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Electrophoretic deposition of organic–inorganic nanocomposites

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Abstract The focus of this review is on a new class of nanocomposites containing inorganic nanoparticles in a polyelectrolyte matrix. The recent advances in the application of electrophoretic deposition for the fabrication of the nanocomposite films are reviewed. New electrochemical strategies are discussed which are based on the use of strong, weak polyelectrolytes, and polymer–metal ion complexes. Many parameters, such as the pH, molecular weight of polyelectrolyte and bath composition influence the deposition process, microstructure and properties of the nanocomposite materials. Various applications, in areas as diverse as catalysis, fuel cells, protection of metals, biomedical implants, quantum dots, superparamagnetic devices, and supercapacitors were proposed for these fascinating new materials.

Introduction

Organic–inorganic composite materials have attracted substantial attention because of the possibility of combining the properties of organic and inorganic components [1–4]. Significant interest has been generated in the fabrication of nanocomposite films containing inorganic nanoparticles in a polyelectrolyte matrix [5–8]. The fabrication of organic–inorganic nanocomposites containing polyelectrolytes and inorganic nanoparticles is usually based on self-assembly [5,6]. This approach involves sequential adsorption of polyelectrolytes and oppositely charged inorganic nanoparticles. Inspired by biomineralization [9, 10], many authors used polyelectrolyte multilayers and polyelectrolyte capsules as reactors for the synthesis of inorganic nanoparticles [11–14]. Composite films containing nanoparticles of metals, oxides, hydroxides, and other materials in a polyelectrolyte matrix were obtained by this technique. Electrophoretic deposition (EPD) is another promising method for fabricating composite films containing polyelectrolytes and inorganic nanoparticles. Various electrochemical strategies are currently under development, which are based on the EPD of polyelectrolytes or polymer–metal ion complexes and the EPD or electrosynthesis of inorganic particles. The advantages of EPD are short processing time and process simplicity. Moreover, uniform films of controlled composition can be obtained on the substrates of complex shape as well as on selected areas of the substrates. The strategy based on the EPD of polyelectrolytes and cathodic electrosynthesis of inorganic materials enables electrosynthesis of nanoparticles in situ in a polymer matrix, preventing particle agglomeration. The properties, composition, nanostructure, and morphology of the composite films can be tailored according to specific requirements for various applications. This can be achieved by variation of bath composition, deposition parameters, and mass transport conditions for organic and inorganic components.

This review paper covers new developments and illustrates various strategies for the fabrication of

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nanostructured organic–inorganic films using EPD. The review is focused on the nanocomposites containing inorganic nanoparticles and polyelectrolytes. New materials and applications are discussed.

Electrophoretic deposition of materials

EPD is essentially a two-step process, which includes the electrophoretic motion of charged inorganic particles or polymers in a liquid towards the electrode and deposit formation [15–21]. Cathodic or anodic deposits can be obtained depending on the charge of the inorganic particles or polymer macromolecules. EPD is an effective technique for the fabrication of advanced coatings. Various materials can be deposited by EPD, including oxides, hydroxides, borides, carbides, nitrides, carbonates, metals, alloys, and polymers [15,16]. The functionality of electrophoretically deposited coatings is numerous and includes electrical conductivity, superconductivity, magnetic, ferroelectric and piezoelectric behavior, corrosion resistance, biocompatibility, and other functional properties. Important advantages gained in using EPD have stimulated accelerated growth in the development and application of this method [15–21].

EPD has excellent potential for the shaping of ceramic materials and fabrication of thin films. However, the sintering of thick ceramic coatings deposited by EPD presents difficulties, related to the sintering shrinkage of the green coatings on dense substrates, difference in thermal expansion coefficients of the substrates and deposited materials, chemical reactions between the substrates and coatings and oxidation of the substrates during sintering at elevated temperatures. The co-deposition of ceramic materials and polyelectrolytes offers the important advantage of room temperature processing of the nanocomposite materials. Therefore the problems related to the high-temperature sintering can be eliminated.

Bath formulations for EPD include various additives, such as surfactants, electrolytes, and polymers. A number of advances have recently contributed to the development of stable suspensions of charged inorganic particles for EPD [21] and considerable attention has been given to the use of polyelectrolytes. It is important to note that electrophoresis results in the accumulation of charged particles or polymer macromolecules at the electrode. Deposit formation is achieved via precipitation and coagulation of the particles or polymers at the electrode surface. Recent studies highlighted the importance of electrode reactions, pH change, and interactions at the electrode surface for the EPD of materials from aqueous solutions. Different electrochemical strategies were developed in order to reduce the electrostatic repulsion of the polyelectrolytes at the electrode surface and achieve co-deposition of the polyelectrolytes and inorganic nanoparticles. The progress in synthesis and application of polyelectrolytes offers important opportunities in the development of advanced nanomaterials using EPD.

Polyelectrolytes

Polyelectrolytes are macromolecules that contain charged functional groups. Figure 1 shows the structures of simple commercial cationic polyelectrolytes used for the fabrication of organic–inorganic nanocomposites by EPD.

The polyelectrolytes can be categorized into two groups: strong polyelectrolytes, for which the degree of ionization is independent of the solution pH, and weak polyelectrolytes, for which the degree of ionization is determined by the solution pH. Poly(diallyldimethylammonium chloride) (PDDA), because of the quaternary ammonium group, is a strong polycation [21]. The degree of dissociation of the ionic groups of

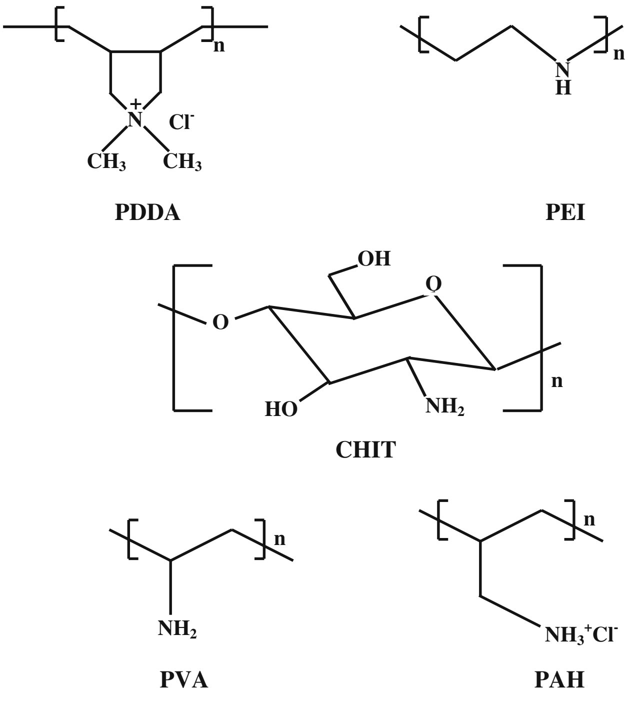

Fig. 1 Cationic polyelectrolytes: poly(diallyldimethylammonium chloride) (PDDA), poly(ethylene imine) (PEI), chitosan (CHIT), poly(vinylamine) (PVA), and poly(allylamine hydrochloride) (PAH)

PDDA is nearly pH independent in a wide pH range below pH 13.

Poly(ethylene imine) (PEI), chitosan (CHIT) poly(vinylamine) (PVA), and poly(allylamine hydrochloride) (PAH) are weak polyelectrolytes, containing amine groups. The amine groups in the branched PEI exist in primary, secondary and tertiary form [22, 23] in the approximate ratio of 1:2:1 with a branching site every 3–3.5 nitrogen atoms along any given chain segment.

PEI is a polybase. The primary amine groups, which are the chain terminating units, are the most basic and chemically reactive. The pH of an aqueous solution containing 1 wt.% PEI is about 11 and at this pH the PEI molecule has no charge [24, 25]. PEI adsorbs protons in the acidic solutions and becomes charged positively, according to the reaction:

$$\mathrm{PEI} + \mathrm{H_3O^+} \rightarrow \mathrm{PEI} - -\mathrm{H^+} + \mathrm{H_2O} \qquad (1)$$

The degree of protonation depends on the amount of acid added.

PVA is another weak polyelectrolyte which is positively charged in acidic solutions [26]. PVA has only primary amino groups linked directly to the main chain. The charge density of PVA can be changed by the pH variation from fully ionized ($\mathrm{pH} < 3$) to completely neutral ($\mathrm{pH} > 10$). A highly charged PVA has an extended coil conformation at pH 3. At $\mathrm{pH} > 9$ a polyelectrolyte chain collapses into a compact globule. Significant interest has been generated in the application of PAH for the polymer-mediated synthesis, surface modification of nanoparticles, and thin film deposition [27, 28]. The PAH macromolecules are positively charged below pH 8 [28].

CHIT is a natural cationic polysaccharide that can be produced by alkaline *N*-deacetylation of chitin [29]. Important properties of this material, such as chemical resistance, biocompatibility, advanced mechanical, antimicrobial, and thermal properties, have been utilized in biotechnology [30, 31]. Water soluble and positively charged chitosan can be prepared by the protonation of amine groups in acidic solutions [32, 33]:

$$\mathrm{CHIT} + \mathrm{H_3O^+} \rightarrow \mathrm{CHIT} - -\mathrm{H^+} + \mathrm{H_2O} \qquad (2)$$

The properties of CHIT in solutions depend on the molecular weight, the degree of deacetylation, pH and ionic strength. At pH 6.5, the primary amine groups of CHIT become deprotonated. As a result of the decreasing charge with the pH increase, dissolved CHIT usually flocculates at pH values about 6 [32, 33].

Several investigations described below have been focused on the applications of PDDA, PEI, PVA, CHIT, and PAH for EPD and the development of novel electrochemical strategies for the fabrication of novel nanocomposites. However, a large variety of other commercial and synthetic polyelectrolytes are currently available, including cationic and anionic polyelectrolytes [34]. The application of the polyelectrolytes for EPD gives researchers a strategy for forming advanced organic–inorganic nanocomposites for a variety of applications.

Polymer–metal ion complexes

Polymer–metal complexes are defined as complexes composed of a polymer ligand and metal ions in which the metal ions are attached to the polymer ligand by a coordinate bond. A polymer chelate is formed when a metal ion is added to a solution of a polymer ligand such as PEI, PVA, or CHIT. There are several excellent reviews of the materials science and applications of polymer–metal ion complexes [22, 35–37]. A soluble polymer–metal ion complex behaves as a polyelectrolyte in aqueous solutions. Therefore the use of polymer–metal ion complexes opens new opportunities in the application of EPD for the fabrication of novel nanocomposites. It is important to note that the protonation of PEI requires the use of significant amounts of acids, which can react with other components of the EPD bath. In contrast, the use of small additives of metal salts enables the formation of polymer–metal ion complexes, which can be utilized for EPD. Moreover, the use of polymer–metal ion complexes paves the way for the fabrication of nanocomposites by a combined method based on EPD and electrosynthesis of inorganic nanoparticles.

It is known that $\mathrm{Ni^{2+}}$, $\mathrm{Mn^{2+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Cd^{2+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Cr^{3+}}$, and some other ions have remarkable binding affinity towards PEI and its derivatives. The complexation of PEI occurs generally through intramolecular formation of chelates in the homogeneous solutions [37]. Figure 2 shows a structure of a charged PEI–$\mathrm{Cu^{2+}}$ complex.

It was demonstrated [37] that a wide variety of PEI–metal ion complexes can be obtained by loading the polymer with different metals. The extent of binding of the ions by PEI depends on the concentration of metal ions in solutions, PEI concentration, pH, and other factors. The pH value is a very important factor in polymer binding since protons and metal ions compete to be bound to the polymer. In the case of metal binding with polybases, like PEI [22], imino groups become

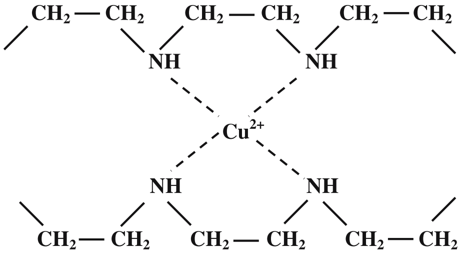

Fig. 2 Idealized structure of the PEI–Cu^{2+} complex

positively charged at low pH due to the protonation and thus unable to form chelates with cations. However, the binding capacity increases with increasing pH [22]. The evaporation of some PEI metal complex solutions can result in the formation of amorphous solids that are generally no longer soluble in water due to the cross-linking. Therefore, it is expected that the use of aqueous solutions of PEI–metal ion complexes for EPD can result in the formation of insoluble deposits. Chelating properties of PEI, PVA, CHIT, and other polyelectrolytes are currently under investigation for biomedical, catalytic, electrochemical, photochemical, and other applications [34–39].

Surface modification of particles using polyelectrolytes

The possibility to obtain stable suspensions and modify the electrokinetic properties of inorganic nanoparticles using polyelectrolytes is important for the application in EPD. Indeed, inorganic particles must be charged and stabilized in suspensions to allow the electrophoresis at a controlled deposition rate. The combination of electrostatic and steric stabilization provided by polyelectrolytes is advantageous for EPD. Note that the adsorption of ions from the solutions of metal salts can result in the electrostatic stabilization of inorganic particles. However, the addition of metal salts to the suspensions results in the decreasing thickness of the electrical double layer and lower suspension stability [21]. The steric stabilization provided by the polyelectrolytes is less sensitive to the increasing ionic strength.

A variety of polyelectrolytes have been studied for the stabilization of colloidal particles [21, 40–44]. The adsorption of polyelectrolytes has been used for particle charging, charge reversal and shifting the isoelectric points to lower or higher pH. Moreover, polyelectrolyte adsorption resulted in lower suspension viscosity and increasing electrophoretic mobility [44]. Recent studies revealed the effect of the molecular weight of polyelectrolytes on the properties of particle dispersions [41, 44]. It was shown that a higher molecular weight polyelectrolyte is more suitable to stabilize the suspensions of nanoparticles. The amount of polymer should be chosen such that a monolayer coverage with the polymer is achieved [44]. Further increase in the polymer concentration can result in particle flocculation [44].

The mechanism of polyelectrolyte adsorption on inorganic materials is the subject of intense experimental works [40, 45–48]. The adsorption of polyelectrolytes is a complicated phenomenon, which is influenced by the solution pH and ionic strength. The attraction of a polyelectrolyte to an oxide surface can be electrostatic, non-electrostatic or a combination of both. The investigations of the pH dependence of the adsorption of weak polyelectrolytes indicate a significant non-electrostatic affinity to the oxide surfaces [40, 47]. However, the studies [48] of PEI adsorption on zirconia showed the importance of the direct interactions of the amine groups and Zr, rather than an adsorption involving oxygen (Zr–O–Zr and Zr–O–H). The amount of the adsorbed polymer depends on the polymer-solvent and particle solvent interactions. Recent studies [49] highlighted the importance of copolymers of a block or graft type for the applications in EPD. It is suggested that the insoluble polymer can serve to anchor the copolymer molecules to the particle surface, whereas the chains of soluble polymers enable the steric stabilization [49].

The application of polyelectrolytes has created important opportunities in the EPD of ceramic materials [50–53]. Cationic and anionic polyelectrolytes were used for the charging and electrosteric stabilization of the suspensions. Further progress in the application of polyelectrolytes for the fabrication of ceramic and organoceramic films requires the understanding of the behavior of polyelectrolytes and inorganic particles with adsorbed polyelectrolytes in electric fields.

Electrophoretic mobility

The electrophoretic mobility of a rigid colloidal particle can be derived from the equation [54]:

$$\mu = \frac{2\varepsilon\varepsilon_0\zeta}{3\eta} f(\kappa a) \tag{3}$$

where ε is the dielectric constant of the solvent, ε_0 the vacuum dielectric permittivity, ζ the zeta potential, η the viscosity of the liquid, $1/\kappa$ the Debye length [54] and a is the particle radius. The function $f(\kappa a) = 1$ for particles that are much smaller than the Debye length ($\kappa a \ll 1$) and $f(\kappa a) = 1.5$ for particles that are large compared with $1/\kappa(\kappa a \gg 1)$.

The electrophoretic mobility of a spherical polyelectrolyte in which fixed charges are distributed at a uniform density ρ_{fix} can be derived from the equation [55]:

$$\mu = \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2}\left[1 + \frac{2}{3}\left(\frac{\lambda}{\kappa}\right)^2 \frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa}\right] \tag{4}$$

where $\lambda = (\gamma/\eta)^{1/2}$, γ is the frictional coefficient of the polyelectrolyte. In contrast to Eq. (3) for the electrophoretic mobility of a rigid particle, Eq. (4) does not include the ζ potential. Ohshima [55] proposed a general theory for soft particles (polyelectrolyte coated particles), which unites the two different theories of electrophoresis for rigid particles and polyelectrolytes. It was shown [55, 56] that when the polyelectrolyte layer is much thicker than the Debye length $1/\kappa$, the concept of zeta potential, which determines the electrophoretic mobility of hard particles, loses its meaning for the soft particles. Instead, the Donnan [55] equilibrium potential in the polyelectrolyte layer plays an essential role in determining the electrophoretic mobility of the soft particles.

The behavior of polyelectrolytes in electric fields exhibits a number of remarkable features, which are due to the interactions between the polyelectrolytes and counterions [57–61]. It was found that at a small field strength the condensed counterions are dragged along with the polyelectrolyte chain, while at an elevated field strength they start gliding along the chain [57]. The mobility is controlled by the electrostatic friction between the chain and condensed counterions. The effective charge of the strong polyelectrolytes is determined by the counterion condensation rather than the nominal charge density [58]. The dissociation of ionizable groups is one of the most important factors controlling the polyelectrolytes behavior in electric fields. It is in this regard that for weak polyelectrolytes the degree of dissociation and electrophoretic mobility depend on pH. The electrophoretic mobility of polyelectrolytes decreases with the increasing ionic strength [59]. The electrophoretic motion can result in stretching of the polyelectrolyte coils due to the hydrodynamic interactions and electric field [61].

Combined methods based on EPD of strong polyelectrolytes and electrosynthesis of inorganic nanoparticles

The ability to deposit composite materials depends on a thorough knowledge of the factors that control the deposition mechanism and structural evolution of the films. Electrophoresis requires the suspension to be colloidally stable. However, deposit formation is achieved via the coagulation of the colloidal particles accumulated at the electrode [21]. The formation of the composite deposits is influenced by the specific behavior and interactions of polyelectrolytes and inorganic particles at the electrode surface.

The charge compensation mechanism has been developed for the fabrication of organic–inorganic nanocomposites containing PDDA [62]. The method is based on the EPD of PDDA and cathodic electrosynthesis of metal oxides and hydroxides. PDDA macromolecules maintain a high positive charge in acidic bulk solutions as well as in basic conditions at the cathode surface. As a result of the strong electrostatic repulsion of the PDDA macromolecules, no deposit formation was achieved from the aqueous PDDA solutions. However, co-deposition of PDDA and the colloidal particles of metal oxides or hydroxides was observed [63–76]. Several initial investigations have been undertaken on the aqueous co-deposition of PDDA and inorganic materials with relatively low isoelectric points, such as oxides/hydroxides of Zr, Ce [62, 65, 68, 72]. It was suggested that the deposit formation is driven by Coulombic attraction between two charged species: cationic PDDA and the negatively charged colloidal particles formed at the electrode surface [21]. Further investigations showed the possibility of co-deposition of other inorganic materials with larger isoelectric point, such as hydroxides of Ni and Co [73, 74]. It was shown that the heterocoagulation of PDDA and inorganic nanoparticles is driven not only by charge attraction, but also by other interactions, such as hydrogen bonding and ion-dipole interactions. Such interactions are significant contributing factors in the deposit formation and determining the stability and microstructure of the deposit. Continuing work on the process resulted in the fabrication of superparamagnetic films [71] based on Fe_3O_4. The combined method was proven to be an important technique for the development of fuel cells and advanced coatings for corrosion protection of metals [65, 67–70, 72]. Figure 3 shows SEM picture of a zirconia–PDDA coating on a porous Ni–yttria stabilized zirconia substrate, developed for the fabrication of fuel cells.

Several investigations have been undertaken on the study of the deposition mechanism, kinetics of deposition, microstructure, and composition of the nanocomposite films [62–65, 74–76]. It was shown that the amount of the deposited material and deposit composition can be controlled by the variation of deposition time, current density, and PDDA concentration in the solutions. Composite coatings of controlled thickness were obtained on conducting substrates of complex shape, such as carbon fibers and felts. Figure 4 shows SEM pictures of zirconia–PDDA coatings of different thickness on carbon fibers.

The proposed method enabled the electrosynthesis of nanoparticles in-situ in a PDDA matrix, preventing particle agglomeration. It was demonstrated that the size of the inorganic nanoparticles and properties of the composite materials be varied by the variation of PDDA concentration in solutions used for the deposition [66, 67]. The possibility to control the size of nanopaticles on the scale of several nanometers paves a way for the fabrication of advanced nanocomposites with important magnetic, optical, and catalytic properties. Another important finding was the influence of PDDA on the crystallization behavior of the inorganic nanoparticles formed by electrosynthesis in situ in the PDDA matrix. It was observed that PDDA promotes the low temperature crystallization of inorganic nanoparticles [66, 70, 71].

The co-deposition of PDDA and oxides is also important for the fabrication of thick oxide films by electrodeposition. The limited thickness achievable without crack formation is one of the factors that discourage the industrial applications of cathodic electrosynthesis. Another problem is related to the low adhesion of the negatively charged oxide/hydroxide nanoparticles formed in the high pH region at the cathode surface. The PDDA acts as a binder, promoting better adhesion of the deposits and preventing cracking. Moreover, the negative charge of the inorganic nanoparticles can be compensated by the positive charge of PDDA. Recent studies showed the possibility to obtain relatively thick ceramic films using small PDDA additives as a binder [70].

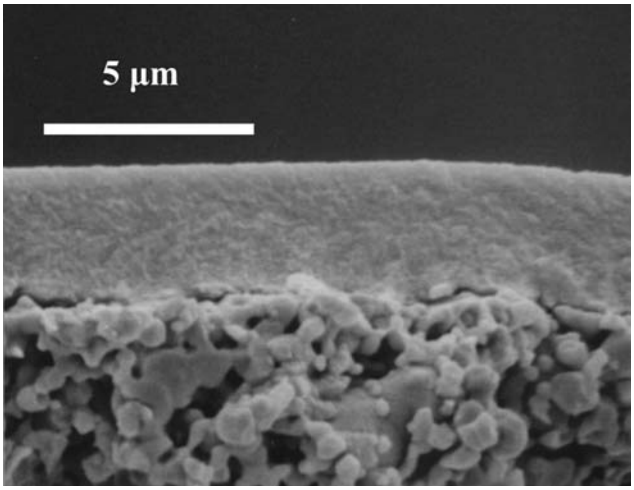

Fig. 3 Zirconia–PDDA film on a porous nickel–yttria stabilized zirconia substrate

Combined methods based on EPD of weak polyelectrolytes and EPD of inorganic nanoparticles

EPD can be applied to both: polyelectrolytes and inorganic nanoparticles for the fabrication of composite materials. The use of weak polyelectrolytes provides an opportunity to use pH as a tool for the manipulation of the charge and solubility of the polymers. Significant interest has been generated in the application of CHIT for the fabrication of advanced films by EPD [77–80]. CHIT has pH-responsible electrostatic and solubility properties that allow it to be deposited on the cathode surface [77–81]. The protonated CHIT is a soluble cationic polyelectrolyte which can be neutralized by the

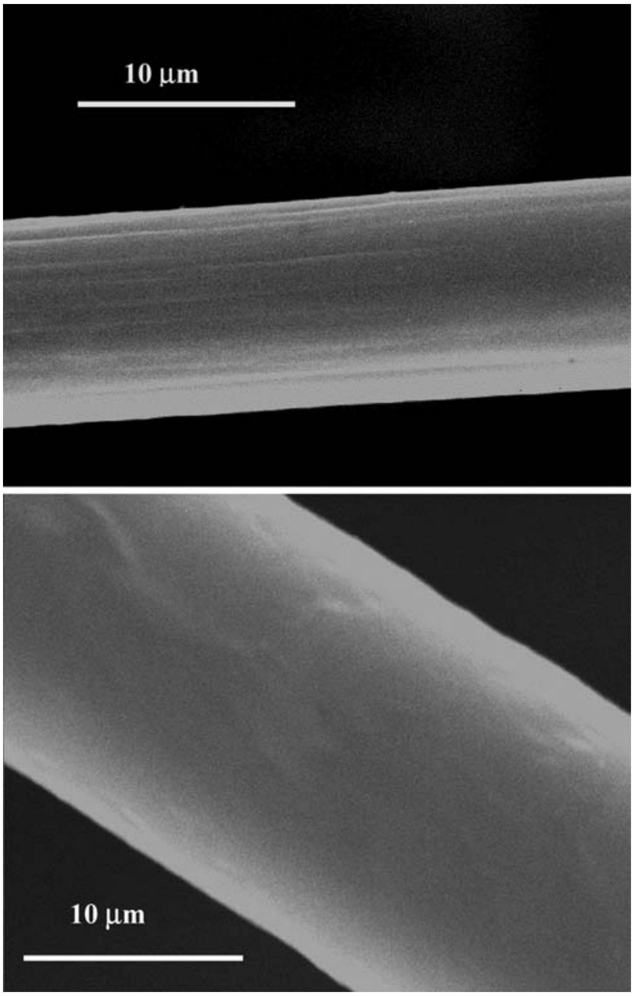

Fig. 4 Zirconia–PDDA coatings of different thickness on carbon fibers

electrogenerated base to form an insoluble deposit at the cathode surface:

$$\mathrm{CHIT}--\mathrm{H}^{+}+\mathrm{OH}^{-}\rightarrow\mathrm{CHIT}+\mathrm{H_2O} \tag{5}$$

The thickness of the CHIT films prepared by EPD was varied in the range from tens of nanometers to micrometers depending on the deposition time, applied voltage, and CHIT concentration in the solutions [77]. CHIT films were deposited selectively onto patterned surfaces for the application in biosensors [77–79]. Several investigations were focused on the electrophoretic co-deposition of CHIT and nanoparticles. It was shown that CHIT promotes the EPD of the latex nanoparticles, which were uniformly distributed in the CHIT film [80]. The mesh sizes of polymer networks are on the order of 10–100 nm and particles below this size range could be attached to CHIT prior to deposition [80]. In another study [82] $\mathrm{MnO_2}$ nanoparticles with particle size of 20 nm were used for the fabrication of nanocomposite CHIT–$\mathrm{MnO_2}$ films. The results of this work indicate that the thickness and composition of the prepared films can be varied by the variation of deposition time and $\mathrm{MnO_2}$ concentration in the solutions used for EPD. The composition and properties of the films were optimized for the application in the glucose biosensors.

Recently the feasibility of the fabrication of hydroxyapatite–CHIT coatings by EPD has been demonstrated [83, 84]. The average length of the needle-like HA crystals prepared by a chemical precipitation method was about 200 nm. The nanocomposite coatings of various thicknesses in the range up to 50 μm were obtained on Ti, stainless steel, and other conducting substrates. The deposit composition was varied by the variation of HA concentration in the solutions. It was shown that obtained coatings provide corrosion protection of metals in the simulated body fluid solutions. The studies revealed preferred orientation of HA nanoparticles with *c*-axis parallel to the coating surface. The orientation of HA in the nanocomposites prepared by EPD was attributed to the interactions of chitosan and HA. It is important to note that the preferred orientation of HA nanocrystals plays an important role in bone properties. The possibility of variation of the hydroxyapatite content and control the particle orientation is important for the fabrication of biomedical implants. The method offers the advantages of room temperature fabrication of the composite coatings. Therefore, the problems related to the sintering of electrophoretic HA deposits can be eliminated. It is expected that HA and chitosan can provide a combination of biocompatibility, corrosion protection, antimicrobial, and other functional properties for the applications in biomedical implants.

Gorelikov and Kumacheva [85] discovered a possibility of the fabrication of composite materials based on poly(vinyl acetate-*co*-crotonic acid) (PVAC) and nanoparticles (NPs) of semiconductors CdS and CdTe. PVAC was deprotonated and dissolved in basic solutions to enable the deposition by anodic EPD. In the proposed method 1-thioglycerol and thioglycolic acid were used as capping and charging agents. The method enabled the formation of the composite films containing well-dispersed NPs in an insoluble polymer matrix. The EPD method has been utilized for the fabrication of patterned films. The results of this work pave the way for the EPD of nanocomposite films containing quantum dots.

Many studies have focused on the use of PEI for the charging of inorganic particles and deposition of nanocomposites by EPD [50, 53, 86]. Hasegawa et al. used PEI to control the surface charge of silica particles. The weight of silica particles deposited on the cathode was maximized at 0.01 mass% PEI in the solutions. The increase in the PEI concentration in solutions resulted in the decreasing deposition rate and particle sedimentation. When PEI content was 1 mass%, the deposits included the regions of the aggregated particles and regions of the deposited PEI without nanoparticles.

It is important to note that PEI must be protonated for the applications in EPD. As pointed out above the PEI protonation requires the use of relatively large amounts of acids, which can react with powders and reduce the suspension stability due to the increasing ionic strength of the solutions. Another approach is based on the use of polymer–metal ion complexes and electrosynthesis of nanoparticles in-situ in a polymer matrix.

Combined methods based on EPD of weak polyelectrolytes and electrosynthesis of inorganic nanoparticles

A critical obstacle in assembling and maintaining a nanoscale material is its tendency to aggregate. To overcome this, the nanoparticles can be formed by electrosynthesis in situ in a polymer matrix using the combined deposition method based on the use of cationic polyelectrolytes or polymer–metal ion complexes.

In the cathodic electrosynthesis method, the high pH of the cathodic region brings about the formation of colloidal particles, which precipitate on the electrode. The charge of weak cationic polyelectrolytes decreases with the increasing pH. Therefore, the pH increase at the cathode surface results in a decreasing charge and promotes the deposition of weak polyelectrolytes. Moreover, EPD of polyelectrolytes can be combined with electrosynthesis of inorganic nanoparticles to form nanocomposite films.

In a series of papers [73–76, 87–91] nanocomposite films containing nanoparticles of Fe, Co, Ni, Mn, Ce, Zr, La oxides/hydroxides in a PEI matrix were deposited on various conducting substrates. Figure 5 shows zirconia–PEI deposit on a carbon fiber. The deposition method enabled the formation of relatively uniform coatings.

The EPD of PEI–Mn complexes has been utilized for the deposition of nanocomposites containing Mn_3O_4 nanoparticles [90]. The proposed method offers important advantages for the fabrication of electrode materials for electrochemical supercapacitors compared to the anodic deposition of MnO_2. The use of polychelates enabled the formation of magnetic $NiFe_2O_4$ films, containing nanowires [88].

The deposition mechanism was discussed in several papers [73, 74, 76, 91]. It is suggested that PEI macromolecules acquire a positive charge as a result of complex formation with metal ions such as Ni^{2+}, Co^{2+}, Mn^{2+}, and Fe^{3+}. In this case, electric field provides the electrophoretic motion of the polymer–metal ion complexes towards the electrode surface. It is suggested that these ions participate in cathodic reactions to form nanoparticles of metal oxides/hydroxides. Free metal ion species, which are not complexed by PEI also exist in solutions and contribute to the elecrosynthesis of the inorganic phase. However, the mechanism of deposition is not fully understood. A difficulty comes from reactions in the solutions, which complicate the complexation chemistry and compete with complex formation. It is known that metal cations in solutions are solvated by water molecules and show a tendency to release protons. In zirconyl chloride solutions, the formation of tetramers $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ can be expected [21]. The tetramers release protons:

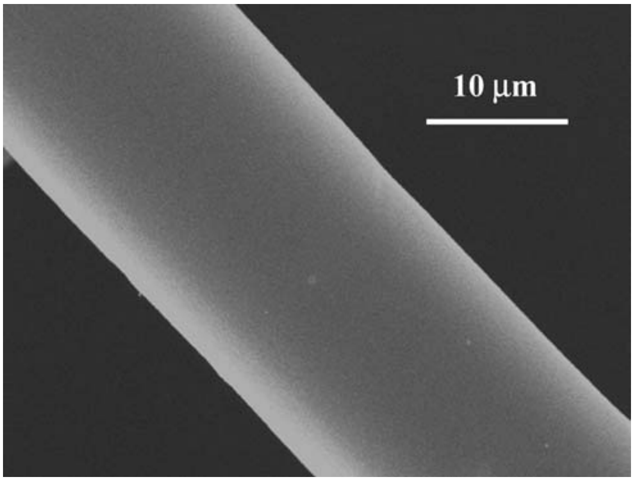

Fig. 5 Zirconia–PEI coating on a carbon fiber

$$[Zr_4(OH)_8(H_2O)_{16}]^{8+} \leftrightarrow [Zr(OH)_{2+x}\cdot(4-x)H_2O]_4^{(8-4x)+} + 4xH^+ \qquad (6)$$

The addition of PEI, which is a polybase, results in shifting the equilibrium to the right. It is suggested that PEI can acquire a positive charge as a result of complex formation with metal ions and partial protonation in the acidic solutions of metal salts.

Several investigations were focused on the fabrication of nanocomposites containing PAH [91–93]. The method is based on the EPD of cationic PAH and electrosynthesis of inorganic nanoparticles. The interest in the electrosynthesis of inorganic particles in a PAH matrix stems from the recent discovery of the room temperature crystallization of complex metal oxides under the influence of PAH [14]. The EPD method enabled the formation of superparamagnetic films containing iron oxide nanoparticles in a PAH matrix [92]. The results of the investigations [73–76, 87–93] indicate that polymer content in the composite films can be varied in the range 0–70 mass% by the variation of the polymer concentration in the solutions. Figure 6 compares the results of the thermogravimetric analysis of cobalt hydroxide films and composite films containing cobalt hydroxide and PVA. The total weight loss of 27.8 mass% for the cobalt hydroxide films is attributed to the dehydration. The composite films show weight loss of 46.6 mass%. The additional weight loss is attributed to burning out of PVA.

Significant interest has been generated in the fabrication of nanocomposites containing CHIT [93–95]. Cathodic electrosynthesis of calcium phosphates was combined with EPD of CHIT to form nanocomposites. It was found that the incorporation of CHIT influenced the electrosynthesis and crystallization of calcium phosphate. The calcium phosphate/chitosan coatings were converted to hydroxyapatite/chitosan coatings after heating in NaOH solutions at 95 °C. The composite coatings contained from 1 to 15 mass% CHIT [95]. The composite coatings showed improved biocompatibility and better adhesion compared to the pure calcium phosphate coatings.

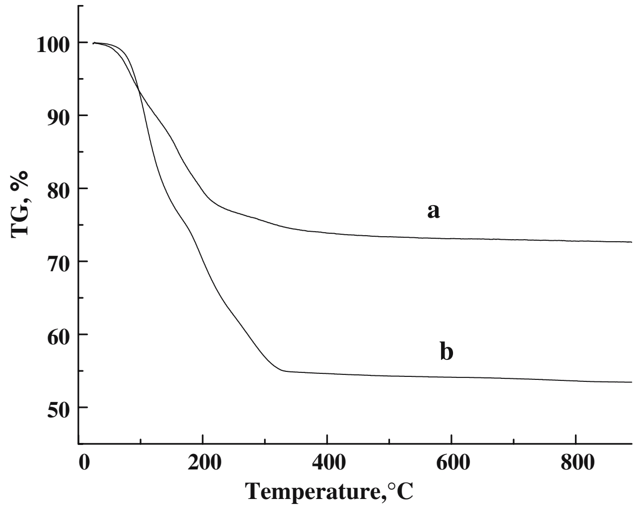

Fig. 6 Results of thermogravimetric analysis of cobalt hydroxide films (**a**) and composite cobalt hydroxide–PVA films (**b**) prepared from 5 mM $CoCl_2$ solutions in a mixed ethanol–water solvent (10% water) without PVA (**a**) and containing 0.5 g/L PVA (**b**)

Conclusions and future trends

Various electrochemical methods based on EPD of polyelectrolytes, polymer–metal ion complexes and inorganic nanoparticles are currently under investigation for the fabrication of the nanocomposite coatings. The combined methods based on the electrosynthesis and EPD open a new avenue for the fabrication of nanostructured materials. One of the important possibilities provided by such methods is the ability of agglomerate-free processing of nanostructured materials. The size of the inorganic particles, formed in situ in a polymer matrix, can be varied on the nanometric scale. Therefore, this approach can be extended to accommodate the formation of quantum dots.

Further development of novel methods based on EPD opens new opportunities in the formation of superparamagnetic films, piezoelectric composites, sensors, thin films for catalytic and electrochemical applications. Composite films based on polyelectrolytes are also of great importance for nanoengineering of particle surfaces, surface modification of fibers, and fabrication of advanced fiber reinforced composites. There is a growing interest in the biomedical application of nanocomposite films.

The majority of studies to date involved simple commercially available cationic polyelectrolytes. The use of advanced polyelectrolytes with important functional properties will result in the development of novel nanomaterials for the applications in various devices. Further progress in the application of polymer–metal ion complexes for EPD can result in new and interesting developments in nanotechnology. It is expected that future research will to a great extent continue to be focused on the development of novel electrochemical strategies and application of new polymer materials. It is foreseen that the realm of new technological applications of EPD will continue an accelerated growth.

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