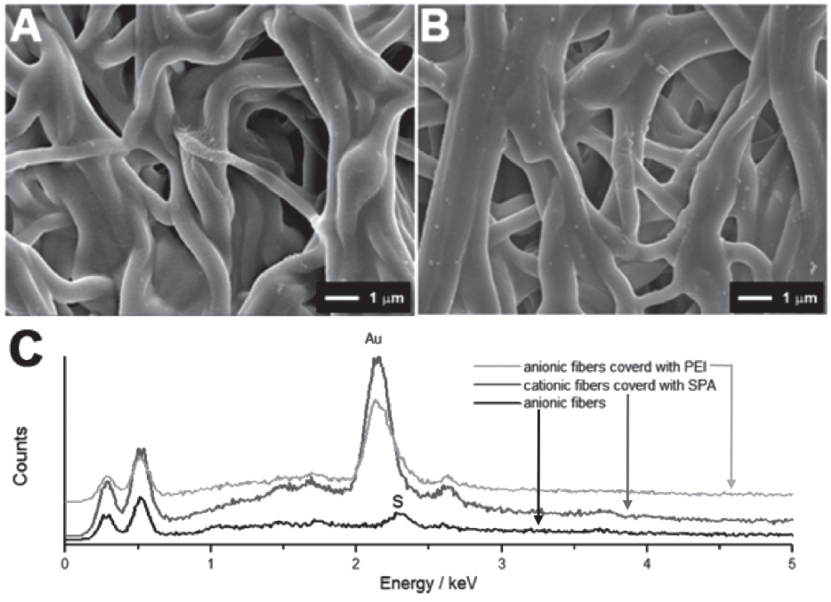


Figure 13. SEM images of fibers after treatment in **$HAuCl_4$**-solution and reduction with $NaBH_4$ A) anionic fiber, B anionic fiber coated with PEI, and C) EDX spectra of fibers.

solution and reduced with $NaBH_4$. SEM images of the cationic fibers showed no visible particles on the fiber surface (**Figure 12**). Treatment of the ion exchanged cationic fibers with SPA resulted in the ability to bind metal ions on the surface. After treatment in the silver salt solution and subsequent reduction the fibers coated with SPA were of a dark brown color, and showed a dense layer of nanoparticles in SEM (Figure 12). The presence of silver on the fiber surface was proven by energy dispersive X-ray analysis (EDX, Figure 12E).

In a similar fashion, the anionically modified chameleon nonwovens turned their color to brown after treatment with $AgNO_3$-solution, which indicated the immobilization of silver nanoparticles on the fiber surfaces as confirmed by SEM and EDX analysis (Figure 12D,E).

The anionically modified chameleon nonwovens coated with silver nanoparticles showed on agar plates inoculated with *E. coli* clearly a strong zone of inhibition while no zone of inhibition was observed with blank anionically modified chameleon nonwovens. The reduction of *E. coli* by the silver nanoparticle modified chameleon nonwovens was 99.9%, which proved the antibacterial activity of the silver nanoparticle coated chameleon nonwovens. Following a similar protocol as for coating with silver nanoparticles chameleon nonwovens were coated with gold nanoparticles by treating the fibers in $HAuCl_4$ solutions and reducing them afterwards by treatment with $NaBH_4$. The pure anionic fibers showed a slight pink color, while the anionic fibers coated with PEI and the cationic fibers coated with SPA showed a rich wine red. The gold nanoparticles were identified by SEM and EDX analysis (**Figure 13**).

3. Conclusions

Water-stable nanofibers could be prepared by green electrospinning of aqueous dispersions of polyacrylates with ionic moieties if the fibers were stabilized in a second step by photo-cross-linking. The ionic moieties could be utilized for coating of the corresponding nonwovens, termed here as chameleon nonwovens, by a variety of different materials by the LBL-process, which opened numerous perspectives for tailoring of optical properties and surface properties of the nonwovens. It has been also shown for coating with metal nanoparticles that the coatings efficiency of the chameleon nonwovens could be further

enhanced by prior coating with polyelectrolytes. An interesting question, which cannot be answered at this this state, is the distribution of the ions on the surface of chameleon fibers. Intuitively, one could expect a homogeneous distribution which has to be proven and will be the topic of our future work. Nevertheless, chameleon nonwovens can be prepared in a safe and efficient way by green electrospinning and thereby open a new platform for the design of novel functional nanofiber-based materials. Further research for the improvement of chameleon nonwovens will focus on spatial confinement of ionic moieties, on selectivity in the coating process as well as on the effect of porosity and surface area change upon morphology-modification by LBL post-functionalization via BET studies.

4. Experimental Section

Materials: BA was obtained from Aldrich and purified by distillation over calcium hydride at reduced pressure. PVA (M_w 195 000 Da, hydrolysis grade 98.0–98.8%) was obtained from Kuraray Specialities Europe. Sodium dodecylsulfate (SDS), potassium peroxo disulfate, sodium styrene sulfonate (SSS) and 2,2′-azobis-2-methyl-propanimidamide dihydrochloride (AAPH) was obtained from Aldrich and used as received. 4-Methacryloyl-oxy-benzophenone (MABP)[34] and 2-methyacryl-oxy-ethyldodecyl dimethyl ammonium bromide (C_{12}-DMAEMA-Br)[35] were prepared according to literature.

Methods: Characterization of latex fibers was done with a JSM-7500F (JEOL) scanning electron microscope operating at an accelerating voltage of 4 kV. The solid content of dispersions was determined by thermogravimetric analysis (TGA) using a Mettler ToledoTGA/STD A 851 at a heating rate of 10 K/min under air. Evaluation was done with 2 STARe software. Glass transition temperatures were measured by a Mettler Toledo DSC 821c at heating/cooling rates of 10 K/min under a nitrogen atmosphere. Evaluation was done with 2 STARe software.

IR-Spectra were taken by a Digilab (Excalibur series) instrument with ATR crystal ZnSe and WinIRPro software version 3.3.

Synthesis of the Anionic Dispersion: A mixture of 37.5 mL (260 mmol) Butylacrylate 3.48 g (13 mmol) MABP, 2.5 g (12 mmol) SSS and 0.35 g (1.2 mmol) SDS was added to 115 mL water and stirred with 1500 rpm in a 1000 mL glass reactor under argon atmosphere at 75 °C. After 15 min 0.375 g (1.3 mmol) potassium peroxo disulfate was added and the stirring speed reduced to 250 rpm. After 60 min the reaction mixture was cooled down to 20 °C. A sample of the dispersion was precipitated in aqueous HCl.

Synthesis of the Cationic Dispersion: A mixture of 27.5 mL (191 mmol) Butylacrylate, 2.75 g (10 mmol) 4- MABP) and 4.25 g (10 mmol C_{12}-DMAEMA-Br was added to 100 mL water and stirred with 1500 rpm in a 1000 mL glass reactor under argon atmosphere at 75 °C. After 15 min 0.100 g (0.4 mmol) AAPH was added and the stirring speed reduced to 250 rpm. After 60 min the reaction mixture was cooled down to 20 °C. A sample of the dispersion was precipitated in saturated NaCl solution

Electrospinning of Dispersions: Each dispersion was mixed with a solution of 25 wt% PVA in deionized water, whereby a ratio among matrix polymer and dispersion of 1:4–referring to the solid content–was applied. These formulations were electrospun on alumina foil with a voltage of 40 kV at a distance of 20 cm and a feed rate of 0.05 mL/min through a needle with a diameter of 0.9 mm.

Nonwovens consisting of a mixture of both fiber types were prepared via a parallel electrospinning set-up, as described previously.[26] In short, two syringes, each charged with cationic or anionic electrospinning formulation, were placed in a distance of 10 cm and a rotating plate was used as collector in order to obtain a regular distribution of both fiber types. Electrospinning was conducted applying the same conditions as with the previously described single syringe set-up.

UV Irradiation: UV irradiation was performed with a medium pressure mercury lamp TQ 150 (power input 150 W) from Heraeus and a quartz cooling tube. The distance between radiation source and sample was 20 cm. Irradiation time was 30 min.

Coating with Polyelectrolytes: The nonwovens consisting of one fiber type were treated with solutions of the polyanion sodium polyacrylate (SPA) and the polyguanidine for 30 min, Both polyelectrolytes were used in a concentration of 0.1 mol monomer units per L. Afterwards the fibers were washed in water for 30 min.

Bactericidal Effect of the Surface: 100 µL of a bacteria suspension containing 10^7–10^8 cfu *E. coli* or *B. subtilis* per mL was spread on a nutrient agar plate and a sample of the nanofiber mats (same size, each) were placed on this plate. The sample was incubated for 24 h at 37 °C. After incubation, the reduction of living bacteria was determined by washing of the samples in 2 mL sterile potassium phosphate buffer (PBS), using a vortex-mixer. A serial tenfold dilution series of 100 µL specimen from this washing solution was prepared in PBS and samples of 10^0, 10^{-2}, and 10^{-4} dilution stages were spread on nutrient agar plates, followed by incubation at 37 °C for 24 h. Subsequently, the colonies were counted and the reduction of viable bacteria was determined regarding a blank control.

Coating with Fluorescent Dyes: Rhodamine 6G was used as cationic dye and fluoresceine as anionic species. The fibers were treated for 5 min in a solution containing 0.1 mol/L of the dye and washed afterwards in water for 30 min.

Coating with Titanium Dioxide: The anionic, cationic, and parallel spun nonwovens were treated in dispersions of titanium dioxide (content of solids 0.1 wt%, particle size 25 nm, anatas conformation) at a pH-value of 2.5 or 11. Afterwards the fibers were washed in water for 30 min.

Test of Photocatalytic Activity: 10 mg nonwoven were added to 2 mL of an aqueous methylene blue solution (0.025 g/L). The sample was irradiated with a medium pressure mercury lamp TQ 150 (power input 150 W) from Heraeus and a quartz cooling tube. The distance between radiation source and sample was 20 cm. The degradation of the dye was detected by UV/vis spectroscopy.

Coating with Metal Nanoparticles: The fibers were coated with metal nanoparticles by treatment the fibers for 30 min in an aqueous solution of a metal salt (0.1 mol/L). After removal of the non bound metal ions via washing in a water bath for 30 min, the metal was reduced by immersion of the fibers in a aqueous $NaBH_4$-solution (0.1 mol/L). Prior to treatment of the cationic fibers with an $AgNO_3$ solution, the counter ion bromide was exchanged with hydroxide by treating the fibers three times with a 1 M NaOH solution.

Acknowledgements

The authors are indebted to the Bundesministerium für Bildung und Forschung (project *Nanofatex*) for financial support.

Received: July 6, 2012
Revised: December 9, 2012
Published online: February 7, 2013

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