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Funkcionalizacija tekstilij z nano TiO_2 in SiO_2 prevlekami

Pregledni znanstveni članek

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Functional Coatings of Textiles Based on TiO_2 and SiO_2 Nanoparticles

Review

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Abstract

Recently functionalisation of different materials by nanocoating is being the target idea of several research projects, however the technology is only limited applied for textiles although it promises a lot. Only functional coatings of textiles based on TiO_2 and SiO_2 nanoparticles are reviewed in this article however, it should be emphasized that different other nano-coatings are of significance likewise.

Key words: nanotechnology, nanocoatings, TiO_2 nanoparticles, SiO_2 nanoparticles

1 Introduction

Recently nanotechnology is introduced for preparing functional textiles. It employs physical or chemical techniques to construct materials, devices or systems on a nanometer scale, thus nanostructured fibres are those with at least one dimension in the range 1–1000 nm. It is a technology that can significantly improve properties of materials compared with those of conventional ones. This remarkable properties improvement is attributed to the significant increase in the fibre's boundary area or its func-

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Izvleček

Funkcionalizacija različnih materialov z uporabo prevlek iz nanodelcev je v zadnjem času predmet mnogih raziskav, vendar pa to tehnologijo na tekstilnem področju uporabljajo le v omejenem obsegu, in to kljub njenemu velikemu potencialu. Članek zajema pregled raziskav s področja nanoprevlek vlaken z delci titanovega in silicijevega dioksida, treba pa je poudariti, da so prevleke iz drugih anorganskih nanodelcev na vlaknih prav tako pomembne, saj z njimi dosegamo nove funkcionalne lastnosti tekstilij.

Ključne besede: nanotehnologija, nanoprevleke, TiO_2 nanodelci, SiO_2 nanodelci

1 Uvod

Nanotehnologija, ki združuje kemijske in fizikalne postopke priprave materialov, naprav ali sistemov nano velikostnega reda, se v zadnjem času vse bolj uporablja tudi v razvoju funkcionalnih tekstilij. Z nanotehnološkimi postopki lahko znatno izboljšamo lastnosti konvencionalnih vlaknatih materialov, kar je posledica povečane funkcionalne površine tekstilije. Tekstilne nanomateriale delimo na nanovlakna, nanokompozite in tekstilije s prevlekami iz nanodelcev [1].

Priprava nanoprevlek na vlaknih ima številne prednosti pred konvencionalnimi apretirnimi postopki, saj so za doseganje enakih učinkov zadostne manjše količine aditivov, poleg tega pa postopki nanoplastenja omogočajo doseganje več funkcionalnosti na tekstilnem substratu sočasno. Prevleke z oksidnimi delci (na primer si-

tional surface. In the textile sector, nanotechnology provides opportunities by creating new materials such as nanofibres, nanocomposites and nanocoated textiles [1].

Replacement of certain conventional finishing procedures with employment of inorganic coatings may prove beneficial, since low quantities of additives are required and various combinations of different functionalities can be simultaneously imparted to a textile substrate. Coatings of particulate oxides, such as silica nano particles, are stable against light, heat, chemical and microbial attack and can, at the same time, act as functional coatings or as carriers for embedded functional additives and inorganic particles or as a base layer for subsequent functionalisation with compounds, which contribute different properties (silanes, fluorinated, phosphorous compounds, etc).

Various functionalities can be enhanced or imparted to a textile material by applying different coatings of nano particles [2, 3]; improved abrasion stability, resistance to thermal deg-

licijevega dioksida), ki so odporne proti svetlobi, toploti, delovanju kemikalij in mikrobov, predstavljajo funkcionalno prevleko vlakna ali pa so osnova za nadaljnjo funkcionalizacijo.

Z nanoprevlekami tekstilij dosegamo različne lastnosti [2, 3], kot so na primer izboljšana obstojnost proti drgnjenju, odpornost proti temperaturnemu razpadu [4, 5, 6], različne odbojne lastnosti (hidrofobnost, oleofobnost, odbojnost za madeže), samočistilne lastnosti, absorpcija UV-svetlobe [7, 8, 9], električna prevodnost, protimikrobna aktivnost itd. [10, 11, 12]. Takšne obdelave tekstilnih materialov so zanimive predvsem za področje tehničnih tekstilij [13].

Članek zajema pregled raziskav na področju prevlek iz delcev silicijevega dioksida in titanovega dioksida. Prevleke iz nanodelcev je mogoče oblikovati neposredno na površini tekstilnega substrata s sol-gel postopkom, z adsorpcijo predhodno oblikovanih delcev iz disperzij ali pa z vključevanjem delcev v mrežno strukturo silike na površini vlakna.

2 Sol-gel postopek

Sol-gel postopek je ena najuporabnejših tehnik za izdelavo tankih filmov [14, 15]. Prednostna lastnost sol-gel postopka je

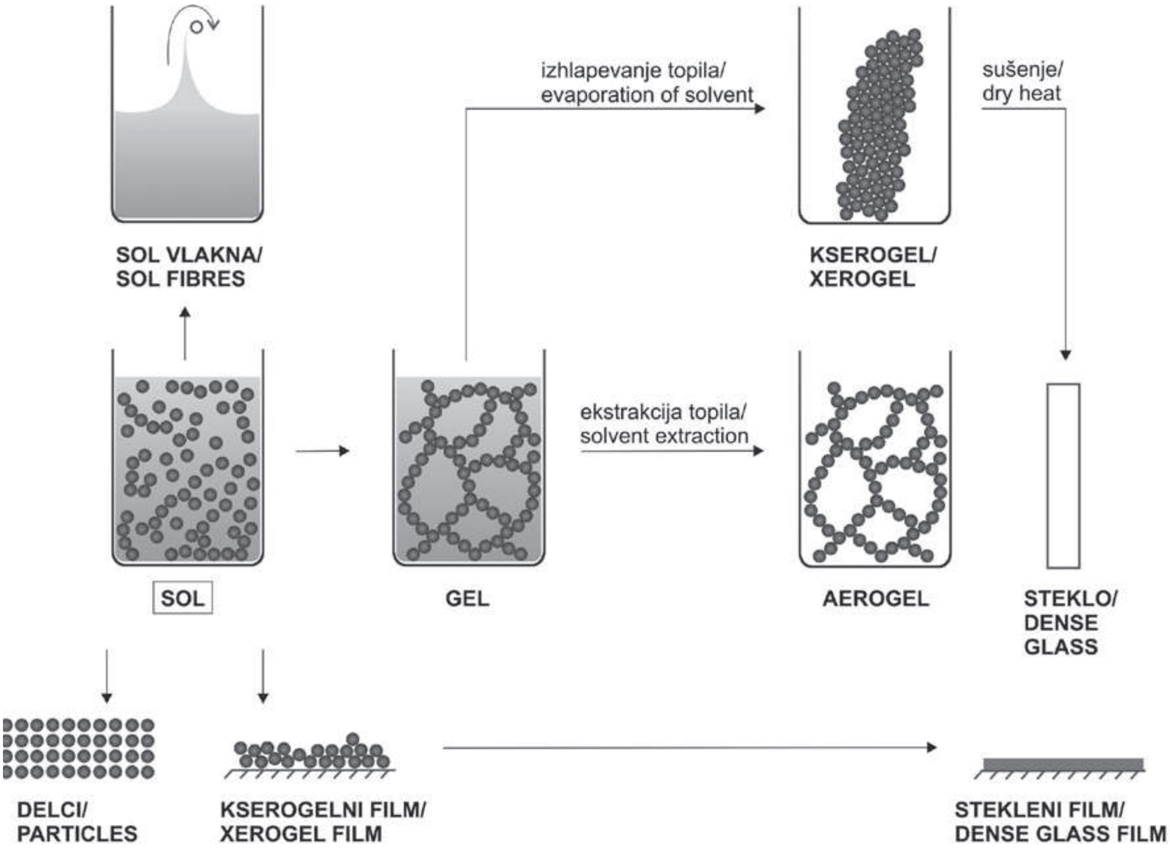


Figure 1: Scheme of the different stages of the sol-gel processing [16]

radiation [4, 5, 6], various repellent properties (water, oil, soil), self-cleaning properties, absorption of UV light [7, 8, 9], electrical conductivity, antimicrobial activity [10, 11, 12]. Such treatments of textiles is especially interesting for the technical textile sector [13].

The article comprises mainly the work done in the field of coatings with silica and titania nanoparticles that are being applied to textile materials for various purposes. Coatings in these cases consist of particles and are either synthesized in-situ on the textile materials' surface via sol gel process, deposited on the textile materials' surface from dispersions or entrapped in the silica network, grown on the surface.

2 Sol-gel process

Sol-gel process is one of the most applicable techniques to manufacture thin films [14, 15]. One of the most advantageous and attractive characteristics of the sol-gel process is the ability to control and manipulate composition and microstructure of the material at the molecular level and at room temperature. Since a sol is defined as a colloidal dispersion of particles in a liquid and gel as a substance that contains a continuous solid skeleton, which serves as an entrapment for continuous liquid phase, than the definition for sol-gel processing is the

predvsem možnost nadzorovanja sestave in mikrostrukture materiala na molekularnem nivoju in pri sobni temperaturi. Sol je definiran kot koloidna disperzija delcev v tekočem mediju, gel pa kot snov, sestavljena iz trdne faze, ki služi kot kletka za tekočo fazo; sol-gel postopek bi tako lahko opisali kot rast koloidnih delcev in njihovo povezovanje v gel. Med sol-gel postopke spadajo tvorbe tankih filmov, vlaken in delcev, kljub temu da v nekaterih primerih, na primer pri delcih, ni faze geliranja (slika 1) [16, 17].

2.1 Sol-gel postopek za izdelavo delcev silicijevega dioksida – SiO_2

Najbolj znan primer uporabe sol-gel postopka je izdelava silicijevega dioksida (silike), in to v obliki delcev, tankih filmov ali gelov. Stöber in sodelavci [18] so leta 1968 objavili metodo za izdelavo sferičnih in monodisperznih nanodelcev silicijevega dioksida; raztopino silicijevega alkoksida v alkoholu in vodi kataliziramo z alkalijo ali kislino. Med najobičajnejše prekurzorje za izdelavo silikatov spadata TMOS (tetramethoxysilane; $Si(OCH_3)_4$) in TEOS (tetraethoxysilane; $Si(OCH_2CH_3)_4$). Sinteza silike v večini primerov poteka preko hidrolize raztopine alkoksida v alkoholu, ki ji sledi reakcija kondenzacije [19, 20, 21, 22, 23, 24, 25]. Sol-gel postopek lahko opišemo z naslednjimi tremi reakcijami:

$$\equiv Si{-}OR + H_2O \longleftrightarrow \equiv Si{-}OH + ROH \tag{1}$$

$$\equiv Si{-}OH + RO{-}Si \longleftrightarrow \equiv Si{-}O{-}Si\equiv + ROH \tag{2}$$

$$\equiv Si{-}OH + HO{-}Si \longleftrightarrow \equiv Si{-}O{-}Si\equiv + H_2O \tag{3}$$

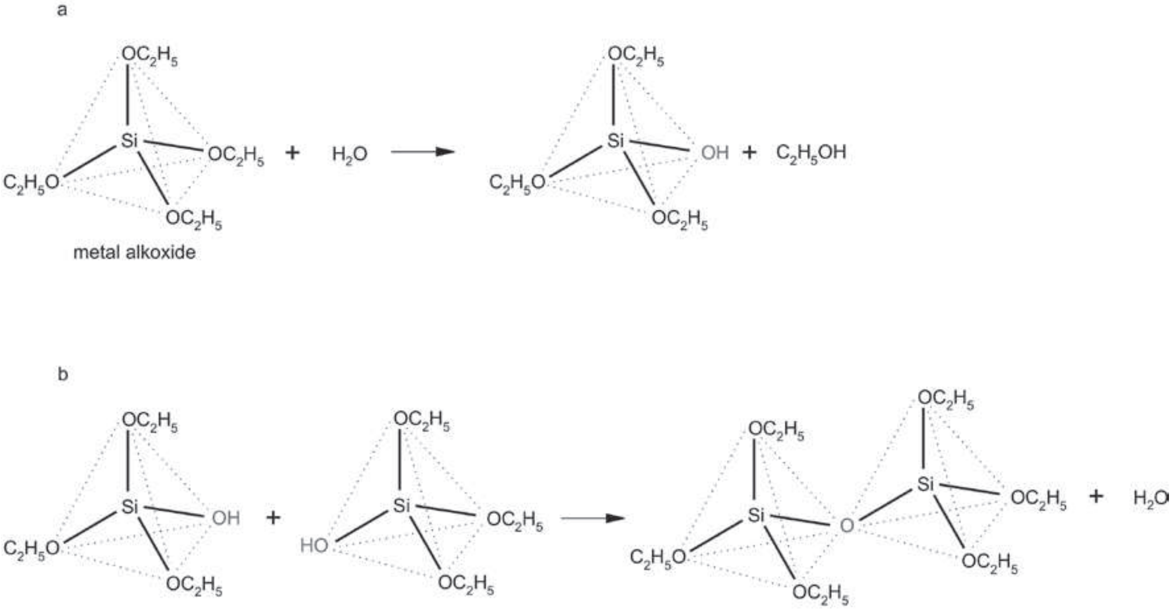


Figure 2: Reactions of a) hydrolysis and b) polycondensation of a silicon precursor

growth of colloidal particles and their linkage together to form a gel. Formation of films, fibres and particles are all considered sol-gel processes, even though gelation may not occur, as in the case of particles formation (Fig. 1). When a sol is composed of extended species, rather than particles, formation of fibres results [16, 17]. Depending on the precursor used, various inorganic oxides can be produced.

2.1 Sol-gel process for formation of silica particles – SiO_2

The most prominent example of a sol-gel process is formation of silica; whether in the form of particles, thin films or gels. Stöber et al. [18] reported a method for synthesis of spherical and monodisperse silica nano particles in 1968. Silicon alkoxide is dissolved in aqueous alcohol solution and the synthesis is catalysed by base or acid. Most commonly used precursors in sol-gel processing of silicates are the following metal alkoxide precursors; TMOS (tetramethoxysilane; $Si(OCH_3)_4$) and TEOS (tetraethoxysilane; $Si(OCH_2CH_3)_4$). Silicate materials are most often synthesized by hydrolysis of the alkoxide, dissolved in an alcohol, followed by a reaction of condensation [19, 20, 21, 22, 23, 24, 25]. Sol-gel process can be described with the following three reactions: (Eq. 1, Eq. 2, Eq. 3).

The hydrolysis reaction (eq 1) replaces alkoxide groups with hydroxyl groups, while subsequent condensation reactions involving the silanol groups produce siloxane bonds and by-products alcohol (eq 2) or water (eq 3). Schematic presentation of the hydrolysis and polycondensation of precursor molecules is given in Fig. 2.

Depending on the type of catalyst used, basic or acidic, different forms of the final product are produced; spherical particles in former case and films in the latter. Under basic conditions hydroxyl anions attack Si directly, while in the case of acid catalysis, protonation of OH or OR substituents attached to Si occurs [19].

2.2 Titania particles – TiO_2

Photocatalytically active (PCA) coating compositions containing a photocatalytically active oxide of a transition metal (MO) or (MO_2) such as titanium dioxide (TiO_2) or zirconium oxide (ZrO_2) catalyst for producing

Pri reakciji hidrolize (enačba 1) se zamenjajo alkoksidne skupine s hidroksilnimi, pri nadaljnjih reakcijah kondenzacije, pri katerih sodelujejo silanolne skupine, pa se tvorijo siloksanske vezi ter stranska proizvoda alkohol (enačba 2) in voda (enačba 3). Na sliki 2 je predstavljena shema reakcij hidrolize in polikondenzacije molekul prekurzorja.

Oblika končnega produkta sol-gel postopka je odvisna od vrste katalizatorja, ki ga uporabimo; v primeru alkalnega katalizatorja nastanejo sferični delci, v primeru kislega pa filmi. V alkalnih pogojih pride do neposredne reakcije med hidroksilnimi anioni in Si, medtem ko v primeru kislo kataliziranega postopka pride do protonacije substituent (skupine OH ali OR) na Si [19].

2.2 Delci titanovega dioksida

Fotokatalitično aktivni oksidi prehodnih kovin (MO ali MO_2), kot sta titanov dioksid (TiO_2) ali cirkonijev dioksid (ZrO_2), reagirajo z organskimi snovmi ali umazanijami iz okolja in jih pod vplivom delovanja sončne svetlobe (še posebej ultravijoličnega sevanja) razgradijo. Organske nečistoče se razgradijo na preproste anorganske komponente, na primer CO_2 in H_2O ter različne mineralne kisline. Razgradne produkte odstranijo toplota, veter in/ali dež. Prevleke so samočistilne zaradi zmogljivosti, ki je odvisna od stopnje fotokatalitične aktivnosti katalizatorja MO_2, ta pa je neposredno sorazmerna s celotno specifično površino delcev MO_2, ki so jim izpostavljene nečistoče [26, 27].

TiO_2 obstaja v treh kristalnih strukturah: rutil, brukit in anataza. Kristalna struktura in velikost kristalov sta pomembni lastnosti TiO_2 prevlek, saj uravnavata učinkovito absorpcijo UV-fotonov [30, 39, 40]. Ker je od vseh treh oblik brukit najbolj nestabilen in ga je zelo težko pripraviti [28], se ta kristalna oblika redko uporablja. V literaturnih virih so opisane predvsem raziskave fotokatalitičnega delovanja TiO_2 na osnovi anatazne polimorfne oblike ali čiste rutilne oblike oziroma mešanice obeh [28]. Anatazna kristalna oblika ima višjo fotokatalitično aktivnost kot rutilna oblika [29, 30, 31, 32, 33, 34, 35, 36, 37] ter širšo vrzel (3,2 eV v primerjavi s 3,0 eV rutilne oblike), višji Fermijev nivo in višjo mobilnost nosilcev naboja v primerjavi s termodinamično stabilnejšo obliko rutil [38]. Zato je kristalna oblika anataza preferenčna oblika za fotokatalitične procese.

TiO_2 lahko sintetiziramo s pomočjo različnih metod, kot so kondenzacija z inertnim plinom [41], sinteza z oksidacijo $TiCl_4$ [42], hidrotermična sinteza iz kovinskega Ti [43] in hidrolitično obarjanje titanovega alkoksida oziroma titanove soli (sol-gel metoda) [44]. Izjemno zanimanje je za sol-gel način, saj dopušča oblikovanje strukture z izbiro prekurzorja in s spreminjanjem procesnih pogojev [44] ter zagotavlja odlično kemijsko homogenost delcev [45, 46, 47, 48, 49, 50].

Poleg TiO_2 se lahko kot fotokatalizatorji uporabljajo tudi kovinski sulfidni polprevodniki, kot so CdS, CdSe ali PbS, ki pa so premalo stabilni, vsaj v vodnih medijih, saj so podvrženi fotoanodni koro-

transparent self-cleaning coatings, such as for glass windows, which react with and decompose organic compounds or pollutants, deposited thereon from the environment, under the effects of exposure to sunlight, particularly the ultraviolet radiation contained therein. The organic pollutants are decomposed to simple inorganic compounds such as CO_2, H_2O and various mineral acids, which re-enter the atmosphere and/or wash away under the effects of heat, wind and/or rain, so that the coatings are self-cleaning with an efficiency which is dependent upon the degree of photocatalytic activity of the MO_2 catalyst, which is directly proportional to the total surface area of the MO_2 particles to which the pollutants are exposed [26, 27].

ziji [51, 52]. Ti materiali so tudi toksični. Prav tako so tudi železovi oksidi podvrženi fotokatodni koroziji in zato niso primerni polprevodniki [53]. Vrzel v frekvenčnem pasu ZnO (3,2 eV) je enaka, kot jo ima anataza, vendar je ZnO nestabilen v vodnih raztopinah [54], v katerih na površini delcev nastaja $Zn(OH)_2$, kar povzroča deaktivacijo katalizatorja [51]. Kot potencialni fotokatalizator so raziskovali tudi WO_3, vendar je manj fotokatalitično aktiven kot TiO_2 [54].

3 Prevleke iz silicijevega dioksida na tekstilnih materialih

Li in drugi avtorji [55] so na različnih tkaninah (bombaž, lan, PA, PET) tvorili tanke plasti silicijeva dioksida, da bi raziskovali interakcije in adhezije delcev silike na vlakna. Prišli so do zaključka, da kemijska sestava in struktura vlaken vplivata na adhezijo plasti

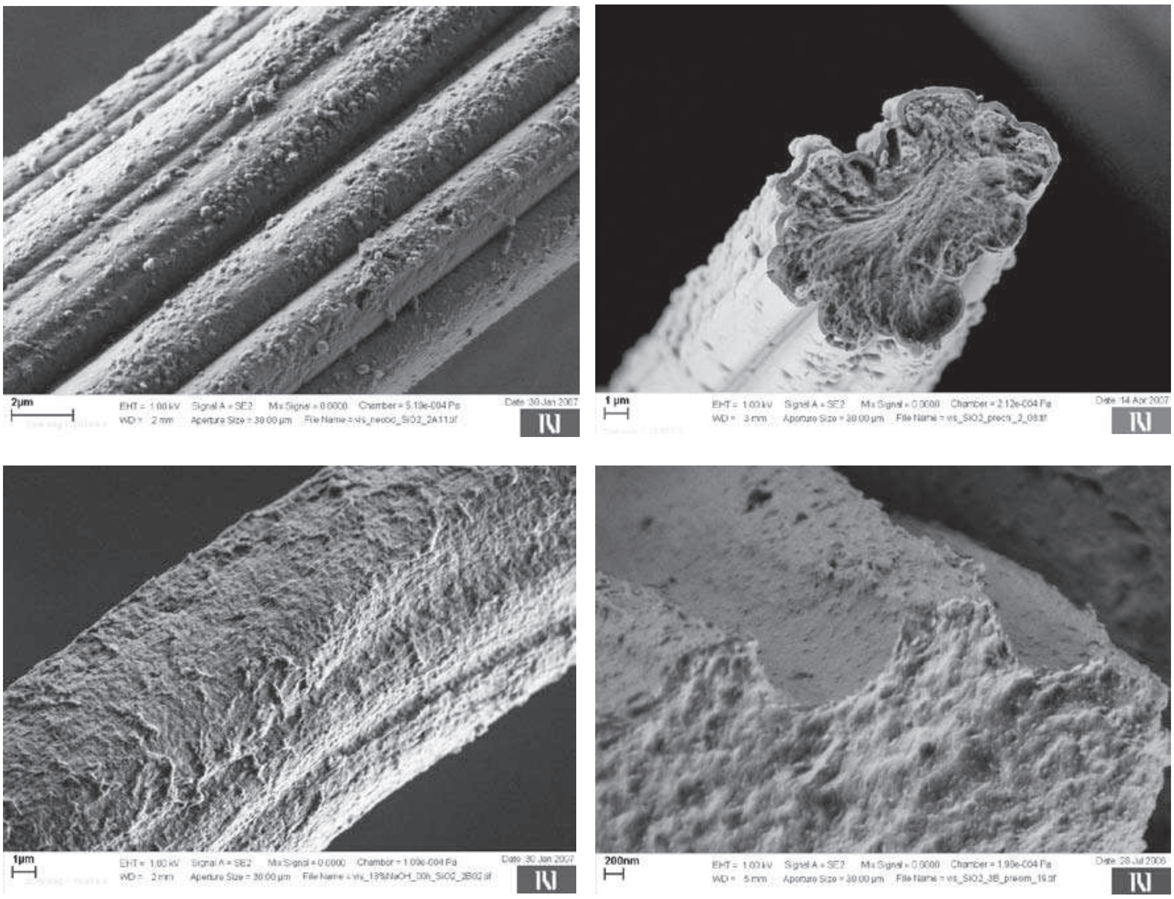


Fig. 3: Effect of pre-treatment of cellulose fibres on subsequent silica growth a) SEM image of a silica layer, formed on a raw, untreated fibre; occurrence of crack and agglomerates, b) cross-section of a raw, untreated fibre with formed silica layer; thick crust with thickness of about 500 nm, c) image of a silica layer, formed on a NaOH-pre-treated fibre; even, homogenous layer of silica particles, d) cross-section of a NaOH-pre-treated fibre with formed silica layer; thin layer with thickness less than 100 nm [6]

Binary metal sulphide semiconductors such as CdS, CdSe or PbS are regarded as insufficiently stable for catalysis, at least in aqueous media as they readily undergo photoanodic corrosion [28, 29]. These materials are also known to be toxic. The iron oxides are not suitable semiconductors as they readily undergo photocathodic corrosion [30]. The band-gap for ZnO (3.2 eV) is equal to that of anatase. ZnO however, is also unstable in illuminated aqueous solutions [71] with $Zn(OH)_2$ being formed on the particle surface. This results in catalyst deactivation [28]. WO_3 has also been investigated as a potential photocatalyst however, it is generally less photocatalytically active than TiO_2 [31].

TiO_2 usually exists in three common crystal structures: rutile, brookite and anatase. Of the three forms, brookite is the most unstable form and is very difficult to prepare [32]. Probably out of these reasons, brookite form is rarely used in photocatalytic studies. Most studies in TiO_2 photocatalysis have been carried out using either pure anatase form or pure rutile form (natural) or a mixture of the two as photocatalysts [32] and therefore only rutile and anatase are commercially important. Often the anatase form of TiO_2 is believed to be more photocatalytically active than rutile form [33, 34, 35, 36; 37, 38, 39, 40, 41]. Anatase has a wider optical band gap (3.2 eV vs 3.0 eV for rutile), a smaller electron effective mass, a higher Fermi level, and a higher mobility of charge carriers than the thermodynamically stable rutile phase [42]. For these reasons the anatase modification is the preferred form for photocatalysis.

The crystalline phase and crystallite size are important properties of the nano-coating, controlling the efficient absorption of UV photons, and the migration of photogenerated holes to the crystallite surface [43, 34, 44].

TiO_2 can be synthesised by several different methods including inert gas condensation [45]; flame synthesis by $TiCl_4$ oxidation [46]; oxidation-hydrothermal synthesis from metallic Ti [47] and hydrolytic precipitation of Titanium alkoxide or titanium salt (sol-gel method) [48]. Of particular interest is the sol-gel approach since it allows compositional and microstructural tailoring through controlling the precursor chemistry and processing conditions [48]. Sol-

na površino tkanine. Avtorji članka smo sintetizirali delce silicijevega dioksida na regeneriranih celuloznih vlaknih in tudi v našem primeru rezultati potrjujejo, da sta rast in morfologija sloja delcev odvisni od mikrostrukture površine vlakna in njegove dostopnosti. Uspelo nam je izdelati enakomerne, goste plasti delcev silicijevega dioksida z debelino pod 100 nm (slika 3) [6]. Določali smo termične lastnosti tako modificiranih vlaken in ugotovili, da enakomerna in celovita pokritost s silicijevim dioksidom lahko upočasni termični razkroj ter poviša temperature, pri katerih pride do vžiga, na višje vrednosti [6]. Kashiwagi je s soavtorji preizkušal ognjevarno aktivnost različnih vrst silike in silikatnih gelov kot aditivov za polipropilen in polietilen oksid [56], Gilman [57] pa je raziskoval kombinacije silikatnega gela in kalijevega karbonata s poliamidom in celulozo, prav tako za doseganje ognjevarnosti. V obeh primerih so avtorji kot preizkusni material uporabili tablete, izdelane iz delcev silicijevega dioksida/silikatnih gelov in različnih organskih polimerov, ne pa dejanskih tekstilnih form.

Delci silicijevega in titanovega dioksida povečajo hidrofilnost vlaken, kar je posledica njihove visoke vsebnosti površinskih hidroksilnih skupin; v primeru takšnih prevlek na regeneriranih celuloznih vlaknih se njihova visoka afiniteta do vode še dodatno poveča [58]. Nanos silike na hidrofobna vlakna lahko izboljša njihovo navzemanje vode (pri čemer se njihove osnovne mehanske lastnosti ne spremenijo) [59]. Sloj delcev silicijevega dioksida, ki je hidrofobno modificiran, pa se lahko uporablja tudi za doseganje hidrofobnosti hidrofilnih vlaken. Yu in drugi avtorji [60] so uporabili kombinacijo delcev silicijevega dioksida in silana s fluorovimi skupinami (PFSC) za zmanjšanje hidrofilnosti bombažne tkanine; z delci silicijevega dioksida so dosegli površinsko hrapavost, medtem ko je plast PFSC znižala površinsko energijo. Tako obdelana bombažna tkanina se ponaša z visokimi vrednostmi vodoodbojnosti in visokimi stičnimi koti (145°). Obdelava bombažne tkanine samo s PFSC, brez delcev silike, daje nižje stične kote. Kombinacija silike in PFSC izboljša tudi oleofobno sposobnost bombažne tkanine. Yang je s sodelavci [61] modificiral lesna celulozna vlakna z večplastno depozicijo polidialildimetilamonijevega klorida (polyDADMAC) in delcev silicijevega dioksida, čemur je sledila plast silana s fluorovimi skupinami (POTS); dosegli so hidrofobno površino vlaken s stičnimi koti, višjimi od 150°. Takšna vlakna se ponašajo tudi z visoko odpornostjo proti delovanju bakterij in zelo dobrimi mehanskimi lastnostmi. Gonçalves in sodelavci [62] so uporabili amorfne delce silicijevega dioksida in perfluorne spojine za izboljšanje vodoodbojnosti celuloznih nanokompozitov; delci silike povečajo površinsko strukturiranost, perfluorne spojine pa znižajo površinsko energijo. Izmerjeni stični koti so se približali vrednosti 150°. Yeh s sodelavci [63] je s kombinacijo silicijevega prekurzorja TEOS in fluoroogljikovimi polimeri dosegel hidro- in oleofobnost bombažnih tkanin ter izboljšanje njihovih mehanskih lastnosti.

Vodoodbojnost tkanin, izdelanih iz ogljikovih vlaken, pa je mogoče doseči z uporabo golih delcev silicijevega dioksida, brez do-

gel processing also provides excellent chemical homogeneity [49, 50, 51, 52, 53]. and is a appropriate method for manipulation of the structure, configuration, composition and chemical characteristics of organic matrices. This property and the ability to immobilize sol-gels covalently on textile support make this technology appealing in surface modification of fibres and other textile structures [54].

3 Silica coatings on textile materials

Li et al. [55] have synthesized thin SiO_2 films from tetraethylorthosilicate by sol–gel method on different fabrics (cotton, flax, nylon-66, poly(ethylene terephthalate)) in order to investigate the interaction and adhesion of silica coatings on fibres. They concluded that the chemical composition and structure of fibres determine the adhesion of the coatings on the fabric surfaces. We have grown a layer of silica particles on regenerated cellulose fibres' surface and reached essentially similar results; growth and formation of particles' layer is dependent on the microstructure of the fibre substrate's surface and its accessibility. We have succeeded to synthesize uniform, dense layers of SiO_2 particles, with a thickness of less than 100 nm (Fig. 3) [6]. Thermal properties of such silica-covered fibres were determined and it was shown that a uniform layer of silica could prolong the thermal degradation of regenerated cellulose fibres, as well as shift temperatures of combustion to higher values [6]. Kashiwagi et al. tested the flame retardant activity of various silicas and silica gels as additives to polypropylene and polyethylene oxide [56], while Gilman et al. [57] examined the combination of silica gel and potassium carbonate in relation to their flame retardant activity, when applied to nylon, cellulose, etc. These last two researches were mainly done from the point of view of effect of silica addition; tested samples were pellets, made of a mixture of silica particles/gels and various organic polymers and not actual textile forms with coatings of nano particles.

Silica and titania coatings, due to their high amount of surface hydroxyl groups, enhance the hydrophilic nature of the fibrous substrate; in case of such coatings on regenerated cellu-

datne površinske modifikacije [64]. V tem primeru je vodoodbojnost posledica površinske morfologije (hrapavosti) delcev silike in ogljikovih vlaken. Premer vlaken znaša od 8 do 10 mikronov, pokrita pa so z delci, katerih povprečna velikost je v rangu od 300 do 500 nm; strukturirana površina ogljikovih vlaken predstavlja primarno površinsko hrapavost, dodaten sloj silike pa sekundarno – tako izdelan kompozit je približek lotosovega lista.

Spojine silanov lahko v obliki površinskih filmov funkcionalizirajo vlaknate materiale [65, 66] ali pa so vezna sredstva med vlakni in različnimi anorganskimi delci, kot so na primer delci silicijevega dioksida. V strukturi silana sta dve reaktivni enoti, ki se – odvisno od prisotnega substrata – različno odzivata.

Alkoksi skupina (OR) poveže molekulo silana s površinskimi hidroksilnimi skupinami anorganskega delca, medtem ko organska funkcionalna skupina (aminska, metakrilna, vinilna itd.) izboljša kompatibilnost ali celo kopolimerizira z organskim substratom (na primer s celuloznim vlaknom) [67]. Za potek kondenzacije med funkcionalno skupino silana in površino vlakna so potrebne visoke temperature. Abdelmouleh je s sodelavci [68] raziskoval interakcije med celuloznim substratom in različnimi spojinami silanov. Ugotovili so, da pri sobni temperaturi predstavljajo privlačne interakcije med njimi le disperzne in polarne sile; do kondenzacije in posledično kovalentne vezave med celuloznim substratom in filmom silana pride šele pri segrevanju nad 100 °C.

Brochier Salon in sodelavci [67] so s segrevanjem med 110 in 120 °C dosegli obstojno vez med veznim silanskim sredstvom in površino celuloze, medtem ko Castellano s sodelavci [69] poroča, da je za pripravo kemijsko modificiranih vlaken, primernih za uporabo v kompozitnih materialih, potrebna kombinacija organskih silanov, katerih skupine ≡Si–OH so bile predhodno hidrolizirane, in temperature nad 80 °C. Ker je pogoj za zagotavljanje trajne vezave silana s površino vlakna visoka temperatura, je lahko postopek pri temperaturno občutljivih tekstilnih materialih problematičen.

Sol-gel postopek se uporablja tudi za izdelavo delcev SiO_2, kjer ti delujejo kot nosilci barvil. Cheng je s sodelavci [70] pripravil volneno tkanino s plastjo silike, ki je vsebovala fotokromna barvila. Ta so se zelo hitro odzvala na UV-svetlobo, saj je porozna struktura silike omogočila potek fotokromne reakcije. Mahltig in sodelavci [71] so prav tako uporabili plast silike na vlaknih kot nosilec barvil; cilj njihovega dela je bil razvoj postopka za barvanje različnih vrst tkanin.

4 Prevleke iz titanovega dioksida na tekstilnih materialih

Transparentni filmi in nanosi titanovega dioksida (TiO_2), zlasti v polimorfni obliki anataza, so predmet mnogih temeljnih znanstvenih raziskav [72]. Zaradi njegovih odličnih fotokatalitičnih lastno-

lose fibres, their already high affinity for water is additionally increased [58]. While formation of a silica coating on hydrophobic fibres could impart hydrophilicity to such substrates (while still retaining their original mechanical properties) [59], modified layers of silica have been investigated for achieving hydrophobicity of otherwise hydrophilic fibres. Yu et al. [60] have used a combination of silica nano particles and perfluorooctylated quaternary ammonium silane coupling agent (PFSC) to impart hydrophobicity to cotton fabrics. Silica particles were used to achieve surface roughness, while layer of PFSC lowered the surface energy. Cotton fabric, treated in such a way, exhibits high water repellent properties and high water contact angle (145°). It must be noted that treatment with pure PFSC, without silica particles, resulted in lower contact angles. Oil repellent properties of silica particles/PFSC treated cotton fabrics were also improved. Yang et al. [61] succeeded in preparing superhydrophobic wood fibres with water contact angles higher than 150°. To achieve this, multi-layer deposition of polydiallyldimethylammonium chloride (polyDADMAC) and silica particles was used, followed by a fluorination with perfluorooctyltriethoxysilane (POTS). This surface treatment also imparted high resistance to bacterial contamination and at the same time retained high tensile strength of the paper, made out of the modified cellulose wood fibres. Gonçalves et al. [62] have prepared superhydrophobic cellulose nano composites by employing amorphous silica particles as a mean to enhance surface roughness and perfluoro moieties for reduction of surface energy. Resultant water contact angles approached a value of 150°. Yeh et al. [63] have used combination of silicon precursor TEOS and fluorocarbon polymer to impart water and oil repellence to cotton fabrics; resultant hybrids have water and oil repellent properties and good physical characteristics.

Silica particles without any additional modification of their surface were used to enhance hydrophobicity of micro-scaled carbon fabrics [64]. In this case, the driving mechanism for achieving hydrophobicity is solely the morphological roughness of silica particles and the base substrate. Carbon fabrics, used in the research,

sti se je tehnološko zanimanje osredotočilo na samočistilne aplikacije [73, 74].

Številni viri poročajo o pridobivanju TiO_2 tankih filmov s sol-gel „dip coating“ tehniko, pri čemer kot prekurzor uporabljajo veliko vrst titanovih alkoksidov [75, 76]; titanov tetraetoksid [77]; titanov etoksid [78]; titanov propoksid [79]; tetraizopropil-ortotitanat [80, 81, 82, 83]; titanov tetra-n-butoksid [84]. Drugi [85, 86] so kot začetni material za izdelavo TiO_2 nanosov uporabili titanov butoksid.

Kot fotokatalizator se pogosto uporabljajo tudi komercialni nano TiO_2 delci P25, ki so sestavljeni iz mešanice rutilne in anatazne kristalne oblike (razmerje med njima je 70 : 30). Značilnosti delcev so: BET-površina 55 ± 15 m^2/g, velikost delcev 30 nm, delci so iz 0,1 nm velikih kristalov. Dokazano je, da je P25 najboljši fotokatalizator za širok spekter organskih onesnaževalcev [87, 88, 89, 90, 91].

Veliko raziskav se nanaša na oblikovanje TiO_2 prevlek s sol-gel postopkom na površinah, ki so obstojne proti visokim temperaturam (steklo, keramika) [92, 93, 94, 39, 53]. Pri tekstilnih materialih pa visoke temperature obdelave predstavljajo omejitev zaradi tveganja poškodb vlaken. Vprašljiva je še obstojnost modifikacije. Omejene procesne temperature, ki jih zahtevajo celulozni substrati, ne vodijo do nastanka anatazne kristalne oblike, kar se odraža v nižji aktivnosti teh delcev v primerjavi s tistimi, ki jih oblikujemo na keramiki pri višjih temperaturah (višja stopnja kristalizacije pomeni višjo fotokatalitično aktivnost) [95]. Kljub temu pa številni poročajo o samočistilnih prevlekah na tekstilnih materialih [96, 97, 98, 99, 100, 101].

4.1 Kompozitni TiO_2–SiO_2 nanosi

Zaradi visoke fotokatalitične sposobnosti TiO_2 delcev obstaja pri oblikovanju nanoprevlek iz teh delcev na vlaknatih površinah nevarnost kemičnih poškodb [102, 103]. Negativen vpliv TiO_2 na vlakna je mogoče omejiti z izdelavo mejne površine med vlakni in TiO_2 delci. Zaščita pa je učinkovita le tedaj, kadar je oplaščenje delcev popolno. Amorfne snovi, kot je na primer silika, SiO_2, ki je obstojna proti visoko fotokatalitičnemu delovanju TiO_2 delcev in se pri izpostavljenosti UV-svetlobi ne razgradi, so primerne za ta namen [104, 105].

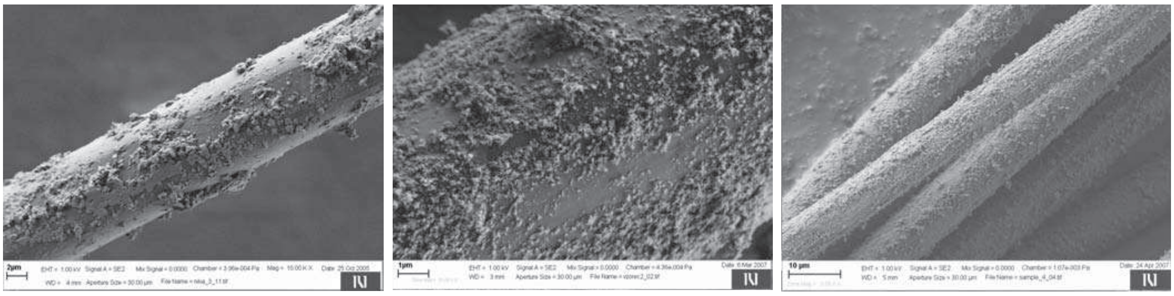
TiO_2–SiO_2 mešani oksidi lahko nastanejo s pomočjo različnih postopkov, na primer s ko-precipitacijo [106, 107, 108, 109] in pirolizo [110, 111], vendar pa izdelava TiO_2–SiO_2 mešanih oksidov najpogosteje poteka po sol-gel metodi [112, 113, 114, 115, 116, 117, 118].

Na lastnosti TiO_2–SiO_2 mešanih oksidov imajo velik vpliv pogoji sol-gel postopka. Ugotovili so, da nastaneta vsaj dva tipa titana: segregirana mikro TiO_2 področja in izolirana Ti-vrsta [119, 118, 120]. V primeru, da je delež titana višji od 15 %, v mešanem oksidu prevladujejo TiO_2 mikro področja [109, 111]. Ti- in Si-prekurzorja imata različne hitrosti kondenzacije. Če želimo izdelati viso-

consisted of carbon fibres with diameter of 8–10 μm, coated with silica particles with an average size of 300–500 nm. Micro-scale of the carbon fabric presents primary surface roughness, added layer of silica secondary roughness and such a composite mimics the lotus leaf.

Silane agents, as mentioned above, are mainly used for imparting additional functionalities and properties to layers of silica particles, formed on the surface of fibres or to impart new functionalities on textile materials by forming surface films [65, 66]. In addition to that, various silanes can be also used as binding/coupling agents between the fibres and silica particles (or various inorganic particles), due to their chemical composition. Two types of reactive moieties, present in the structure of silanes, respond in different ways, depending on the substrate they approach. Alkoxy groups (OR) connect the silane molecule with the hydroxylated surface, while the organic functional groups (amine, methacrylic, vinylic, etc improve compatibility or even copolymerize with an organic substrate (e.g. cellulose fibre) [67]. In order to trigger actual condensation reaction between the silane functional group and the surface of a fibre, higher temperatures have to be employed. Abdelmouleh et al. [68] studied the interactions between cellulose substrate and various silane agents. At room temperature only dispersive and polar attractive interactions are present, it

ko homogene TiO_2–SiO_2 okside, je treba uporabiti dvostopenjsko katalizirano hidrolizo [109, 111, 120, 121, 122]. Za pripravo TiO_2–SiO_2 mešanih katalizatorjev se uporabljajo različni prekurzorji [118, 123, 124, 125]. Avtorji, ki so TiO_2–SiO_2 nanose pripravili na površinah vlaken, so uporabili različne postopke; sol-gel postopek, pri katerem so kot prekurzor uporabili titanov tetraizopropoksid [105], oziroma postopek z uporabo že pripravljenih TiO_2 nanodelcev P25 (slika 4) [126, 58].



a) TIP precursor b) P25 c) P25 + SiO_2

Fig. 4: Effect of different coating procedures on resultant titania layers a) SEM image of a surface layer of titania, obtained by in-situ growth from titania precursor; uneven distribution of agglomerates with uncovered areas, b) SEM image of a surface layer of titania, obtained by deposition of pre-formed particles from a dispersion; some areas of fibres are still not covered, but overall coverage is much more homogenous and particles are much more monodisperse, c) SEM image of a surface layer of titania, obtained by combination of pre-formed titania particles, embedded in a SiO_2 layer; full coverage of fibres is achieved with a homogenous layer – silica particles act as means for even titania distribution [126]

5 Zaključek

Funkcionalizacija vlaken na osnovi prevlek iz nanodelcev je modifikacijska tehnika z izjemnimi možnostmi oblikovanja novih funkcionalnih materialov, ki pa je še vedno nezadostno zastopana na področju tekstilstva.

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was only after heating above 100°C that condensation occurred, resulting in covalent bonding between the cellulose fibre and silane film. Brochier Salon et al. [67] used heating at 110–120°C to create permanent bonding of the coupling agent to the cellulose surface. Castellano et al [69] have reported that use of pre-hydrolyzed ≡Si–OH groups of organic silanes and temperatures above 80°C are required in order to chemically modify cellulose fibres for their use in composite materials. Since elevated temperatures, following the coating process of a fibre with silane, are necessary for achievement of a satisfactory attachment between the two components, this requirement may prove hard to meet when dealing with temperature-sensitive textile materials.

Silica has served as well as a carrier for incorporation of dye-stuffs. Cheng et al. [70] have prepared dye-containing silica sol-covered wool fabrics. Photocromic dyes were able to provide a very fast response to UV light, since highly porous silica matrix enabled free space for photocromatic reaction to be accomplished. Mahltig et al. [71] have incorporated dyes into sol-gel coatings on textile fibres. Aim of the work is to develop a "one-type" recipe for dyeing different kinds of fabrics.

4 Titania coatings on textile materials

Transparent films and coatings of titanium dioxide (anatase) have been studied for a number of years now [72]. Technological interest has focussed around their potential in self-cleaning applications due to their photocatalytic properties [73, 74].

Numerous literature reports on the fabrication of TiO_2 *thin films by sol-gel dip coating technique using many types of titanium alkoxides as precursors [75, 76]; titanium tetraethoxide [77]; titanium ethoxide [78]; titanium propoxide [79]; tetraisopropyl-orthotitanate [80, 81, 82, 83]; titanium tetra-n-butoxide [84]. Others [85, 86] have used titanium butoxide as starting materials for making* TiO_2 *thin films.*

However, P 25, a commercial TiO_2 *catalyst containing a mixture of rutile and anatase crystalline forms (70% : 30% anatase/rutile mixture),*

flame retardancy properties of new halogen-free phosphorous doped SiO_2 thin films on fabrics. *Journal of Applied Polymer Science*, 2007, vol. 105, p. 3748–3756.

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with a BET surface area of 55 ± 15 m^2/g and crystalline sizes of 0.1 nm in 30 nm aggregates is the most widely used photocatalyst and has proven to be the best photocatalyst towards a broad range of organic pollutants [87, 88, 89, 90, 91].

Much work has been carried out depositing TiO_2 *on heat resistant surfaces like glass, ceramics and silica by sol-gel methods, where temperatures up to 500 °C can be used [92, 93, 94, 39, 53]. By applying the procedure to the textile surfaces some hindrances may appear, i.e. high temperature treatment conditions, fibre damage risks, problems connected with durability of the modification, etc. Limited process temperatures allowed for cellulose substrates, reduce a degree of anatase crystallization, which results in lower photocatalytic activity of generated coatings in comparison to coatings on high temperature resistant materials [95]. However, some reports on* TiO_2 *application in the textile industry can be found [96, 97, 98, 99, 100, 101].*

4.1 Mixed titania (TiO_2) and silica (SiO_2) coatings

TiO_2 *acting as a photocatalyst (that is, holes and electrons escape from the surface of the* TiO_2 *particles), can participate in the chemical damages of the organic fibre [102, 103]. To diminish the role* TiO_2 *may plays in the degradation of the fibre, it is possible to encapsulate the* TiO_2 *to prevent the electron from escaping and provide a barrier between the organic fibre and the* TiO_2 *surface. Encapsulation consists in placing an insulator on the surface of the* TiO_2*. In order to be effective, the insulation barrier must completely encapsulate the* TiO_2 *particle. Amorphous solids like silica are used because they completely coat the entire* TiO_2 *surface.* SiO_2 *is resistant to high photocatalytic activity of* TiO_2 *particles and doesn't degrade under exposure to UV light [104, 105].*

Titanium-silica mixed oxides can be produced by different ways like coprecipitation [106, 107, 108, 109] and flame pyrolysis [110, 111], but the most common way is the sol-gel method [112, 113, 114, 115, 116, 117, 118]. The conditions of the sol-gel process have a major influence on the properties of titanium-silica mixed oxides. It was found that at least two types of Ti

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species are present: segregated TiO_2 micro domains and isolated Ti species [119, 118, 120] When the titanium content was higher than 15 wt% (nominal TiO_2), the TiO_2 micro domains became more prominent in the mixed oxides [109, 111]. Since Si and Ti precursors have different condensation rates, a two-stage acid catalyzed hydrolysis was introduced to prepare atomically mixed TiO_2–SiO_2 oxides with high homogeneity [109, 111, 120, 121, 122]. TiO_2–SiO_2 mixed catalysts were prepared using different precursors [118, 123, 124, 125]. We have found publications about TiO_2–SiO_2 nanocoatings on fibres. Sol–gel TiO_2-based thin layers were obtained from two processes; using sol-gel process, where the precursor titanium tetra-isopropoxide was used [105] or using already prepared TiO_2 P25 nanoparticles (Fig. 4) [126, 58].

5 Conclusion

Nanocoating represents a modification technique with great potential for synthesis of novel functional materials, however nanocoating technology is still inadequately employed in the textile production.

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