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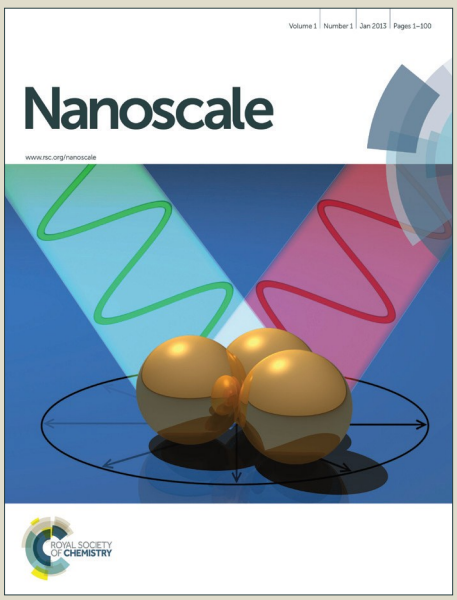

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REVIEW

Recent Development of Polydopamine: An Emerged Soft Matter for Surface Modification and Biomedical Applications

Meiying Liu[a], Guangjian Zeng[a], Ke Wang[b], Qing Wan[a], Lei Tao[b], Xiaoyong Zhang[a,]*, and Yen Wei[b,]*

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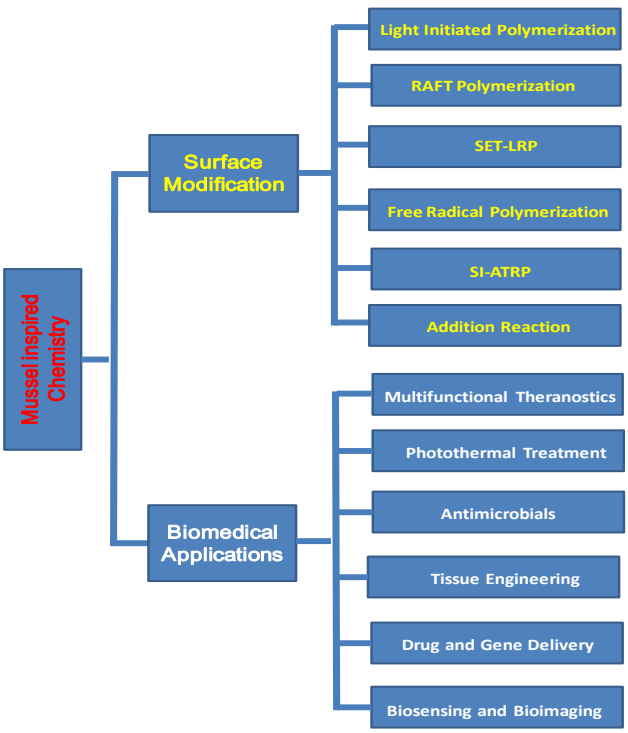
After more than four billion years' evolution, nature creates a large number of fascinating living organisms, which showed many peculiar structure and wonderful properties. Nature could provid plentiful inspiration source for scientists to create various materials and devices with special function and utilization. Since Messersmith proposed the fabrication of multifunctional coating through mussel inspired chemistry, it has attrated considerable attention in recent years for their promising and exiciting applications. Polydopamine (PDA), an emerged soft matter, has demonstrated to be a crucial component in mussel inspired chemistry. In this review, the recent development of PDA for mussel inspired surface modification was summarized and discussed. The biomedical applications of PDA based materials were also highlighted. We trust this review can provide important and timely information for mussel inspired chemistry and will be of great interest for scientists' from chemistry, materials, biology, medicine and interdisciplinary.

1. Introduction

Nature should be the treasury for scientists, that provides us plentiful inspiration source to advance our research and improve the quality of our daily life. After four and half billion years evolution, nature has reached its optimality. A large number of fascinating living organisms with special structure, extraordinary properties and outstanding performances have been created.[1] Learning from nature and understanding the underline mechanism of these creatives, we could construct various artificial advanced materials and devices with wonderful properties for different applications. The terminology of biomimetics originates from the Greek "bios" and "mimesis" and was proposed in the 1960s. Many excellent biomimic examples were intensively investigated and great advances have been achieved.[2-4] For example, Jiang et al have explored many biomimic systems inspired by lotus leaves, rice leaves, butterfly wings, mosquito eyes, moth eyes, red rose petals, cicada wings, gecko feet, desert beetle, spider silks, and fish scales.[5-9] Many functional materials and devices with adjustable surface wettability have been designed and fabricated, which can be utilized for diverse applications ranging from self-cleaning, antifogging, water harvesting, antireflection, and water/oil seperation.[10-14]

Marine mussel Mytilus edulis is another important example in the biomimetic fields because of its strong adhesion towards various substrates in the presence of water.[15, 16] It has demonstrated that the strong and universal adhesion of marine mussel was attributed to the adhesive proteins, which contained large amounts of lysine, dopa and 3- and 4-hydroxyproline.[17] The catechol funcitonal groups of dopa has regarded as the essential component for the adhesion of mussel towards various substances.[18-20] After uncovering the molecular mechanism of mussel adhesion, a number of factors that may influence the adhesion properties of dopa have also investigated by Waite et al in detail.[21, 22] Results suggested that the amino compounds, metal ions etc will effect the adhesion strength.[23-35] The mussel inspired chemistry has not received great attention until Messersmith et al reported the fabrication of multifunctional coating using mussel inspired chemistry.[36] In their work, dopamine was used to mimic the composition of adhesive proteins, that can be self-polymerized in water to form adherent polydopamine (PDA) thin films. More importantly, the PDA films can provide an important platform for secondary reactions, which can be used to create various ad-layers, including self-assembly monolayers, metal films, grafting of macromolecules through Michael addition reaction and controlled living polymerization.[36-38] After this pioneer work, the mussel inspired chemistry has attracted considerable research attention for surface modification and the potential applications of these multifunctional materials from mussel inspired chemistry for diverse fields has been explored.[39-54] Some excellent reviews focused on the PDA based materials have also been published in very recent years.[55-59] For example, Städler et al have summarized the biomedical applications of PDA based materials for interfacing with cells, drug delivery and biosensing in 2011.[57] More recently, the recent advance of PDA and its derivative materials for energy, environmental and biomedical applications has been reviewed by Lu et al.[55] However, a comprehensive review with focus on the surface modification strategies and biomedical applications of PDA based materials is still lacking.

The review article will summarize the recent progress and development of surface modification strategies based on PDA and biomedical applications of PDA based materials (**Scheme 1**). The types of PDA based materials and emerged surface modification strategies based on PDA were summarized in the first part of this review. The biomedical applications of PDA based materials for biosensing, bioimaging, drug delivery, antibacterial, and tissue engineering are subsequently discussed and prospected. Especially, the design and fabrication of luminescent PDA nanoparticles and photothermal conversion of PDA nanoparticles for cancer treatment were highlighted. We hope this revierw article will significantly advance the surface modification and biomedical applications of PDA based materials. It should be of great interest for scientists from chemistry, materials, biology, medicine and interdisciplinary.



Scheme 1 Schematic showing the surface modification strategies based on mussel inspired chemistry and the biomedical application of polydopamine based materials.

2. Mussel inspired surface modification

Surface modification of materials play a crucial role to adjust their properties, extend their applications and improve their performance. Great effort has been devoted to the surface modification of materials through the layer by layer assembly, self-assembly monolayer formation, hydrolysis of functional silanes, Langmuir-Blodgett deposition and plasma surface modification etc.[60-74] However, many of these existing strategies have their limitations, including the chemical specificity, the size and shape of substrates, requirement of complex instruments and multistep procedures. Mussel inspired surface modification is a novel and useful surface modification method, which was first reported by Lee and Messersmith in 2007.[36] Inspired by the adhesion capability of marine mussel, Lee et al demonstrated that dopamine, a small molecule containing both of amine and catechol groups, that could be self-polymerized into PDA thin films in aqueous solution under weak alkaline aqueous environment (**Fig. 1**). These PDA thin films can strongly attach to almost any inorganic and organic material surfaces (noble metals, oxides, semiconductors, ceramics and polymers) regardless of their shape and size. More importantly, the formed PDA thin films can further react with many other compounds through secondary reaction. Thus different functional components such as biomacromolecules, long-chain molecules, metal films etc can be introduced onto these PDA films to form functional ad-layers. It is therefore multifunctional coatings can be facilely introduced on various material surfaces taken advantage of the universal adhesion capability and high reactivity of PDA films. After the pioneering work by Lee and Messersmith, the utilization of mussel inspired chemistry to fabricate multifunctional materials have attracted great research attention.

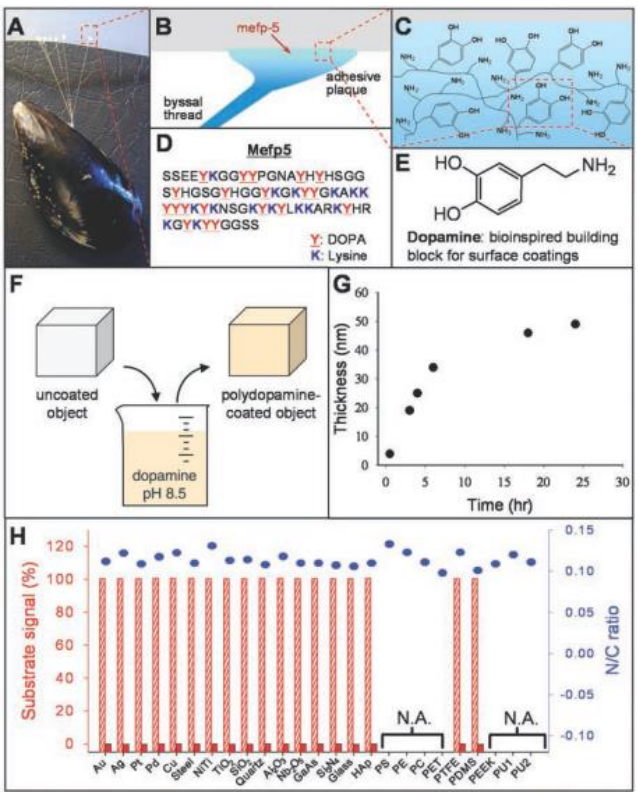


Fig. 1 (A) Photograph of a mussel attached to commercial PTFE. (B and C) Schematic illustrations of the interfacial location of Mefp-5 and a simplified molecular representation of characteristic amine and catechol groups. (D) The amino acid sequence of Mefp-5. (E) Dopamine contains both amine and catechol functional groups found in Mefp-5 was used as a molecular building block for polymer coatings. (F) A schematic illustration of thin film deposition of PDA by dip-coating an object in an alkaline dopamine solution. (G) Thickness evolution of PDA coating on Si as measured by AFM of patterned surfaces. (H) XPS characterization of 25 different PDA-coated surfaces. The bar graph represents the

intensity of characteristic substrate signal before (hatched) and after (solid) coating by PDA. (reprinted with permission from Ref. [36]).

2.1 PDA based materials

To date, several types of PDA based nanocomposites have been reported.[46, 75, 76] For example, Zhou et al have demonstrated that PDA nanocapsules can be fabricated via mussel inspired chemistry. In their work, the PDA thin films were first coated on silica nanoparticles, which were served as the templates. After removal of silica nanoparticles, the PDA based nanocapsules were obtained. These nanocapsules can be used as the containers for carrying some molecules.[75] Based on this work, the stimuli responsive PDA based nanocapsules can also be fabricated via the combination of self-polymerization of dopamine to form PDA and subsequently surface polymerization with thermo and pH responsive polymers. These responsive PDA nanocapsules can be used for controlled release of pesticide.[77] The luminescent PDA based nanoparticles were first reported by Wei group in 2012.[78] In the work, the luminescent PDA nanoparticles were prepared via self-polymerization of dopamine in Tris buffer solution after oxidation with concentrated H_2O_2. Results demonstrated that the emission wavelength of these luminescent PDA nanoparticles is dependent on the excitation wavelength. The excitation wavelength dependent optical behavior of these PDA nanoparticles is possibly ascribed to the wide size distribution. These luminescent PDA nanoparticles possess excellent water dispersibility, high fluorescent quantum yield, and excellent biocompatibility. These properties make these luminescent PDA nanoparticles promising probes for bioimaging and biosensing applications. The preapration of luminescent PDA based nanocapsules was also demonstrated by Caruso et al.[79] In their work, the PDA based nanocapsules were fabricated via self-polymerization of dopamine using silica particles and polystyrene particles as the templates and then removal of these templates to leave the PDA shells. To endow luminescence from these PDA nanocapsules, the H_2O_2 was utilized to oxidize PDA nanocapsules. As compared with Wei's report, the size and morphology of PDA based nanocapsules can be well controlled because templates were used.[78] Furthermore, the uniform PDA based nanospheres with well controlled size and morphology were first prepared by Lu et al in the absence of templates. In this work, the PDA based carbon nanospheres can be formed by self-polymerization of dopamine in a mixture solution containing water, ethanol and ammonia at room temperature.[46] The size of these PDA based carbon nanospheres could be easily controlled ranging from 120 to 780 nm by tuning the ratios of ammonia and dopamine (**Fig. 2**). After carbonization, the resultant N-doped carbon nanospheres still maintained their morphology, and showed higher electroconductivity, higher oxygen reduction catalytic activity. These results implied that the obtained N-doped carbon nanospheres are promising for energy storage and conversion application. Furthermore, these uniform PDA based nanospheres also exhibited excellent photothermal conversion effect, which makes these PDA based nanospheres promising candidates for cancer photothermal treatment and fabrication of multifunctional theranostic systems.[49]

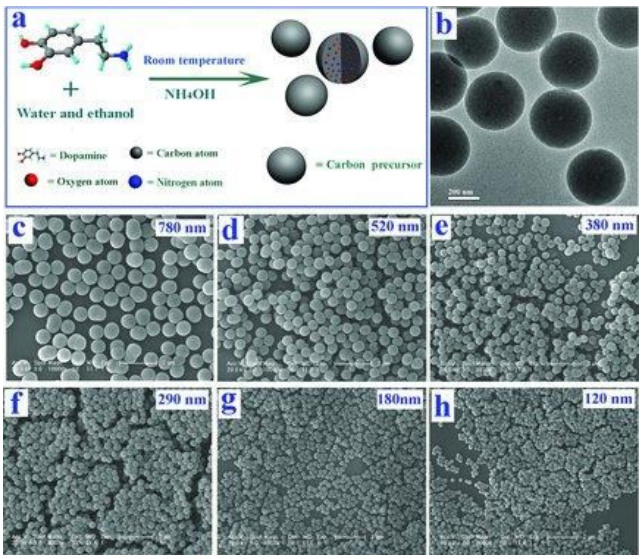


Fig. 2 a) Schematic illustration of the synthesis of PDA SMSs. b) Typical TEM image of PDA SMSs with an average diameter of 380 nm. c–h) SEM images of PDA SMSs with different diameter prepared at different ratios of ammonia and dopamine. (reprinted with permission from Ref.[46]).

2.2 Mussel inspired surface modification strategies

Surface modification of material surfaces is an important research topic and can be utilized to adjust the physicochemical properties of materials and fabrication of composites with combined properties. In this section, several surface modification strategies based on mussel inspired chemistry were summarized and discussed. These surface modification strategies were focused on the polymer modification relied on the PDA thin films, which mainly included addtion reactions, surface-initiated atom transfer radical polymerization (SI-ATRP), single-electron transfer living radical polymerization (SET-LRP), reversible addition-fragmentation chain transfer (RAFT) polymerization and light irradiation initiated surface polymerization.[80-83]

2.2.1 Addition reactions

It has been demonstrated that PDA films can further react with the amino and thiol containing compounds such as biomacromolecules, commercial available small molecules and polymers and amino containing synthetic polymers. For example, the immobilization of biomolecules such as peptides, proteins and enzymes can be achieved through combination of mussel inspired chemistry and Michael addition reaction.[47] These functionalized materials and surfaces can be used for enzyme immobilization, tissue engineering and biosensing etc.[47, 84-87] The commercial available small molecules and polymers that contained amino and thiol groups were also immobilized onto nanomaterials and surfaces. For example, combination of mussel inspired chemsitry and Michael addition reaction, we fabricated the water and organic dispersed carbon nanotubes using the N-dodecyl mercaptan and 3-mercapto-1-propanesulfonic acid sodium salt and

polyethyleneimine as the modification agents.[83] Furthermore, the alkyl chain contained thoil groups can also be facilely immobilized on the PDA coated stainless steel mesh films through Michael addition reaction.[88] The resultant films displayed superhydrophobic properties and could be used for oil/water separation (**Fig. 3**). Finally, the Michael addition reaction can also be adopted for immobilization of synthetic polymers on the surface of different nanomaterials such as graphene oxides, carbon nanotubes, molybdenum disulfide nanosheets and silica nanoparticles.[89-98] For example, amino- and thiol-terminated polymers such as PPEGMA, PMAA and PNIPAM et al can be prepared via chain transfer living radical polymerization, RAFT polymerization and free radical living polymerization, that could subsequently conjugate with the PDA modified nanomaterials through Michael addition reaction.[89-98] These polymer nanocomposites could not only show improved dispersibility and biocompatibility, but also exhibit pH and thermo responsiveness. Furthermore, some reports have demonstrated that a chemical bond and electrostatic interactions could contribute to the mussel inspired surface modfication strategy.[99]

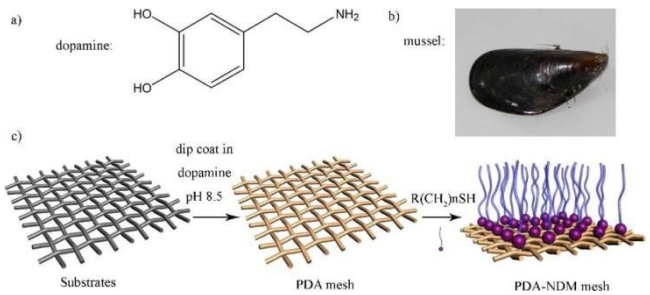


Fig. 3 a) Chemical structure of dopamine; b) photograph of a mussel; c) schematic description of the preparation of polydopamine coated stainless steel mesh film and N-dodecyl mercaptan modified surface through Michael addition reaction. (reprinted with permission from Ref.[88]).

2.2.2 SI-ATRP

SI-ATRP is one of the most commonly adopted strategies to render the materials and surfaces with different properties. However, the SI-ATRP initiators should be first immobilized on the materials or surfaces through conjugation reaction. These initiators can be further utilized for growth of polymers on materials and surfaces through ATRP. It is well known that the dopamine molecule contains both amino and catechol groups. After the dopamine was self-polymerized into PDA, the amino and hydroxyl groups can be simultaneously introduced on the materials. These functional groups can be further utilized to immobilize initiators for ATRP.[80, 100-105] For example, the combination of mussel inspired chemistry and SI-ATRP for preparation of thermoresponsive coated multi-element compound fertilizer was first reported by Zhou et al. They demonstrated that the fertilizer core coated by polydopamine-graft-poly(N-isopropylacrylamide) bilayer can show controlled release behavior over a long term.[106] As shown in **Fig. 4**, it can be seen that the release speed of Cu from MCFs and PMCFs at 37 °C was greater than that of at 25 °C. This was mainly ascribed to that the average molecular speed and diffusion was faster at high temperature. On the contrary, the nutrients release speed was much slower at high temperature after the surface of PDA thin films were further coated with thermoresponsive polymers poly(N-isopropylacrylamide. All of these above results implied that stimuli-sensitive controlled release systems can be facilely and effectively fabricated via combination of PDA coating and SI-ATRP. Because of the universality of mussel inspired chemistry and monomer adaptability of ATRP, this strategy can be also prepared for various polymer coating with different stimuli, that should be promising for fabrication of many other controlled delivery systems. Furthermore, the PDA thin films can also link with ATRP initiators, which can be used for surface modfication of materials through SI-ATRP relied on the adhesion capability of PDA.[107-111]

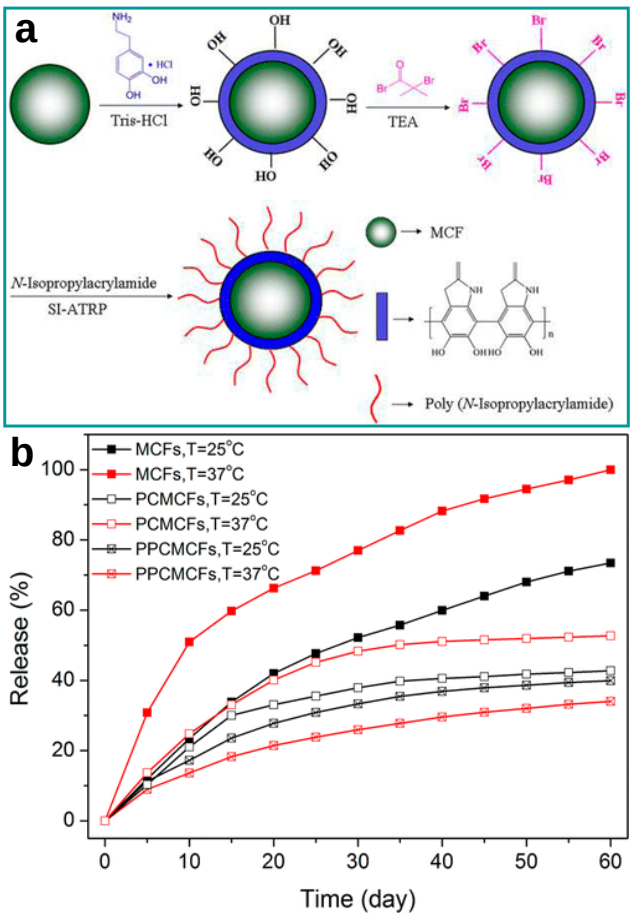


Fig. 4 (a) Schematic illustration of the ATRP Grafted with PNIPAm from Pdop-Coated Fertilizers. (b) Stimuli–responsive release behavior of Cu from fertilizers at different temperatures. (reprinted with permission from Ref. [106]).

2.2.3 SET-LRP

SET-LRP is a recently emerged controlled/living radical polymerization similar to ATRP, that has been first proposed by Percec in 2006.[112] Compared with ATRP, SET-LRP can be used for synthesizing polymers with controlled polymer properties under more mild conditions such as in aqueous solution, air atmosphere, room temperature. More importantly, the polymerization speed of SET-LRP is rather fast because of

the outer-sphere SET mechanism with a low activation energy.[113-121] The Cu(0) atomtic species have demonstrated to be the catalyst for the SET-LRP. Although there are still some dispute between SET-LRP and ATRP, SET-LRP at least has provide a more convenient route for synthesis of polymers with designable polymer properties. Therefore, great research attention has been devoted to the emerged living radical polymerization method. A series of solvents such as H_2O, alcohols, dipolar aprotic solvents, ethylene, propylene carbonate, ionic liquids, their mixture and even the beverages, different monomers included acrylates, methacrylates, vinyl chloride, poly(ethylene glycol) monomethyl ether methacylate (PEGMA), N-isopropylacrylamide (NIPAM), styrene sulfonate have been adopted for SET-LRP.[122-126] The SET-LRP has also recently utilized for surface modification of different materials such as graphene oxide, carbon nanotubes, silica nanoparticles and wheat straw etc.[119, 127-131] These modified materials were utilized for improving their dispersibility and enhancing environmental polluntant adsorption capability. For example, Zhang et al have demonstrated that multiwalled carbon nanotubes can be first coated by PDA via self-polymerization of dopamine to introduce the amino and hydroxyl groups on their surfaces.[127] These functional groups can be further utilized for immobilization of initiator, which can control growth of PPEGMA polymer brushes (**Fig. 5**). The successful formation of CNT-PDA-PPEGMA nanocomposites was confirmed by a series of characterization techniques. Apart from PPEGMA, other polymers can be also grafted on the PDA coating due to the good monomer adaptability of SET-LRP.[128, 132]

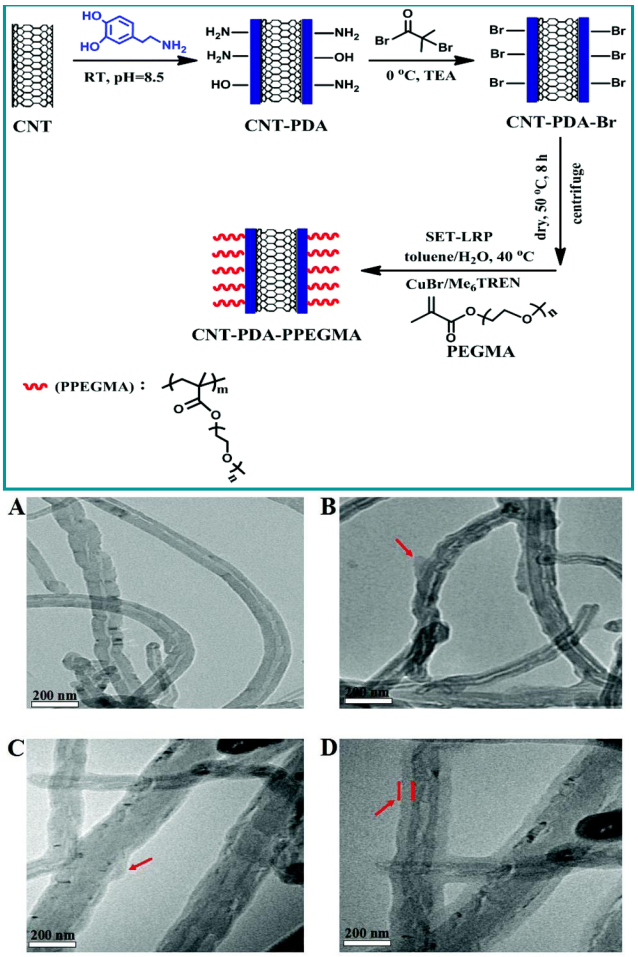


Fig. 5 Schematic representation for the synthesis of CNT-PDA-PPEGMA by the combination of mussel inspired chemistry and SET-LRP strategy. PDA films were first coated on the surface of pristine CNTs via mussel inspired chemistry to obtain CNT-PDA, which contained a number of amino and hydroxyl groups. After that, the initiator (2-bromo-2-methylpropionyl bromide) was further conjugated on CNT-PDA to obtain CNT-PDA-Br. Finally, the monomer (PEGMA) was further introduced on the surface of CNT-PDA-Br via SET-LRP. Representative TEM images of (A) pristine CNTs, (B) CNT-PDA, (C) CNT-PDA-Br and (D) CNT-PDA-PPEGMA. Scale bar = 200 nm. The PDA and polymer films coated on the surface of CNTs could be clearly observed via TEM images (B–D). TEM characterization gave direct evidence that the CNTs were successfully functionalized by PDA and polymers by the combination of mussel inspired chemistry and the SET-LRP method. (reprinted with permission from Ref.[127]).

2.2.4 RAFT polymerization

Zhang et al. recently developed a novel strategy that combination of the mussel inspired chemistry and RAFT polymerization to fabricate thermo-responsive graphene oxide based polymer nanocomposites in aqueous solution.[91] In this work, the graphene oxide was first coated with PDA films under weak alkaline aqueous solution. Then the thermo-responsive polymers (PNIPAM) synthesized from RAFT polymerization were immobilized onto GO-PDA through Michael addition reaction. As shown in **Fig. 6**, the thickness of graphene oxide sheets was obviously increased after they were coated with PDA and subsequently linked with PNIPAM through Michael addition reaction. After surface

functionalized with PNIPAM, the resultant GO-PDA-PNIPAM composites showed thermo-responsive properties. Of cause, the method described in the work is also useful for fabrication of many other polymer nanocomposites with different properties and functions because of the universal adhesion of PDA towards almost any material surfaces and the well applicability of RAFT polymerization. As compared with other controlled radical polymerization methods such as ATRP and SET-LRP etc, the method combines mussel inspired chemistry and RAFT polymerization can occur under aqueous solution, room temperature, air atmosphere and without using any metal catalysts. Therefore, this method could provide a facile, green and universal route for fabrication of various polymer nanocomposites with promising application potential. Apart from controlled radical polymerization methods, some other free radical polymerization strategies could also be utilized for surface modification of materials and surfaces with the combination of mussel inspired chemistry. The excellent and interest ones will be described in the following sections, that contained free radical polymerization and light irradiation initiated surface polymerization.

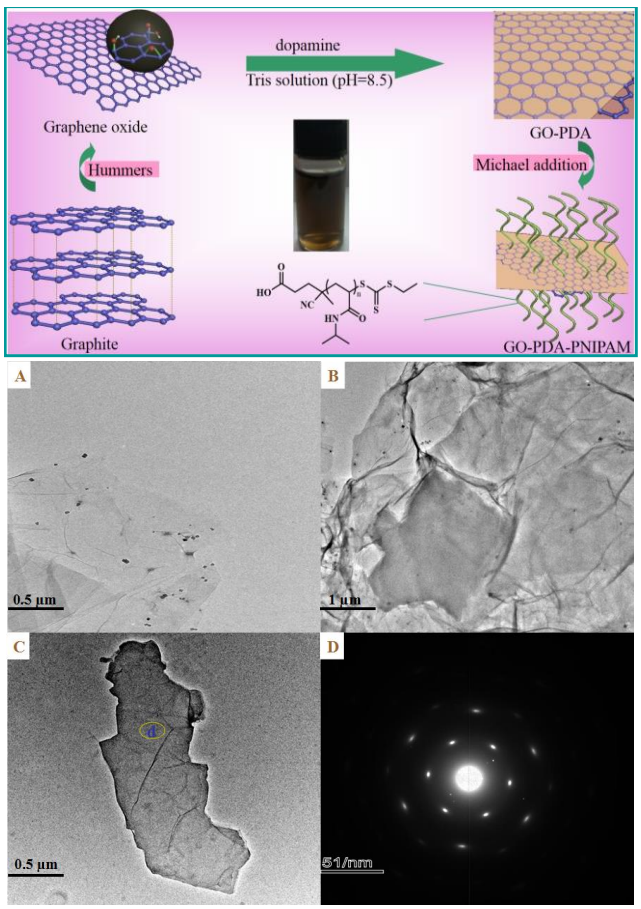


Fig. 6 Schematic representation for the preparation of GO-PDA-PNIPAM. Step 1: graphite was first oxidized and exfoliated into a single layer of slices through a modified Hummers' method. Step 2: GO was coated with PDA in Tris solution through mussel adhesion. Step 3: the intermediate, GO-PDA, was grafted with poly(N-isopropylacrylamide) (PNIPAM) through a Michael addition reaction. (A) A TEM image of GO observed at low magnification; (B) a TEM image of GO-PDA, revealing the PDA wrapped on the GO surface; (C) a TEM image of GO-PDA-PNIPAM; (D) diffraction pattern of GO-PDA-PNIPAM in the region shown in (C). (reprinted with permission from Ref.[91]).

2.2.5 Free radical polymerization

In a recent report, Zhang et al. demonstrated that the monomers itaconic anhydride (IA) and PEGMA can be polymerized using Azobisisobutyronitrile as the radical initiator to active these monomers and form poly(PEGMA-*co*-IA).[133] The resultant polymers contained the active pendant IA groups can be easily reacted with the amino group of dopamine in anhydrous organic solvents to obtain dopamine pendant polymers (DA-poly(PEGMA-*co*-IA)). Taking advantage of the adhesion of dopamine towards material surfaces, these dopamine pendant polymers are expected to attach to any material surfaces. As shown in **Fig. 7**, the GO sheets can be facilely functionalized by DA-poly(PEGMA-*co*-IA) through a one-step route in aqueous solution, air atmosphere, at room temperature and without using any metal catalysts. During the ring-opening reaction between the IA and dopamine, a large number of carboxyl groups were generated on DA-poly(PEGMA-*co*-IA). These carboxyl groups can coordinate with the anticancer agent cisplatin, which can be controlled release from the GO-DA-poly(PEGMA-*co*-IA) at different pH values. Combined with the excellent biocompatibility of GO-DA-poly(PEGMA-*co*-IA) and the controlled drug release behavior, the obtained GO based polymer nanocomposites should be one of the promising candidates for drug delivery applications. On the other hand, the dopamine containing copolymers could also obtain from copolymerization of dopamine-methacrylamide derivatives and other monomers through free radical polymerization.[108, 134, 135] More importantly, the universal adhesion of dopamine also provided the potential for surface modification of many other materials and surfaces. Therefore, the strategy described in this section, that combined the mussel inspired chemistry and free radical polymerization should be a rather simple and universal method for fabrication of various polymer nanocomposites with prospective applications.

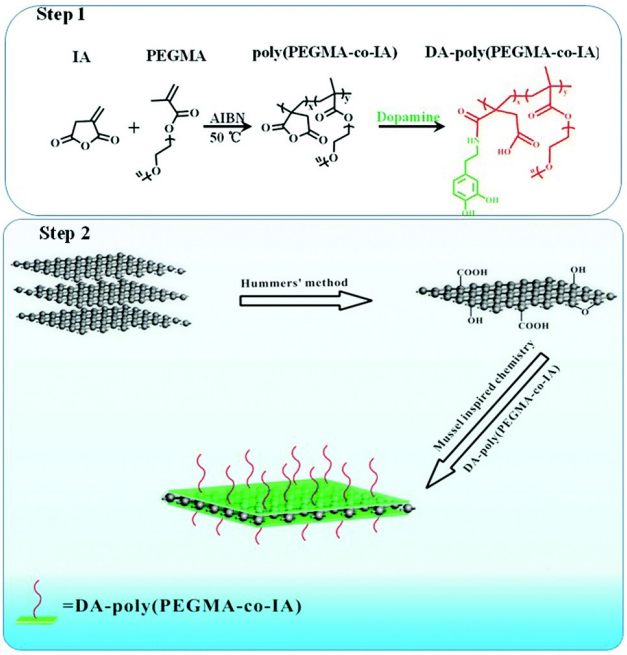


Fig. 7 Schematic illustration of the preparation of DA-poly(PEGMA-co-IA) modified GO via mussel inspired chemistry. Step 1 shows the synthesis of poly(PEGMA-co-IA) by free radical living polymerization, which was subsequently reacted with DA to get DA-poly(PEGMA-co-IA). Step 2 illustrates the attachment of DA-poly(PEGMA-co-IA) onto GO via mussel inspired chemistry. (reprinted with permission from Ref.[133]).

2.2.6 Light initiated surface polymerization

Light is a very useful tool for initiating polymerization through generation of radical during the light irradiation.[136-138] As compared with other polymerization methods, the light initiated/controlled polymerization has its specific advantages, which included mild reaction conditions, fast polymerization rate, low toxicity and biocompatibility and capability for lithographic patterning of substrates. A number of photosensitizers or photoinitiators such as AIBN, benzophenone, tertiary amines, and peroxides *etc* have been utilized for surface grafting or polymerization. However, these initiators are expensive and toxic. It is therefore highly desirable to develop novel photoinitiators for generating radical species under rather mild conditions. In a recent report by Zhou et al., the PDA thin films were found to be utilized as novel radical generation agents, which can initiate polymerization just using light irradiation (**Fig. 8**).[139] In their work, PDA thin films simultaneously acted as adhesive layers and the photoactive species, which can be further used for surface initiated photopolymerization under simulated sunlight irradiation. In a more recently reported by Jia et al, the surface modification of PDA based nanocapsules through this photopolymerization was also demonstrated. In this work, the silica nanoparticles were used as the templates for preparation of PDA based hollow spheres. Then the thermo-responsive polymer thin film poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) was grafted onto these PDA microcapsules through surface initiated photopolymerization strategy. The obtained PDA based microcapsules were utilized for thermo-controlled release of pesticide.[77]

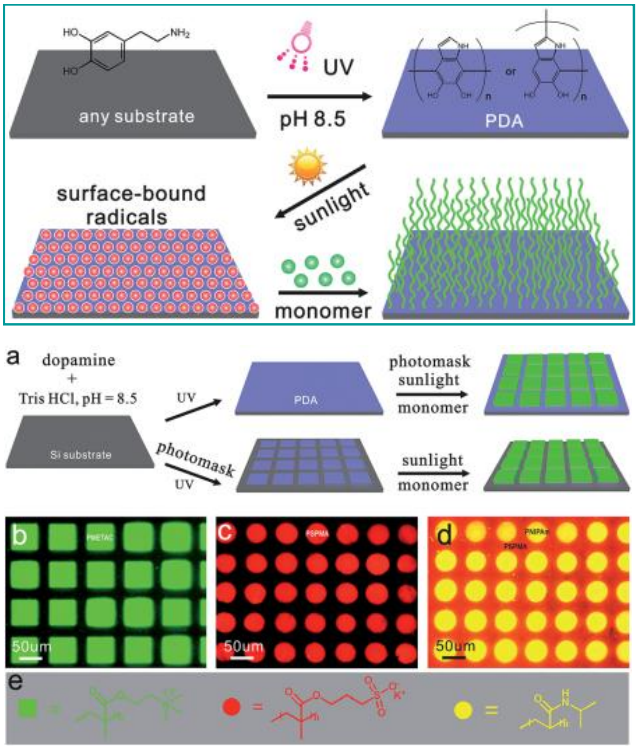


Fig. 8 (a) Outlined procedures for preparing patterned polymers. (b) Fluorescence image of methyl orange-stained PMETAC, (c) Rhodamine 6G-stained PSPMA, (d) binary pattern of acridine-stained PSPMA/PNIPAm, and the corresponding chemical structures (e). The bright green area is PMETAC, the red area is PSPMA, the yellow area is PNIPAm. (reprinted with permission from Ref.[139]).

3. Biomedical applications of PDA based materials

The PDA based materials have attracted great research attention for various application fields since the first report of fabrication of multifucntional coating by Messersmith et al.[36] In the following sections, PDA based materials for the biomedical applications such as biosensing, bioimaging, drug/gene delivery, tissue engineering, antibactrials, theranostics are introduced.

3.1 PDA based materials for biosensing

Detection of cancers at eary stage plays a pivotal role for cancer treatment and prognosis. The development of novel detection methods with high sensitivity and selectivity is therefore of great interest. Among them, electrochemical sensing is a very simple and high sensitive method for detection of cancer biomarkers. Matrix metalloproteinases (MMPs) are a family of secreted zinc-dependent endopeptidases, which are crucial for regulating the degradation and process of extracellular matrices, and are up-regulated in almost every type of human cancers. Highly sensitive and selective dection of these MMPs therefore play a very important role in monitoring the cancer and disease state. In a recent work, Zhu et al fabricated an electrochemical

immunosensing device by taking advantage of the features of Au nanoparticles and graphene oxide.[140] To fabricate these sensor devices, Au nanoparticles were immobilized on N-doped graphene sheets, which were used for conjugating the Ab1 and then attached on the electrodes. On the other hand, the HRP-Ab2 was immobilized on the graphene oxide sheets through the combination of mussel inspired chemistry and Michael addition reaction (**Fig. 9**). In the presence of MMP-2, the HPR-Ab2 modified on the graphene oxide sheets can be linked on the eletrodes through formation of Ab1/MMP-2/HPR-Ab2 sandwich structure, which can significantly amplify the signal output. Therefore, ultrasensitive electrochemical immunosensor for detection of cancer markers with good precision, stability and reproducibility can be fabricated. More importantly, the formation of PDA can be used for immobilization of a number of antibodies, and different immunosensing devices could be fabricated via mussel inspired chemistry.[141-145]

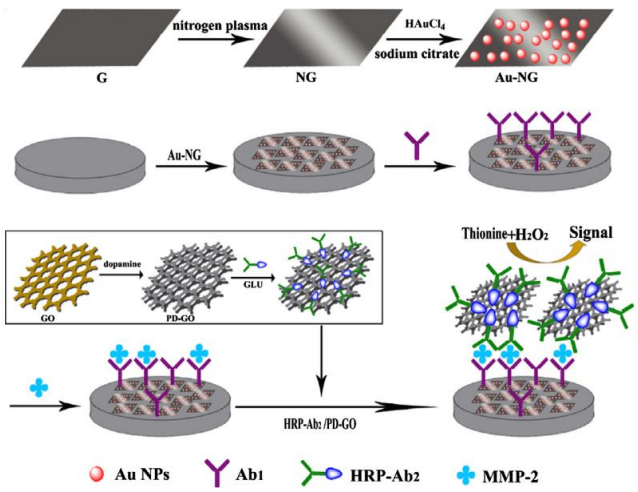


Fig. 9 Schematic illustration of the preparation and detection procedure of MMP-2 immunosensing. (reprinted with permission from Ref.[140]).

Development of simple, rapid, sensitive and cost-effective method for detection of specific DNA sequences is very important for identification of the genetic disease, disease related pathogens and other biological activities. The introduction of fluorescence labeled nucleic acids has been generally considered as the most effective and simple strategy to detect the nucleic acid sequences. It has been demonstrated that the adsorption behavior of single and double chain nucleic acids is significantly different. For example, the single chain nucleic acids are readily adsorbed onto many nanomaterials, which can quench the fluorescence of nucleic acids. However, when the matched nucleic acids were added, double chain nucleic acids were formed that were detached from these nanomaterials. Therefore the fluorescence was turned on and could be used for detection of the specific nucleic acids effectively. To date, a large number of nanomaterials such as carbon nanotubes, graphene related materials, carbon dots, and MoS_2 etc were used for the fluorescence quenchers.[146-150] For example, Sun et al have demonstrated that the PDA nanospheres with uniform size and morphology can be obtained via a rather facile method in a mixture of alkaline water and ethanol mixture (**Fig. 10**).[150] Results demonstrated that the PDA nanospheres can be used as effective quenchers for detection of oligonucleotide sequence associated with human immunodeficiency virus (HIV). As compared with other nanomaterial quenchers, the PDA nanospheres can be prepared in rather mild experimental conditions with good biocompatibility and water dispersibility. Therefore, they should be promising candidates for the nucleic acid detection.

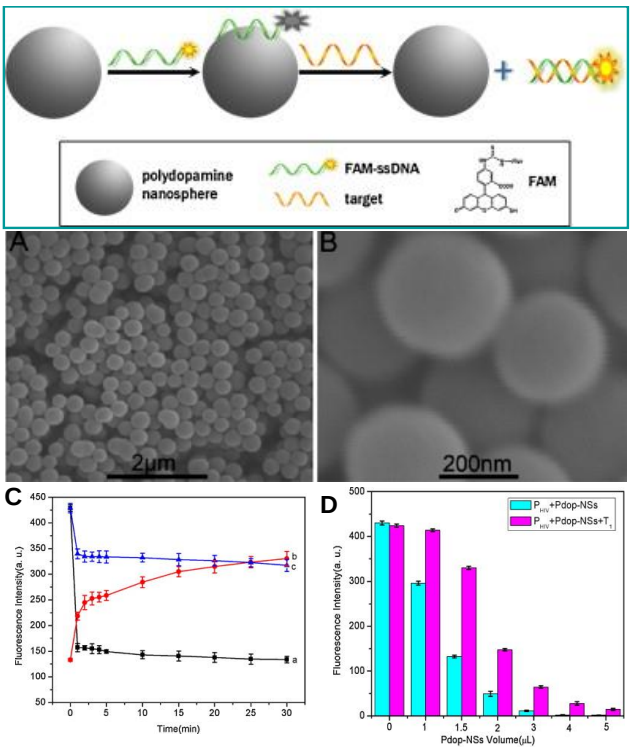


Fig. 10 A schematic diagram (not to scale) illustrating the Pdop-NSs-based fluorescent nucleic acid detection. (A) Low and (B) high magnification SEM images of Pdop-NSs. Effect of incubation time on the (a) fluorescence quenching of PHIV in the presence of Pdop-NSs, (b) fluorescence recovery of PHIV–Pdop-NSs by T1, and (c) fluorescence quenching of PHIV–T1 complex in the presence of Pdop-NSs. In each sample the volume of Pdop-NSs is 1.5 μL. Fluorescence intensity histogram of PHIV + Pdop-NSs and PHIV + Pdop-NSs + T1 with different volume of Pdop-NSs. (reprinted with permission from Ref.).

Protein phosphorylation is one of the most important and ubiquitous post translational modifications, that is related to many biological events of eukaryotic cells such as cell division, growth, differentiation, migration and intercellular communication. However, when determination of phosphorylation profiles of proteins in phosphoproteome research, the existence of nonphosphopeptides will suppress the mass spectrometry (MS) signal intensity for detection of phosphopeptides. Therefore seperation of phosphoproteins or phosphopeptides from protein mixtures with high effectiveness is very improtant for MS based phosphoproteomics. In a recent work by Deng et al, the Fe_3O_4@PDA microspheres were prepared and used for immobilization of Ti^{4+} through the coordinated interaction

between Ti^{4+} and catechol group of PDA.[151] The final nanocomposites (Fe_3O_4@PD-Ti^{4+} microspheres) were further utilized for selective enhancement of phosphopeptides because Ti^{4+} ions can fish the phosphorylated peptides from the biological samples with high percentage of non-phosphorylated peptides (**Fig. 11**). The authors demonstrated that the obtained Fe_3O_4@PD–Ti^{4+} microspheres show a high sensitivity for detection of phosphopeptides from a solution with ultra-low concentration. On the other hand, the PDA functionalized magnetic nanoparticles can also be used for molecularly imprinted polymer coating for protein recognition, ribonuclease A and enantioseparation etc.[152-154] Therefore, the PDA based materials and PDA functionalized are hold great application prospect in the analytic fields.

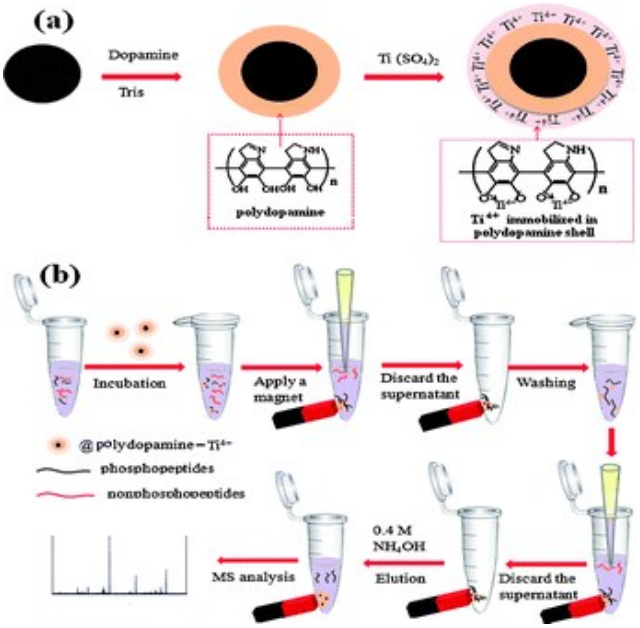


Fig. 11 (a) Synthetic route to Fe_3O_4@PD–Ti^{4+} microspheres; (b) workflow of phosphopeptides enrichment from a biological sample using Fe_3O_4@PD–Ti^{4+} microspheres. (reprinted with permission from Ref. [151]).

3.2 Luminescent PDA based materials for bioimaging

Fluorescent imaging has demonstrated to be one of the most popular tools in disease diagnosis, imaging guided therapeutic and theranostics. As compared with other imaging models such as radioactive imaging, magnetic resonance imaging, Raman imaging and ultrasound imaging, the fluorescent imaging showed some outstanding features including high sensitivity, well adjustment of fluorescent properties, cost-effective and facile for detection.[70, 155-164] To date, a large number of luminescent nanomaterials have been developed, that can be mainly divided into fluorescent inorganic nanoparticles (e.g. semiconductor quantum dots, metal nanoclusters, rare earth ions doped nanomaterials, carbon quantum dots and silica quantum dots etc) and fluorescent organic nanomaterials based on conventional organic dyes, conjugated polymers and aggregation-induced emission dyes and other types of organic dyes.[164-187] As compared with the fluorescent inorganic nanoparticles, the fluorescent organic nanomaterials have arouse great attention recently due to their good designability of fluorescent properties, biodegradability and good biocompatibility.[188-196] However, the procedure for the synthesis of organic dyes is often rather complex and less effective. On the other hand, the organic dyes are hydrophobic in nature and should be further conjugated with hydrophilic components to render them water dispersible. Moreover, the fluorescent intensity will largely decrease when they were encapsulated in organic fluorescent nanomaterials because of their aggregation caused quenching effect.[197-199] Therefore, the preparation of novel fluorescent organic nanomaterials that could overcome some of these shortcomings is of great interest. In a recent work by Zhang et al, they demonstrated for the first time that PDA based fluorescent organic nanoparticles with tunable fluorescent properties can be facilely fabricated via the combination of self-polymerization of dopamine in the presence of Tris buffer and subsequent oxidation.[78] The obtained fluorescent organic nanoparticles showed desirable biocompatibility, low toxicity and tunable fluorescent emission, that can be used for cell imaging applications (**Fig. 12**). The PDA based fluorescent organic nanoparticles can be fabricated under room temperature, air atmosphere, without metal catalysts in short term and only using dopamine as the precursor. As compared with the conventional methods for fabrication of fluorescent organic nanoparticles, this method can avoid the complex organic synthesis procedure, expensive chemical agents and post modification. Therefore, they can act as a novel type of fluorescent organic nanoparticles, which are deserved for further investigation. Following our work, some other PDA based fluorescent organic nanoparticles have also been prepared through a similar route. For example, the fabrication of PDA based fluorescent organic nanocapsules using silica nanoparticles and polystyrene micronanoparticles as templates were reported by Caruso and colleagues.[76, 79] Compared to our previous work, the size and morphology of these PDA based luminescent nanocapsules can be well controlled because the templates were used to direct the self-polymerization of dopamine.

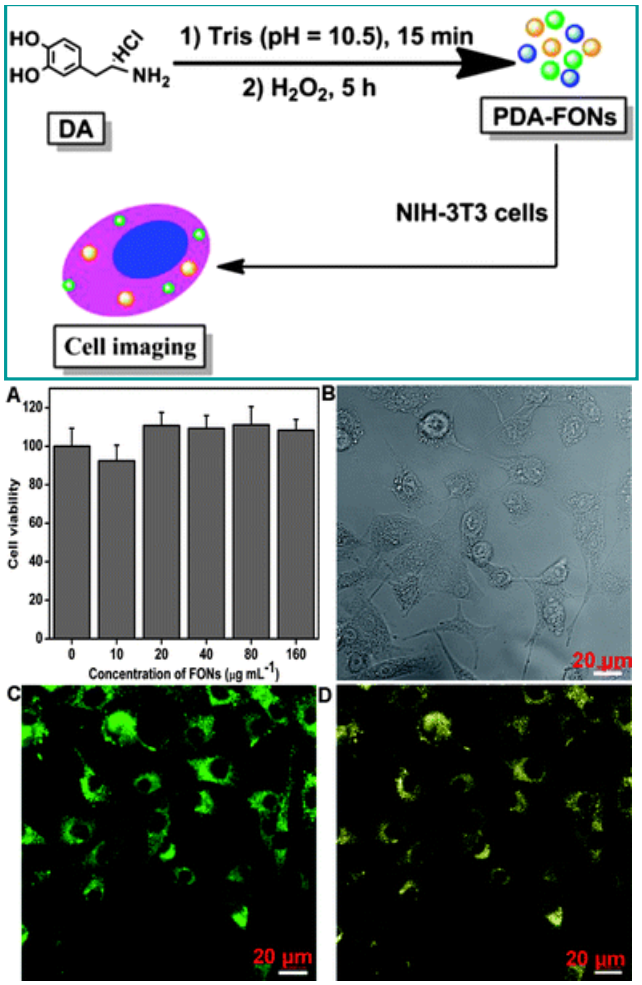


Fig. 12 Schematic showing the preparation of PDA–FONs by oxidation of polydopamine (PDA) and the subsequent utilization of the PDA–FONs for cell imaging (the above picture). The below pictures showed the Cellular toxicity and cellular imaging of PDA–FONs. (A) Effect of PDA–FONs on NIH-3T$_3$ cells. (B), (C) and (D) are CLSM images of cells imaged under bright field 405 nm and 458 nm excitations, respectively. (reprinted with permission from Ref. [78]).

Inspired by the above results, an alternative strategy has recently been developed by Zhang and colleagues to fabricate PDA based fluorescent organic nanoparticles. In this study, fluorescent organic nanoparticles with green fluorescence can be facilely prepared via just mixing of dopamine and an amino compound such as polyethyleneimine (PEI) or polyethylene polyamine in water at room temperature for 2 h without inert gas protection and metal catalysts.[200] These PDA-PEI fluorescent organic nanoparticles exhibited well water dispersibility, good biocompatibility and can be potentially utilized for cell imaging applications (**Fig. 13**). Different from the fluorescent properties as described in the above report, the emission wavelength of PDA-PEI fluorescent organic nanoparticles was fixed at about 526 nm, that is independent on the excitation wavelengths. Moreover, the pH values could influence the fluorescent intensity of PDA-PEI fluorescent organic nanoparticles but will not affect their emission wavelengths. Although the detailed mechanism for the formation of PDA-PEI fluorescent organic nanoparticles was not clear yet, the successful preparation of these PDA based fluorescent organic nanoparticles through self-polymerization of dopamine and amino compounds could provide a simple and novel route for fabrication of polymeric luminescent nanoparticles. However, in case of PDA fluorescent organic nanoparticles and PDA-PEI fluorescent organic nanoparticles, it is difficult to control their morphology and fluorescent properties. Therefore the future research direction should focus on design novel PDA based fluorescent organic nanoparticles to adjust their size, morphology and fluorescent properties.[201] Following this route, Zhang et al have recently developed many multifunctional PDA based fluorescent organic nanoparticles through the combination of mussel inspired chemsitry and controlled living polymerization. The size and morphology can be controlled in some extent, and these exciting results will be published in near future.

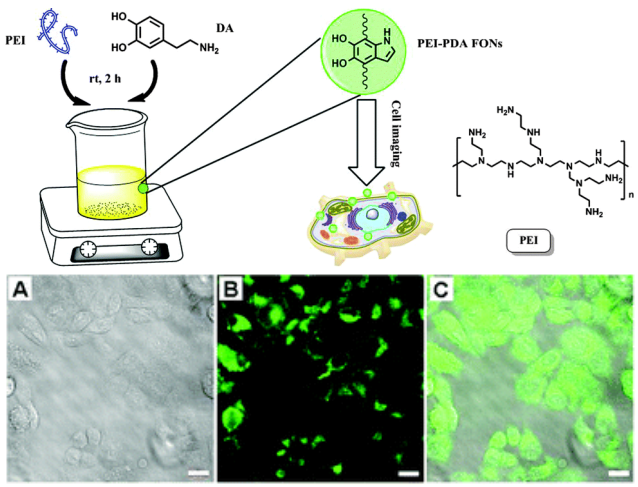


Fig. 13 Schematic showing the preparation of PEI-PDA FONs through self-polymerization using polyetheniemine (PEI) and dopamine (DA) as the precursors and cell imaging applications of PEI-PDAFONs. CLSM images of A549 cells when they were incubated with 10 μg mL^{-1} of PEI-PDA FONs for 3 h. (A) Bright field, (B) excited with 405 nm laser, (C) merged image of A and B. Scale bar = 20 μm. (reprinted with permission from Ref. Self-polymerization of dopamine and polyethyleneimine: novel fluorescent organic nanoprobes for biological imaging applications).

3.3 Drug/gene delivery applications

The delivery of drugs/genes using polymers have arouse great research interest recently due to the designability and properties of polymers. Taking advantage of the universal adhesion of PDA towards various materials and surfaces, the utilization of PDA based coatings could not only improve the solution stability of polymeric nanocarriers, but also provide active platforms for secondary reactions to immobilize other functional components such as PEG molecules, therapeutic agents and targeting agents.[202-204] For example, Yeo et al have demonstrated that poly(lactic-co-glycolic acid) PLGA nanoparticles based drug delivery systems can be fabricated through mussel inspired chemistry and subsequent immobilization of PEG and TAT peptides.[205] The intracellular delivery of an anticancer drug (PTX) was also investigated. The results demonstrated that the PLGA NPs showed relative

high cell uptake ratio in MMP-2 pretreatment group as compared to the control group. The PTX showed desirable cell killing capability after loading onto PDA modified biodegradable PLGA nanoparticles, suggesting the potential use of PDA coated PLGA nanoparticles for drug delivery applications. In previous reports, Zhang et al also demonstrated that PDA modified graphene oxide sheets, carbon nanotubes and silica nanoparticles can be used for immobilization of functional polymers and loading drugs such as DOX and cisplatin for pH controlled drug delivery applications.[128, 133, 206] More importantly, the PDA based nanomaterials have demonstrated to possess excellent photothermal conversion effect, thus these PDA based drug delivery systems can potentially be used as photothermal treatment agents.[49] Considering of the universal adhesion capability, high reactivity for secondary reaction and excellent photothermal conversion effect of PDA based nanomaterials, mussel inspired chemistry should be a novel, general and promising strategy for fabrication of multifunctional theranostic systems.[207-212]

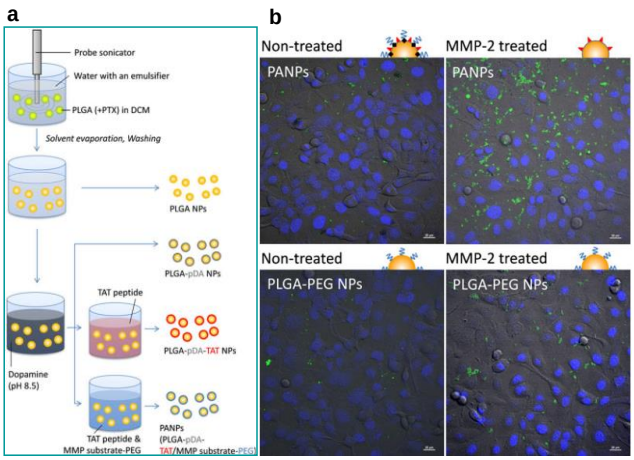


Fig. 14 (a) Schematic diagram of preparation of NPs used in this study. (b) Cellular uptake of *PANPs and *PLGA-PEG NPs with or without MMP-2 pre-treatment. Scale bar=20 μm. (reprinted with permission from Ref. [205]).

As compared with the nanoparticles, nanocapsules hold greater spaces for loading guest molecules such as drugs, therefore the PDA based nanocapsules for drug delivery are of specific interest.[213-221] For example, the PDA based nanocapsules with different size were fabricated by using emulsion droplets as templates.[79] These PDA capsules were used for conjugating the thiol containing polymers, which were synthesized by thiol-maleimide chemistry using thiolated poly(methacrylic acid) (PMASH) and a maleimide hydrazone derivative of doxorubicin. Because the hydrazone bond is an acid-labile group, the drugs loaded on these PDA capsules can release from drug carriers under acidic environment such as endosomes and lysosomes but are stable in the physiological solution. Therefore, the DOX release can be easily controlled by the pH values and utilized for controlled drug delivery in biological systems (**Fig. 15**). The controlled release behavior of DOX from these PDA capsules were confirmed by the deconvolution of microscope images. As shown in **Fig. 15**, it can be seen that the AF488-labeled PDA capsules can be readily internalized by HeLa cells and are mainly distributed in the cytoplasms (**Fig. 15c**). However, some of DOX internalized by cells can detach from the PDA capsules and enter into cell nuclei (**Fig. 15b**). After DOX was released from the PDA capsules, the DOX could exhibit comparable and even greater cell killing effects as compared with free DOX. It is therefore, these PDA capsules are promising candidates for pH controlled drug delivery applications, that could greatly decrease the adverse effect of DOX and enhanced its anticancer effects. In another report by our group, we have fabricated graphene oxide based polymer nanocomposites taking advantage of the strong and universal adhesion of dopamine towards graphene oxide.[133] In this work, the copolymers with pendant dopamine and PEGMA molecules were first synthesized via free radical polymerization using PEGMA and itaconic anhydride as the monomers. To attach dopamine to these copolymers, the ring-opening reaction between the amino group of dopamine and the anhydride groups was adopted. The PEGylated graphene oxide based polymer nanocomposites can therefore be facilely obtained via mixing of dopamine-contained copolymers and graphene oxide in aqueous solution. The graphene oxide based polymer nanocomposites can be used for high efficient loading cisplatin and controlled release of the drug in acidic solution. On the other hand, the graphene oxide based polymer nanocomposites displayed excellent biocompatibility, making them potential for drug delivery applications. Moreover, the dopamine could also attach onto stainless steel by taking advantage of the adhesion of dopamine. The dopamine and PDA modified stainless steel can be used for binding and sustaining release of siRNA.[222]

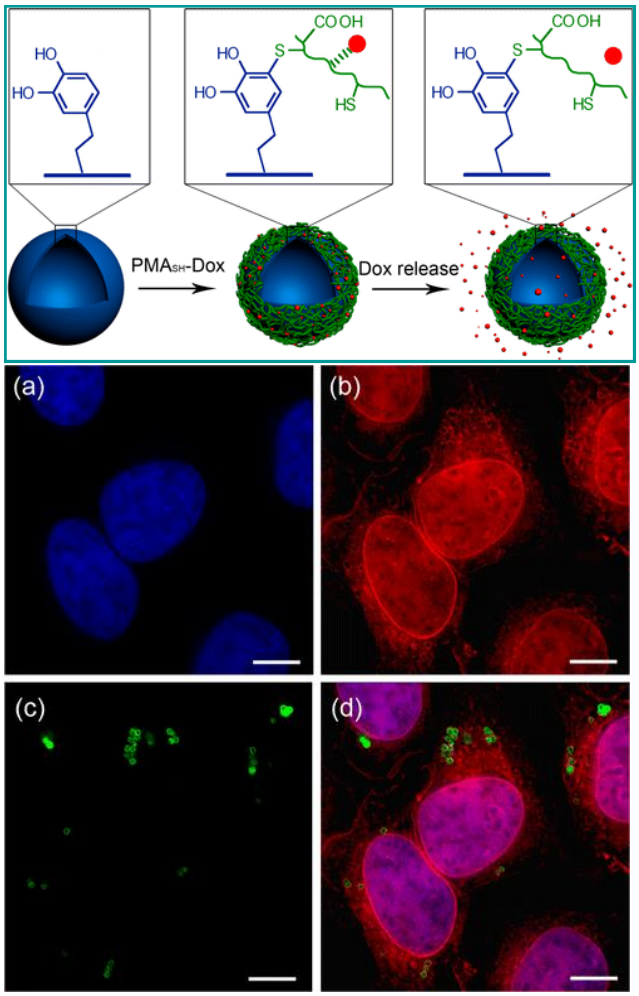


Fig. 15 Immobilization and pH-Responsive Release of Dox from PDA Capsules. Representative deconvolution microscope images of HeLa cells treated with Dox-loaded capsules. (a) Nuclei were stained blue with Hoechst 33342. (b) Red fluorescence arises from Dox. (a) Green fluorescence represents internalized AF488-labeled PDA capsules. (d) Merged image of AF488, Hoechst and Dox signals. All scale bars are 10 μm. (reprinted with permission from Ref. [79].)

3.4 PDA based materials for antimicrobials

The outbreak of infectious diseases and development of antibiotic resistance, the search for novel antimicrobial agents has arouse great research attention. Due to their small size, high specific surface areas and unique chemical and physical properties, a large number of nanomaterials such as carbon nanotubes, graphene oxide, copper nanoparticles, Ag nanoparticles and polymeric nanoparticles have been examined as antimicrobial agents.[45, 223-234] In a recent report from Tang et al. it was demonstrated that the Ag nanoparticles can be in situ deposited on the graphene oxide sheets taken advantage of the adhesion of dopamine and reductivity of PDA thin films.[235] To fabricate such nanocomposites for antimicrobial applications, the graphene oxide sheets were first coated by PDA thin films through self-polymerization of dopamine under aqueous solution. Then Ag nanoparticles were formed via just mixing PDA functionalized graphene oxide sheets and $AgNO_3$. The antimicrobial activity of the final product (Ag-PDA-GNS) to Gram-positive bacteria E. coli cells and Gram-negative bacteria B. subtilis was examined. Results demonstrated that Ag-PDA-GNS hybrid materials could be facilely fabricated and showed strong antimicrobial activity to both Gram-negative and Gram-positive bacteria. These results suggested that mussel inspired chemistry is a facile and useful method for fabrication of Ag nanoparticles based antimcrobial nanocomposites for the universal adhesion of PDA thin films and their capability for in situ formation of Ag nanoparticles. In another report by Messersmith, the Au@Ag-NRs were facilely fabricated via surface coating of Au NRs with PDA thin films in rather mild conditions, followed by spontaneous electroless silver metallization. The results demonstrated that the release of silver can be well controlled by light irradiation, which can be related to the antimicrobial activity.[236]

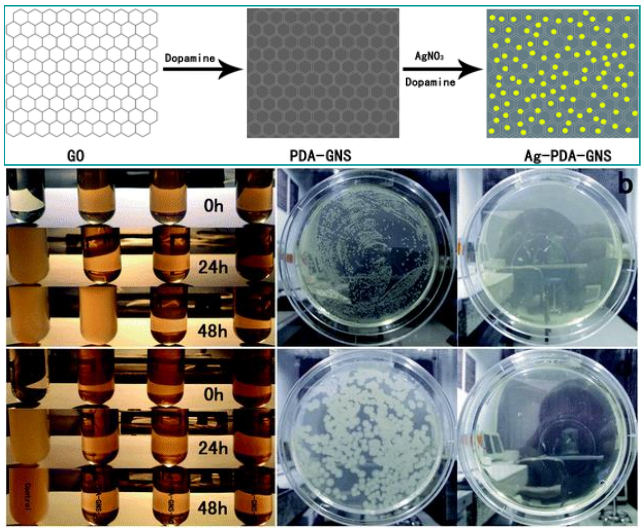


Fig. 16 The up image shows the illustration of the procedure for preparing Ag-PDA-GNS. The bottom images are the antibacterial activities of Ag-PDA-GNs. LB liquid medium turbidity assays (a and c) and LB–agar plate tests (b and d) were employed to evaluate antibacterial activities toward Gram-negative bacteria E. coli cells (a and b) and Gram-positive bacteria B. subtilis (c and d). (reprinted with permission from Ref. [235])

3.5 Tissue engineering

Biodegradable electrospun fibers have demonstrated to be promising scaffolds for supporting the growth of cells for fabrication of artificial tissues.[237-240] To fabricate suitable scaffolds for cell growth, adjustment of the surface properties of scaffolds is generally required. Due to the universal adhesion of dopamine towards a variety of materials and surfaces, the mussel inspired chemistry should be of great potential for surface property adjustment.[38, 241-253] For example, Park and colleagues have demonstrated that the biodegradable electrospun polycaprolactone (PCL) nanofibers can be modified by gelatin and PDA thin films.[254] These PCL electrospun nanofibers were used as the scaffolds for human endothelial cell growth. They demonstrated that the PDA modified PCL electrospun nanofibers displayed highly enhanced adhesion and viability, positive expression of endothelial cell markers and increased stress fiber formation

as compared with the unmodified and gelatin modified nanofibers. All of these results implied that the PDA coating plays a crucial role for enhancement of cell growth. Furthermore, some biocompatible hydrogels based on PDA have also prepared and showed promising properties for tissue engineering applications.[255] And the mussel inspired modification strategy should be a facile and useful route for surface modification of different scaffolds, which should be of great interest for tissue engineering applications.

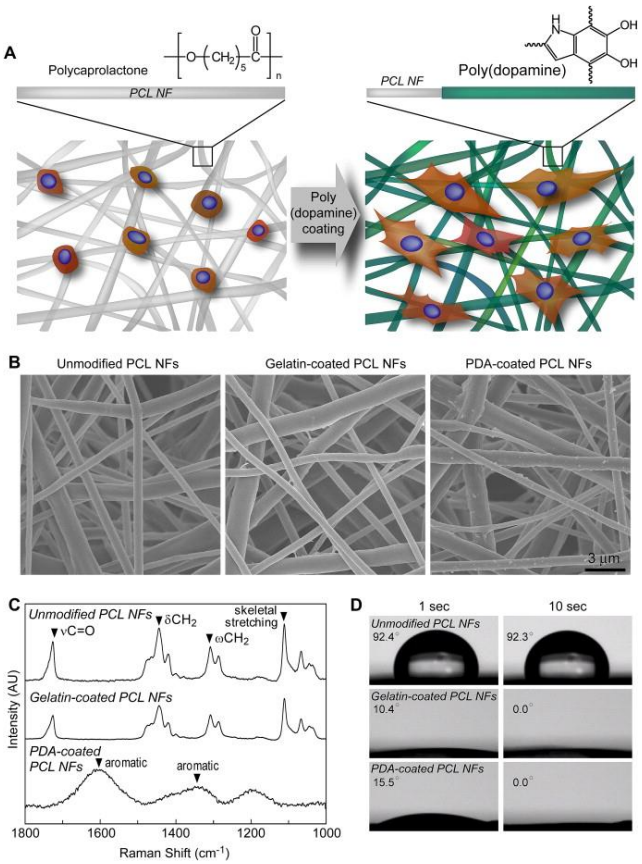


Fig. 17 (A) Schematic illustration of cell adhesion on PDA-coated polycaprolactone nanofibers (PCL NFs). (B) SEM images, (C) Raman spectra, and (D) water contact angle measurement of unmodified, gelatin-coated, and PDA-coated PCL NFs. The increase of fiber diameter, new Raman peaks at 1350/1600 cm^{-1}, and a decrease in the water contact angle indicate the formation of a PDA ad-layer on electrospun PCL NFs. (reprinted with permission from Ref. [254])

3.6 Enhancement of biocompatibility

Biocompatibility is related to the host responses of materials for specific biomedical applications.[256] Surface modification of materials and surfaces to enhance their biocompatibility is crucial for biomaterials include the drug delivery carriers, scaffolds and other implants. Previous reports have demonstrated that PDA not only possesses universal adhesion towards almost any materials and surfaces, but also could provide the active platforms for secondary modification reactions.[257-260] More importantly, the surface modification of nanomaterials with PDA coatings could reduce the toxicity of different nanomaterials such as semiconductor quantum dots, carbon nanotubes, graphene oxides, metal nanoparticles, and magnetic nanoparticles.[257-260] For example, Zhao et al have demonstrated that graphene oxide sheets can be facilely modified by the proteins such as BSA and Hep via combination mussel inspired chemistry and Michael addition reaction (**Fig. 18**). Results showed that the surface modfication of graphene oxide sheets with these biopolymers could not only improve the dispersibility of graphene oxide sheets, but also could affect the toxicity of graphene oxide sheets towards human cell lines and red blood cells.[84] These results implied that PDA modification is of great attention for surface modification of many different scaffolds and implant devices due to the biocompatibility enhancement and facile for secondary immobilization of biological active molecules through mild experimental conditions. In anther report, Ji et al have demonstrated the fabrication of PDA coated Au nanocomposites via mussel inspired chemistry. The cell uptake behavior, biodistribution and biodegradability of GNP@PDA was also inverstigated.[260] They demosntrated that PDA coated Au nanoparticles did not display toxicity to a number of tissues such as liver, spleen and kidneys after a single injection of GNP@PDA for 1 and 42 days.[260] These results suggested that surface modification of materials with PDA thin films is a useful route for fabrication of biocompatibile PDA coated nanocomposites, which are of great importance for biomedical applications.

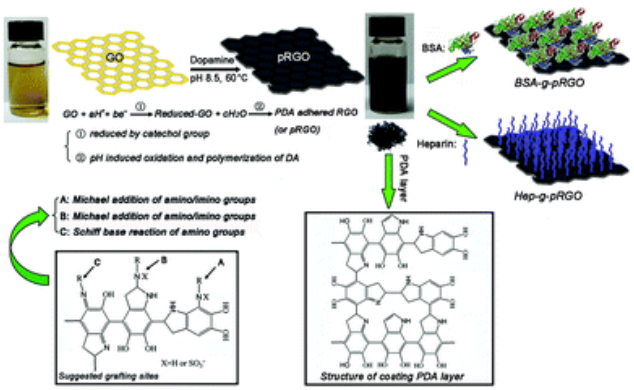


Fig. 18 Approach for constructing the aqueous stable and biocompatible RGO by a biomimetic method, and the possible PDA chemical structure as well as the suggested reaction mechanism. Note: the PDA coating layer could immobilize the biopolymer which contained thiols, imino, and amines groups, such as heparin or protein. (reprinted with permission from Ref. [84])

3.7 Cancer photothermal treatment

Cancer photothermal treatment is a recently emerged cancer therapy method. The photothermal treatment is based on the conversion of light energy into thermal and thus can kill the abnormal cells in situ. For a number of materials such as carbon nanotubes, graphene oxides, gold nanorods and conjugated polymeric nanomaterials, MoS_2 sheets and PDA nanospheres it has been demonstrated that they possess desirable photothermal conversion effects.[49, 261-266] However, fabrication of nanomaterials with good photothermal conversion capability, desirable biocompatibility and

biodegradability, high water dispersibility, easy for surface functionalization and low cost is still challenging. For example, many carbon nanomaterials based photothermal conversion agents such as carbon nanotubes and graphene oxide sheets are difficult to be degradable *in vivo*, which will cause subsequently toxicity to the living organisms.[262] Some other inorganic photothermal conversion agents such as MoS_2 sheets and Au nanorods etc have suffered the issues about the toxicity as well as high cost.[264] The previously utilized polymeric photothermal conversion agents such as polypyrrole nanoparticles are difficult to be dispersed in the aqueous solution and to resist degradation *in vivo*.[267] Therefore, development of novel photothermal conversion agents that could overcome the above problems is of great interest. Lu et al have recently demonstrated that PDA nanospheres can be prepared via self-polymerization of dopamine under the alkaline water and ethanol mixture at room temperature.[49] The size of these PDA nanospheres can be easily adjusted through changing the reaction conditions. More importantly, these PDA nanospheres showed desirable biocompatibility and very excellent photothermal conversion efficiency, which is much greater than that of gold nanorods. The photothermal treatment of cancer using these PDA nanospheres was confirmed through cell and animal models. For example, these PDA nanospheres showed almost no toxicity towards 4T1 cells even the concentration of PDA nanospheres is as high as 1.2 mg mL^{-1}, However, all cells were almost death when they were incubated with 50 μg mL^{-1} of PDA nanospheres and irradiated by near-infrared laser irradiation for 5 min (**Fig. 19**). Furthermore, the PDA nanospheres can effectively eliminate the tumors after they were irradiated using near-infrared laser irradiation. As compared with other types of methods, the photothermal treatment could focus on the tumor sites, thus can avoid the adverse effects to other tissues. Given the excellent photothermal conversion effects of PDA based nanomaterials and facile for surface modification, the PDA based nanocomposites should be an promising candidates for cancer photothermal treatment.[268, 269]

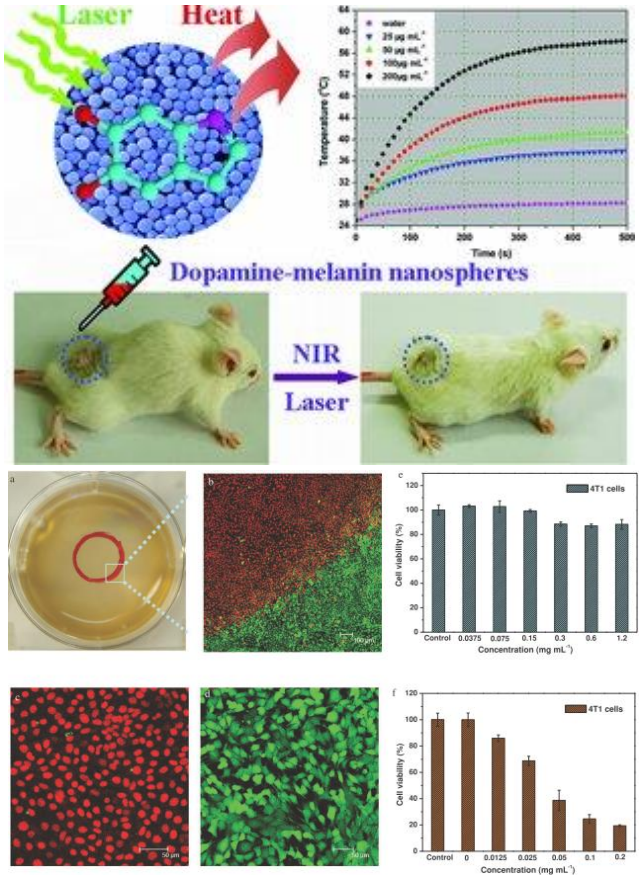


Fig. 19 The up images show the preparation of PDA nanospheres and their cancer photothermal treatment. The bolow images are the biocompatibility and photothermal treatment of PDA nanospheres. a) A digital photo of the 4T1 cell culture dish after incubation with Dpa-melanin CNSs. The red circle shows the laser spot. b–d) Confocal images of calcein AM (green, live cells) and propidium iodide (red, dead cells) co-stained 4T1 cells after laser irradiation. e) Cell viability of 4T1 cells after incubation with increased concentrations of Dpa-melanin CNSs. f) Cell viability of 4T1 cells treated with different concentrations of Dpa-melanin CNSs and laser irradiation (808 nm, 2 W cm^{-2}, 5 min). (reprinted with permission from Ref. [49])

3.7 Multifunctional theranostics

Theranostic is a novel cancer treatment concept that was intergated the therapeutic and diagnosis components into one entity. Over the past few decades, great progress has been made in the design and fabrication of theranostic agents through combination of different imaging and therapeutic models.[270-282] However, facile fabrication of promising therapeutic agents is still not easy due to the limitations such as low efficiency and toxicity. Based on the excellent photothermal conversion effect of PDA nanospheres, Lu et al have demonstrated a novel multifunctional nanotheranostic systems based on the PDA nanocomposites.[283] To fabricate these theranostic systems, the PDA nanospheres were coated with coordinating polymers, which were formed by the coordination of benzene-1,3,5-tricarboxylic acid with iron ion. The biomedical applications of the resultant PDA based multifunctional nanocomposites for MRI imaging, DOX delivery and photothermal cancer treatment were evaluated. Results demonstrated that PDA based nanocomposites can be

used for T1/T2 dual mode MRI imaging. More importantly, these PDA nanospheres can be used to encapsulate DOX, which can be controlled release from drug carriers by NIR laser. It is therefore, the PDA based nanocomplexes can be used for MRI guided chemo-thermal synergistic treatment. In another report by Liu et al, the PEGylated PDA nanospheres were examined as chemo-radiotherapy. The PEGylated PDA nanospheres were first labeled with radionuclides such as ^{131}I and ^{99m}Tc, which were utilized for radiotherapy. The anticancer agent (DOX) can be further loaded onto radionuclide labeled PDA nanospheres. The results suggested that these PDA nanospheres could exhibit strong antitumor effect and excellent biocompatibility to animals.[284] All of these results implied that PDA based nanocomposites are promising candidates for fabrication of multifunctional nanotheranostic systems.

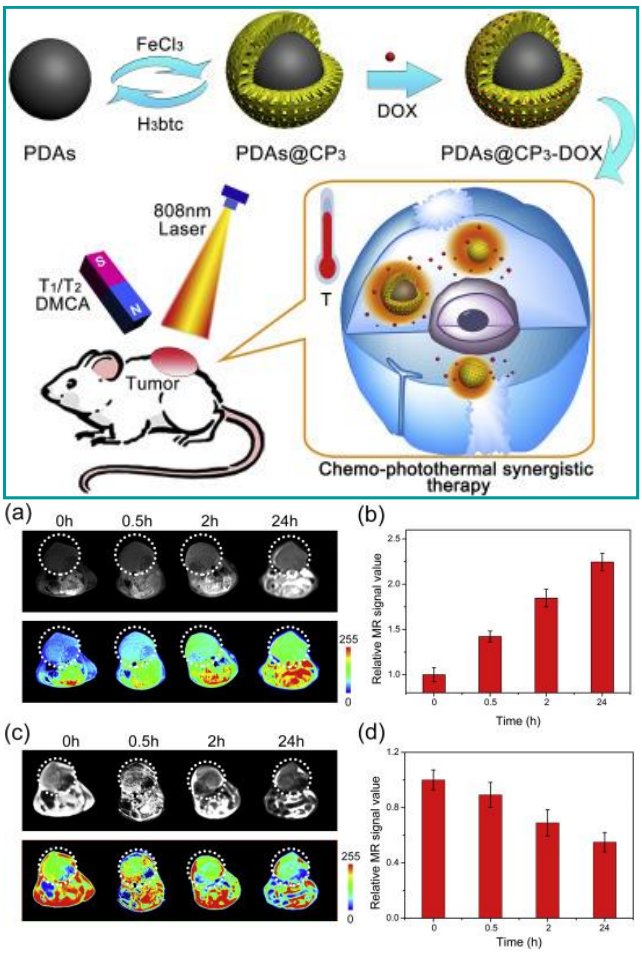


Fig. 20 Schematic illustration of the synthesis and application of PDAs@CP_3-DOX. *In vivo* T_1 (a) and T_2 (c) MR images of mice after intravenous injection of PDAs@CP_3 at different time intervals (0 h means pre-injection), and corresponding data analysis of T_1 (b) and T_2-weighted (d) MRI measurements, respectively. (reprinted with permission from Ref. [283].)

4. Conclusion

This reivew summarized the recent advanced surface modification and their biomedical applications of PDA based materials in recent years. A number of surface modification strategies that relied on the mussel inspired chemistry have been discussed including the Michael addition reation of amino- and thiol-contained compounds, combination of mussel inspired chemistry and chain transfer free radical polymerization, surface-initiated ATRP, surface-initiated SET-LRP, combination of RAFT polymerization and Michael addition reaction, and light irradiation initiated surface polymerization etc. Recently, the biomedical applications of these PDA based nanocomposites have extensively explored and many exciting results were achieved. The topic biomedical applications are mainly included PDA materials based biosensing, luminescent PDA nanoprobes for biological imaging, PDA based nanocomposites for antimacrobial applications, controlled drug delivery, siRNA delivery, improvement of biocompatibility, tissue engineering, photothermal cancer treatment and PDA based multifunctional nanotheranostics. Although great progress has been made in the surface modification and biomedical applications of PDA based materials, there still has many spaces for the development of PDA based materials for practical biomedical applications. For example, some reports have demonstrated that dopamine can be used for fabrication of polymeric luminescent nanoparticles or nanocapsules, however, the mechanism for generation of fluorescence is still not clear. On the other hand, no rational design principle for fabrication and regulating the luminescent properties, morphology and functional groups of these PDA based luminescent materials. Furthermore, the detailed information about pharmacokinetics behavior and long-term toxicity data of these PDA based materials is still lacking.

Acknowledgements

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Notes

a Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China.

b Department of Chemistry and the Tsinghua Center for Frontier Polymer Research, Tsinghua University, Beijing, 100084, P. R. China.

Xiaoyongzhang@1980@gmail.com , weiyen@tsinghua.edu.cn

References

1. L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang and D. Zhu, *Adv. Mater.*, 2002, **14**, 1857-1860.
2. T. Sun, L. Feng, X. Gao and L. Jiang, *Acc. Chem. Res.*, 2005, **38**, 644-652.
3. G. D. Bixler and B. Bhushan, *Nanoscale*, 2013, **5**, 7685-7710.
4. W.-L. Min, B. Jiang and P. Jiang, *Adv. Mater.*, 2008, **20**, 3914-3918.
5. X. Gao and L. Jiang, *Nature*, 2004, **432**, 36-36.

6. L. Jiang, Y. Zhao and J. Zhai, *Angew. Chem. Int. Ed*, 2004, **116**, 4438-4441.

7. Y. Zheng, H. Bai, Z. Huang, X. Tian, F.-Q. Nie, Y. Zhao, J. Zhai and L. Jiang, *Nature*, 2010, **463**, 640-643.

8. K. Liu, J. Du, J. Wu and L. Jiang, *Nanoscale*, 2012, **4**, 768-772.

9. K. Liu, X. Yao and L. Jiang, *Chem. Soc. Rev.*, 2010, **39**, 3240-3255.

10. K. Liu and L. Jiang, *Nano Today*, 2011, **6**, 155-175.

11. J. Ju, H. Bai, Y. Zheng, T. Zhao, R. Fang and L. Jiang, *Nat. Commun.*, 2012, **3**, 1247.

12. J. Wu, N. Wang, Y. Zhao and L. Jiang, *Nanoscale*, 2015, **7**, 2625-2632.

13. M. Liu, H. Zhang, K. Li, L. Heng, S. Wang, Y. Tian and L. Jiang, *Adv. Funct. Mater.*, 2015, **25**, 421-426.

14. W. Liu, X. Liu, J. Fangteng, S. Wang, L. Fang, H. Shen, S. Xiang, H. Sun and B. Yang, *Nanoscale*, 2014, **6**, 13845-13853.

15. J. H. Waite and M. L. Tanzer, *Science*, 1981, **212**, 1038-1040.

16. K. J. Coyne, X.-X. Qin and J. H. Waite, *Science*, 1997, **277**, 1830-1832.

17. J. H. Waite, *J. Biol. Chem.*, 1983, **258**, 2911-2915.

18. Q. Lin, D. Gourdon, C. Sun, N. Holten-Andersen, T. H. Anderson, J. H. Waite and J. N. Israelachvili, *Proc. Natl. Acad. Sci. U.S.A.*, 2007, **104**, 3782-3786.

19. L. A. Burzio and J. H. Waite, *Biochemistry*, 2000, **39**, 11147-11153.

20. B. P. Lee, P. B. Messersmith, J. N. Israelachvili and J. H. Waite, *Annu. Rev. Mater. Chem.*, 2011, **41**, 99.

21. S. W. Taylor, D. B. Chase, M. H. Emptage, M. J. Nelson and J. H. Waite, *Inorg. Chem.*, 1996, **35**, 7572-7577.

22. E. W. Danner, Y. Kan, M. U. Hammer, J. N. Israelachvili and J. H. Waite, *Biochemistry*, 2012, **51**, 6511-6518.

23. M. J. Harrington, A. Masic, N. Holten-Andersen, J. H. Waite and P. Fratzl, *Science*, 2010, **328**, 216-220.

24. H. Zeng, D. S. Hwang, J. N. Israelachvili and J. H. Waite, *Proc. Natl. Acad. Sci. U.S.A.*, 2010, **107**, 12850-12853.

25. N. Holten-Andersen, M. J. Harrington, H. Birkedal, B. P. Lee, P. B. Messersmith, K. Y. C. Lee and J. H. Waite, *Proc. Natl. Acad. Sci. U.S.A.*, 2011, **108**, 2651-2655.

26. W. Wei, J. Yu, C. Broomell, J. N. Israelachvili and J. H. Waite, *J. Am. Chem. Soc.*, 2012, **135**, 377-383.

27. S. C. Nicklisch and J. H. Waite, *Biofouling*, 2012, **28**, 865-877.

28. J. Heo, T. Kang, S. G. Jang, D. S. Hwang, J. M. Spruell, K. L. Killops, J. H. Waite and C. J. Hawker, *J. Am. Chem. Soc.*, 2012, **134**, 20139-20145.

29. J. Yu, W. Wei, M. S. Menyo, A. Masic, J. H. Waite and J. N. Israelachvili, *Biomacromolecules*, 2013, **14**, 1072-1077.

30. Y. Kan, E. W. Danner, J. N. Israelachvili, Y. Chen and J. H. Waite, *Plos One*, 2014, DOI: 10.1371/journal.pone.0108869.

31. Q. Wan, M. Liu, J. Tian, F. Deng, Y. Dai, K. Wang, Z. Li, Q. Zhang, X. Zhang and Y. Wei, *RSC Adv.*, 2015, **5**, 38316-38323.

32. Q. Wan, J. Tian, M. Liu, G. Zeng, Z. Li, K. Wang, Q. Zhang, F. Deng, X. Zhang and Y. Wei, *RSC Adv.*, 2015, **5**, 25329-25336.

33. Y. Xie, C. He, L. Liu, L. Mao, K. Wang, Q. Huang, M. Liu, Q. Wan, F. Deng and H. Huang, *RSC Adv.*, 2015, **5**, 82503-82512.

34. Y. Xie, Q. Huang, M. Liu, K. Wang, Q. Wan, F. Deng, L. Lu, X. Zhang and Y. Wei, *RSC Adv.*, 2015, **5**, 68430-68438.

35. X. Liu, J. Deng, L. Ma, C. Cheng, C. Nie, C. He and C. Zhao, *Langmuir*, 2014, **30**, 14905-14915.

36. H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426-430.

37. W. Kwon, S. Do and S.-W. Rhee, *RSC Adv.*, 2012, **2**, 11223-11226.

38. W.-B. Tsai, W.-T. Chen, H.-W. Chien, W.-H. Kuo and M.-J. Wang, *Acta Biomater.*, 2011, **7**, 4187-4194.

39. D. Zhong, Q. Yang, L. Guo, S. Dou, K. Liu and L. Jiang, *Nanoscale*, 2013, **5**, 5758-5764.

40. D. Hong, H. Lee, B. J. Kim, T. Park, J. Y. Choi, M. Park, J. Lee, H. Cho, S.-P. Hong and S. H. Yang, *Nanoscale*, 2015, **7**, 20149-20154.

41. J. WonáKim, S. JaeáLee and B. GilláChoi, *Nanoscale*, 2015, **7**, 324-329.

42. X. Wu, C. Yang, J. Ge and Z. Liu, *Nanoscale*, 2015, **7**, 18883-18886.

43. Y. Jin, D. Deng, Y. Cheng, L. Kong and F. Xiao, *Nanoscale*, 2014, **6**, 4812-4818.

44. A. R. K. Sasikala, A. GhavamiNejad, A. R. Unnithan, R. G. Thomas, M. Moon, Y. Y. Jeong, C. H. Park and C. S. Kim, *Nanoscale*, 2015, **7**, 18119-18128.

45. S. M. Kang, S. Park, D. Kim, S. Y. Park, R. S. Ruoff and H. Lee, *Adv. Funct. Mater.*, 2011, **21**, 108-112.

46. K. Ai, Y. Liu, C. Ruan, L. Lu and G. M. Lu, *Adv. Mater.*, 2013, **25**, 998-1003.

47. H. Lee, J. Rho and P. B. Messersmith, *Adv. Mater.*, 2009, **21**, 431-434.

48. Y. Lee, H. Lee, Y. B. Kim, J. Kim, T. Hyeon, H. Park, P. B. Messersmith and T. G. Park, *Adv. Mater.*, 2008, **20**, 4154-4157.

49. Y. Liu, K. Ai, J. Liu, M. Deng, Y. He and L. Lu, *Adv. Mater.*, 2013, **25**, 1353-1359.

50. M.-H. Ryou, J. Kim, I. Lee, S. Kim, Y. K. Jeong, S. Hong, J. H. Ryu, T.-S. Kim, J.-K. Park and H. Lee, *Adv. Mater.*, 2013, **25**, 1571-1576.

51. M.-H. Ryou, Y. M. Lee, J.-K. Park and J. W. Choi, *Adv. Mater.*, 2011, **23**, 3066-3070.

52. C. Cheng, S. Li, J. Zhao, X. Li, Z. Liu, L. Ma, X. Zhang, S. Sun and C. Zhao, *Chem. Eng. J.*, 2013, **228**, 468-481.

53. Q. Wei, F. Zhang, J. Li, B. Li and C. Zhao, *Polym. Chem.*, 2010, **1**, 1430-1433.

54. J. Wang, H. Zhu, G. Chen, Z. Hu, Y. Weng, X. Wang and W. Zhang, *Macromol. Rapid Commun.*, 2014, **35**, 1061-1067.

55. Y. Liu, K. Ai and L. Lu, *Chem. Rev.*, 2014, DOI: 10.1021/cr400407a.

56. Q. Ye, F. Zhou and W. Liu, *Chem. Soc. Rev.*, 2011, **40**, 4244-4258.

57. M. E. Lynge, R. van der Westen, A. Postma and B. Sttädler, *Nanoscale*, 2011, **3**, 4916-4928.

58. E. Faure, C. Falentin-Daudré, C. Jérôme, J. Lyskawa, D. Fournier, P. Woisel and C. Detrembleur, *Prog. Polym. Sci.*, 2011, **38**, 236-270.

59. J. Sedó, J. Saiz-Poseu, F. Busqué and D. Ruiz-Molina, *Adv. Mater.*, 2013, **25**, 653-701.

60. S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi and R. Kumar, *Prog. Polym. Sci.*, 2013, **38**, 1232-1261.

61. B. Yang, Y. Zhao, X. Ren, X. Zhang, C. Fu, Y. Zhang, Y. Wei and L. Tao, *Polym. Chem.*, 2015, **6**, 509-513.

62. X. Ren, B. Yang, Y. Zhao, X. Zhang, X. Wang, Y. Wei and L. Tao, *Polymer*, 2015, **64**, 210-215.

63. X. Zhang, J. Yin, C. Peng, W. Hu, Z. Zhu, W. Li, C. Fan and Q. Huang, *Carbon*, 2011, **49**, 986-995.

64. X. Zhang, J. Yin, C. Kang, J. Li, Y. Zhu, W. Li, Q. Huang and Z. Zhu, *Toxicol. Lett.*, 2010, **198**, 237-243.

65. X. Zhang, Y. Zhu, J. Li, Z. Zhu, J. Li, W. Li and Q. Huang, *J. Nanopart. Res.*, 2011, **13**, 6941-6952.

66. X. Zhang, C. Fu, L. Feng, Y. Ji, L. Tao, Q. Huang, S. Li and Y. Wei, *Polymer*, 2012, **53**, 3178-3184.

67. X. Zhang, S. Wang, C. Fu, L. Feng, Y. Ji, L. Tao, S. Li and Y. Wei, *Polym. Chem.*, 2012, **3**, 2716-2719.

68. X. Zhang, J. Hui, B. Yang, Y. Yang, D. Fan, M. Liu, L. Tao and Y. Wei, *Polym. Chem.*, 2013, **4**, 4120-4125.

69. J. Hui, X. Zhang, Z. Zhang, S. Wang, L. Tao, Y. Wei and X. Wang, *Nanoscale*, 2012, **4**, 6967-6970.

70. X. Zheng, M. Liu, J. Hui, D. Fan, H. Ma, X. Zhang, Y. Wang and Y. Wei, *Phys. Chem. Chem. Phys.*, 2015, **17**, 20301-20307.

71. T. Desmet, R. Morent, N. D. Geyter, C. Leys, E. Schacht and P. Dubruel, *Biomacromolecules*, 2009, **10**, 2351-2378.

72. R. Morent, N. De Geyter, T. Desmet, P. Dubruel and C. Leys, *Plasma Process. Polym.*, 2011, **8**, 171-190.

73. R. Morent, N. De Geyter, S. Van Vlierberghe, P. Dubruel, C. Leys and E. Schacht, *Surf. Coat. Tech.*, 2009, **203**, 1366-1372.

74. N. De Geyter, R. Morent, T. Desmet, M. Trentesaux, L. Gengembre, P. Dubruel, C. Leys and E. Payen, *Surf. Coat. Tech.*, 2010, **204**, 3272-3279.

75. B. Yu, D. A. Wang, Q. Ye, F. Zhou and W. Liu, *Chem. Commum.*, 2009, 6789-6791.

76. X. Chen, Y. Yan, M. Muúllner, M. P. van Koeverden, K. F. Noi, W. Zhu and F. Caruso, *Langmuir*, 2014, **30**, 2921-2925.

77. W. Sheng, W. Li, B. Li, C. Li, Y. Xu, X. Guo, F. Zhou and X. Jia, *Macromol. Rapid Commun.*, 2015, **36**, 1640-1645.

78. X. Zhang, S. Wang, L. Xu, Y. Ji, L. Feng, L. Tao, S. Li and Y. Wei, *Nanoscale*, 2012, **4**, 5581-5584.

79. J. Cui, Y. Yan, G. K. Such, K. Liang, C. J. Ochs, A. Postma and F. Caruso, *Biomacromolecules*, 2012, **13**, 2225-2228.

80. H. Hu, B. Yu, Q. Ye, Y. Gu and F. Zhou, *Carbon*, 2010, **48**, 2347-2353.

81. C. Heng, M. Liu, K. Wang, F. Deng, H. Huang, Q. Wan, J. Hui, X. Zhang and Y. Wei, *Ceram. Int.*, 2015, **41**, 15075-15082.

82. X. Zhang, J. Ji, X. Zhang, B. Yang, M. Liu, W. Liu, L. Tao, Y. Chen and Y. Wei, *RSC Adv.*, 2013, **3**, 21817-21823.

83. X. Zhang, M. Liu, Y. Zhang, B. Yang, Y. Ji, L. Feng, L. Tao, S. Li and Y. Wei, *RSC Adv.*, 2012, **2**, 12153-12155.

84. C. Cheng, S. Nie, S. Li, H. Peng, H. Yang, L. Ma, S. Sun and C. Zhao, *J. Mater. Chem. B*, 2013, **1**, 265-275.

85. C. Nie, L. Ma, C. Cheng, J. Deng and C. Zhao, *Biomacromolecules*, 2015, **16**, 992-1001.

86. Y. Xia, C. Cheng, R. Wang, C. He, L. Ma and C. Zhao, *Colloids Surf. B Biointerfaces*, 2016, doi:10.1016/j.colsurfb.2015.1012.1018.

87. L. Xu, N. Liu, Y. Cao, F. Lu, Y. Chen, X. Zhang, L. Feng and Y. Wei, *ACS Appl. Mater. Interf.*, 2014, **6**, 13324-13329.

88. Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng and Y. Wei, *ACS Appl. Mater. Interf.*, 2013, **5**, 4438–4442.

89. X. Zhang, Q. Huang, M. Liu, J. Tian, G. Zeng, Z. Li, K. Wang, Q. Zhang, Q. Wan and F. Deng, *Appl. Surf. Sci.*, 2015, **343**, 19-27.

90. X. Zhang, G. Zeng, J. Tian, Q. Wan, Q. Huang, K. Wang, Q. Zhang, M. Liu, F. Deng and Y. Wei, *Appl. Surf. Sci.*, 2015, **351**, 425-432.

91. Y. Shi, M. Liu, K. Wang, F. Deng, Q. Wan, Q. Huang, L. Fu, X. Zhang and Y. Wei, *Polym. Chem.*, 2015, **6**, 5876-5883.

92. L. Fu, Y. Shi, K. Wang, P. Zhou, M. Liu, Q. Wan, L. Tao, X. Zhang and Y. Wei, *New J. Chem.*, 2015, **39**, 8172-8179.

93. J. Tian, H. Zhang, M. Liu, F. Deng, H. Huang, Q. Wan, Z. Li, K. Wang, X. He and X. Zhang, *Appl. Surf. Sci.*, 2015, **357**, 1996-2003.

94. Q. Wan, J. Tian, M. Liu, G. Zeng, Q. Huang, K. Wang, Q. Zhang, F. Deng, X. Zhang and Y. Wei, *Appl. Surf. Sci.*, 2015, **346**, 335-341.

95. C. Hou, Z. Qi and H. Zhu, *Colloids Surf. B Biointerfaces*, 2015, **128**, 544-551.

96. E. D. Giol, D. Schaubroeck, K. Kersemans, F. De Vos, S. Van Vlierberghe and P. Dubruel, *Colloids Surf. B Biointerfaces*, 2015, **134**, 113-121.

97. D. Schaubroeck, Y. Vercammen, L. Van Vaeck, E. Vanderleyden, P. Dubruel and J. Vanfleteren, *Appl. Surf. Sci.*, 2014, **303**, 465-472.

98. G. Zeng, M. Liu, X. Liu, Q. Huang, D. Xu, L. Mao, H. Huang, F. Deng, X. Zhang and Y. Wei, *Appl. Surf. Sci.*, 2016, doi:10.1016/j.apsusc.2016.1005.1093.

99. F. Bernsmann, B. Frisch, C. Ringwald and V. Ball, *J. Colloid Interf. Sci.*, 2010, **344**, 54-60.

100. Z. Ma, X. Jia, J. Hu, G. Zhang, F. Zhou, Z. Liu and H. Wang, *Langmuir*, 2013, **29**, 5631-5637.

101. X. Wang, Q. Ye, T. Gao, J. Liu and F. Zhou, *Langmuir*, 2012, **28**, 2574-2581.

102. J. Yan, B. Li, F. Zhou and W. Liu, *ACS Macro Lett.*, 2013, **2**, 592-596.

103. W.-x. Wang, M.-h. Wang and J.-m. Sun, *Chin. J. Polym. Sci.*, 2015, **33**, 1260-1270.

104. T. Sun, C.-l. Chen and X.-z. Gong, *Chin. J. Polym. Sci.*, 2014, **32**, 880-891.

105. J.-l. Pan, Z. Li and L.-f. Zhang, *Chin. J. Polym. Sci.*, 2014, **32**, 1010-1018.

106. Z. Ma, X. Jia, J. Hu, Z. Liu, H. Wang and F. Zhou, *J. Agric. Food Chem.*, 2013, **61**, 12232-12237.

107. X. Fan, L. Lin, J. L. Dalsin and P. B. Messersmith, *J. Am. Chem. Soc*, 2005, **127**, 15843-15847.

108. P. Glass, H. Chung, N. R. Washburn and M. Sitti, *Langmuir*, 2009, **25**, 6607-6612.

109. C. Li, W. Wang, F. Xu, L. Zhang and W. Yang, *J. Membrane Sci.*, 2011, **367**, 7-13.

110. J. Liu, Q. Ye, B. Yu, X. Wang and F. Zhou, *Chem. Commun.*, 2012, **48**, 398-400.

111. B. Zhu and S. Edmondson, *Polymer*, 2011, **52**, 2141-2149.

112. V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro and S. Sahoo, *J. Am. Chem. Soc.*, 2006, **128**, 14156-14165.

113. F. Alsubaie, A. Anastasaki, P. Wilson and D. M. Haddleton, *Polym. Chem.*, 2015, **6**, 406-417.

114. B. M. Rosen and V. Percec, *Chem. Rev.*, 2009, **109**, 5069-5119.

115. S. R. Samanta, V. Nikolaou, S. Keller, M. J. Monteiro, D. A. Wilson, D. M. Haddleton and V. Percec, *Polym. Chem.*, 2015, **6**, 2084-2097.

116. S. R. Samanta, R. Cai and V. Percec, *Polym. Chem.*, 2015, **6**, 3259-3270.

117. S. R. Samanta, H.-J. Sun, A. Anastasaki, D. M. Haddleton and V. Percec, *Polym. Chem.*, 2015, **5**, 89-95.

118. D. Konkolewicz, Y. Wang, P. Krys, M. Zhong, A. A. Isse, A. Gennaro and K. Matyjaszewski, *Polym. Chem.*, 2014, **5**, 4396-4417.

119. C. Waldron, Q. Zhang, Z. Li, V. Nikolaou, G. Nurumbetov, J. Godfrey, R. McHale, G. Yilmaz, R. K. Randev and M. Girault, *Polym. Chem.*, 2014, **5**, 57-61.

120. C. Waldron, A. Anastasaki, R. McHale, P. Wilson, Z. Li, T. Smith and D. M. Haddleton, *Polym. Chem.*, 2014, **5**, 892-898.

121. H.-n. Li, F.-j. Zhang, S. Xie and Z.-j. Liu, *Chin. J. Polym. Sci.*, 2015, **33**, 362-370.

122. O. Bertrand, P. Wilson, J. A. Burns, G. A. Bell and D. M. Haddleton, *Polym. Chem.*, 2015, **6**, 8319-8324.

123. S. R. Samanta and V. Percec, *Polym. Chem.*, 2015, **5**, 169-174.

124. S. R. Samanta, R. Cai and V. Percec, *Polym. Chem.*, 2014, **5**, 5479-5491.

125. A. Simula, V. Nikolaou, F. Alsubaie, A. Anastasaki and D. M. Haddleton, *Polym. Chem.*, 2015, **6**, 5940-5950.

126. T. Zhang, Y. Du, F. Müller, I. Amin and R. Jordan, *Polym. Chem.*, 2015, **6**, 2726-2733.

127. Q. Wan, M. Liu, J. Tian, F. Deng, G. Zeng, Z. Li, K. Wang, Q. Zhang, X. Zhang and Y. Wei, *Polym. Chem.*, 2015, **6**, 1786-1792.

128. C. Heng, M. Liu, K. Wang, X. Zheng, H. Huang, F. Deng, J. Hui, X. Zhang and Y. Wei, *RSC Adv.*, 2015, **5**, 91308-91314.

129. D. J. Wang, H. Chen, H. Xu, J. M. Sun and Y. Y. Xu, *ACS Sustain. Chem. Eng.*, 2014, **2**, 1843-1848.

130. J. Liu, W. Yang, L. Tao, D. Li, C. Boyer and T. P. Davis, *J. Polym. Sci. A Polym. Chem.*, 2010, **48**, 425-433.

131. Y. Deng, Y. Li, J. Dai, M. Lang and X. Huang, *J. Polym. Sci. A Polym. Chem.*, 2011, **49**, 4747-4755.

132. J. Tian, D. Xu, M. Liu, F. Deng, Q. Wan, Z. Li, K. Wang, X. He, X. Zhang and Y. Wei, *J. Polym. Sci. A Polym. Chem.*, 2015, **53**, 1872-1879.

133. Q. Wan, L. Mao, M. Liu, K. Wang, G. Zeng, D. Xu, H. Huang, X. Zhang and Y. Wei, *Polym. Chem.*, 2015, **6**, 7211-7218.

134. H. Chung, P. Glass, J. M. Pothen, M. Sitti and N. R. Washburn, *Biomacromolecules*, 2010, **12**, 342-347.

135. J. K. Park, K. S. Kim, J. Yeom, H. S. Jung and S. K. Hahn, *Macromol. Chem. Phys.*, 2012, **213**, 2130-2135.

136. T. Zhang, T. Chen, I. Amin and R. Jordan, *Polym. Chem.*, 2014, **5**, 4790-4796.

137. Z. Liu, G. Zhang, W. Lu, Y. Huang, J. Zhang and T. Chen, *Polym. Chem.*, 2015, **6**, 6129-6132.

138. Y. Hou, P. Xiao, J. Zhang, M. Peng, W. Lu, Y. Huang, C. Ouyang and T. Chen, *RSC Adv.*, 2015, **5**, 60990-60992.

139. W. Sheng, B. Li, X. Wang, B. Dai, B. Yu, X. Jia and F. Zhou, *Chem. Sci.*, 2015, **6**, 2068-2073.

140. G. Yang, L. Li, R. K. Rana and J.-J. Zhu, *Carbon*, 2013, **61**, 357-366.

141. B. Xing and X.-B. Yin, *Plos One*, 2009, **4**, e6451.

142. Y. Wan, D. Zhang, Y. Wang, P. Qi and B. Hou, *Biosens. Bioelectron.*, 2011, **26**, 2595-2600.

143. G. Wang, H. Huang, G. Zhang, X. Zhang, B. Fang and L. Wang, *Langmuir*, 2010, **27**, 1224-1231.

144. A. Tretjakov, V. Syritski, J. Reut, R. Boroznjak, O. Volobujeva and A. Öpik, *Microchim. Acta*, 2013, **180**, 1433-1442.

145. S. Shi, L. Wang, R. Su, B. Liu, R. Huang, W. Qi and Z. He, *Biosens. Bioelectron.*, 2013, **74**, 454-460.

146. X. Tang, S. Bansaruntip, N. Nakayama, E. Yenilmez, Y.-l. Chang and Q. Wang, *Nano Lett.*, 2006, **6**, 1632-1636.

147. S. He, B. Song, D. Li, C. Zhu, W. Qi, Y. Wen, L. Wang, S. Song, H. Fang and C. Fan, *Adv. Funct. Mater.*, 2010, **20**, 453-459.

148. S. Liu, L. Wang, Y. Luo, J. Tian, H. Li and X. Sun, *Nanoscale*, 2011, **3**, 967-969.

149.H. Li, J. Zhai and X. Sun, *Nanoscale*, 2011, **3**, 2155-2157.

150.Q. Liu, Z. Pu, A. M. Asiri, A. O. Al-Youbi and X. Sun, *Sensor. Actuat. B-Chem.*, 2014, **191**, 567-571.

151.Y. Yan, Z. Zheng, C. Deng, X. Zhang and P. Yang, *Chem. Commun.*, 2013, **49**, 5055-5057.

152.W.-H. Zhou, C.-H. Lu, X.-C. Guo, F.-R. Chen, H.-H. Yang and X.-R. Wang, *J. Mater. Chem.*, 2010, **20**, 880-883.

153.M. Zhang, X. Zhang, X. He, L. Chen and Y. Zhang, *Nanoscale*, 2012, **4**, 3141-3147.

154.R.-P. Liang, X.-N. Wang, C.-M. Liu, X.-Y. Meng and J.-D. Qiu, *J. Chromatogr. A*, 2014, **1323**, 135-142.

155.M. Liu, X. Zhang, B. Yang, Z. Li, F. Deng, Y. Yang, X. Zhang and Y. Wei, *Carbohyd. Polym.*, 2015, **121**, 49-55.

156.X. Zhang, S. Wang, C. Zhu, M. Liu, Y. Ji, L. Feng, L. Tao and Y. Wei, *J. Colloid Interf. Sci.*, 2013, **397**, 39-44.

157.X. Zhang, S. Wang, M. Liu, B. Yang, L. Feng, Y. Ji, L. Tao and Y. Wei, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19013-19018.

158.X. Zhang, X. Zhang, S. Wang, M. Liu, Y. Zhang, L. Tao and Y. Wei, *ACS Appl. Mater. Interf.*, 2013, **5**, 1943-1947.

159.X. Zhang, X. Zhang, B. Yang, Y. Zhang and Y. Wei, *ACS Appl. Mater. Interf.*, 2014, **6**, 3600-3606.

160.Y. Liu, X. Feng, J.-g. Zhi and B. Tong, *Chin. J. Polym. Sci.*, 2012, **30**, 443-450.

161.X. Hui, D. Xu, K. Wang, W. Yu, H. Yuan, M. Liu, S. Zhengyu, X. Zhang and Y. Wei, *RSC Adv.*, 2015, **5**, 107355-107359.

162.X. Zhang, J. Li, Y. Zhu, Y. Qi, Z. Zhu, W. Li and Q. Huang, *Nucl. Sci. Tech.*, 2011, **22**, 99-104.

163.Q. Wan, M. Liu, D. Xu, H. Huang, L. Mao, G. Zeng, F. Deng, X. Zhang and Y. Wei, *J. Mater. Chem. B*, 2016, **4**, 4033-4039.

164.M. Liu, H. Huang, K. Wang, D. Xu, Q. Wan, J. Tian, Q. Huang, F. Deng, X. Zhang and Y. Wei, *Carbohyd. Polym.*, 2016, **142**, 38-44.

165.Q. Wan, K. Wang, H. Du, H. Huang, M. Liu, F. Deng, Y. Dai, X. Zhang and Y. Wei, *Polym. Chem.*, 2015, **6**, 5288-5294.

166.Q. Wan, K. Wang, C. He, M. Liu, G. Zeng, H. Huang, F. Deng, X. Zhang and Y. Wei, *Polym. Chem.*, 2015, **6**, 8214-8221.

167.X. Zhang, M. Liu, B. Yang, X. Zhang, Z. Chi, S. Liu, J. Xu and Y. Wei, *Polym. Chem.*, 2013, **4**, 5060-5064.

168.X. Zhang, X. Zhang, B. Yang, J. Hui, M. Liu, Z. Chi, S. Liu, J. Xu and Y. Wei, *Polym. Chem.*, 2014, **5**, 318-322.

169.X. Zhang, X. Zhang, B. Yang, J. Hui, M. Liu, Z. Chi, S. Liu, J. Xu and Y. Wei, *Polym. Chem.*, 2014, **5**, 683-688.

170.X. Zhang, X. Zhang, B. Yang, J. Hui, M. Liu, W. Liu, Y. Chen and Y. Wei, *Polym. Chem.*, 2014, **5**, 689-693.

171.X. Zhang, X. Zhang, B. Yang, M. Liu, W. Liu, Y. Chen and Y. Wei, *Polym. Chem.*, 2013, **4**, 4317-4321.

172.X. Zhang, X. Zhang, B. Yang, M. Liu, W. Liu, Y. Chen and Y. Wei, *Polym. Chem.*, 2014, **5**, 356-360.

173.X. Zhang, X. Zhang, B. Yang, M. Liu, W. Liu, Y. Chen and Y. Wei, *Polym. Chem.*, 2014, **5**, 399-404.

174.Y. Zhao, B. Yang, Y. Zhang, S. Wang, C. Fu, Y. Wei and L. Tao, *Polym. Chem.*, 2014.

175.X. Zhang, X. Zhang, B. Yang, L. Liu, F. Deng, J. Hui, M. Liu, Y. Chen and Y. Wei, *RSC Adv.*, 2014, **4**, 24189-24193.

176.X. Zhang, X. Zhang, B. Yang, L. Liu, J. Hui, M. Liu, Y. Chen and Y. Wei, *RSC Adv.*, 2014, **4**, 10060-10066.

177.X. Zhang, X. Zhang, B. Yang, S. Wang, M. Liu, Y. Zhang and L. Tao, *RSC Adv.*, 2013, **3**, 9633-9636.

178.M. Liu, K. Wang, X. Zhang, X. Zhang, Z. Li, Q. Zhang, Z. Huang and Y. Wei, *Tetrahedron*, 2015, **71**, 5452-5457.

179.Q. Wan, C. He, K. Wang, M. Liu, H. Huang, Q. Huang, F. Deng, X. Zhang and Y. Wei, *Tetrahedron*, 2015, **71**, 8791-8797.

180.X. Zhang, M. Liu, B. Yang, X. Zhang and Y. Wei, *Colloids Surf. B Biointerfaces*, 2013, **112**, 81-86.

181.X. Zhang, X. Zhang, B. Yang, M. Liu and Y. Wei, *Colloids Surf. B Biointerfaces*, 2014, **116**, 739-744.

182.X. Zhang, X. Zhang, B. Yang, Y. Zhang, M. Liu, W. Liu, Y. Chen and Y. Wei, *Colloids Surf. B Biointerfaces*, 2014, **1**, 435-441.

183.A. Bhirde, J. Xie, M. Swierczewska and X. Chen, *Nanoscale*, 2011, **3**, 142-153.

184.S. Chandra, P. Das, S. Bag, D. Laha and P. Pramanik, *Nanoscale*, 2011, **3**, 1533-1540.

185.I. Díez and R. H. A. Ras, *Nanoscale*, 2011, **3**, 1963-1970.

186.Y. P. Ho and K. W. Leong, *Nanoscale*, 2010, **2**, 60-68.

187.A. Shiohara, S. Prabakar, A. Faramus, C. Y. Hsu, P. S. Lai, P. T. Northcote and R. D. Tilley, *Nanoscale*, 2011, **3**, 3364-3370.

188.M. Liu, X. Zhang, B. Yang, F. Deng, Y. Yang, Z. Li, X. Zhang and Y. Wei, *Macromol. Biosci.*, 2014, **14**, 1712-1718.

189.M. Liu, X. Zhang, B. Yang, L. Liu, F. Deng, X. Zhang and Y. Wei, *Macromol. Biosci.*, 2014, **14**, 1260-1267.

190.Q. Lv, K. Wang, D. Xu, M. Liu, Q. Wan, H. Huang, S. Liang, X. Zhang and Y. Wei, *Macromol. Biosci.*, 2016, **16**, 223-230.

191.M. Liu, X. Zhang, B. Yang, F. Deng, Z. Li, J. Wei, X. Zhang and Y. Wei, *Appl. Surf. Sci.*, 2014, **322**, 155-161.

192.Y. Gao, H. Zhang, T. Jiang, J. Yang, B. Li, Z. Li and J. Hua, *Sci. China Chem.*, 2013, **56**, 1204-1212.

193.Q. Li and Z. Li, *Sci. China Chem.*, 2015, DOI: 10.1007/s11426-11015-15517-11424

194.J. Liang, G. Feng, R. T. K. Kwok, D. Ding, B. Tang and B. Liu, *Sci. China Chem.*, 2015, doi: 10.1007/s11426-11015-15470-11422.

195.A. Qin, Y. Zhang, N. Han, J. Mei, J. Sun, W. Fan and B. Z. Tang, *Sci. China Chem.*, 2012, **55**, 772-778.

196.D. Wang, W. Cao and J. Fan, *Sci. China Chem.*, 2014, **57**, 791-796.

197.X. Zhang, K. Wang, M. Liu, X. Zhang, L. Tao, Y. Chen and Y. Wei, *Nanoscale*, 2015, **7**, 11486-11508.

198.X. Zhang, X. Zhang, L. tao, Z. Chi, J. Xu and Y. Wei, *J. Mater. Chem. B*, 2014, **2**, 4398-4414.

199.X. Zhang, X. Zhang, B. Yang, J. Hui, M. Liu, Z. Chi, S. Liu and J. Xu, *J. Mater. Chem. C*, 2014, **2**, 816-820.

200.M. Liu, J. Ji, X. Zhang, X. Zhang, B. Yang, F. Deng, Z. Li, K. Wang, Y. Yang and Y. Wei, *J. Mater. Chem. B*, 2015, **3**, 3476-3482.

201.A. Kaur, T. Raj, S. Kaur, N. Singh and N. Kaur, *Org. Biomol. Chem.*, 2015, **13**, 1204-1212.

202.J. Park, T. F. Brust, H. J. Lee, S. C. Lee, V. J. Watts and Y. Yeo, *ACS nano*, 2013, **8**, 3347-3356.

203.M. E. Lynge, B. M. Teo, M. B. Laursen, Y. Zhang and B. Städler, *Biomat. Sci.*, 2013, **1**, 1181-1192.

204.J. Li, Y. Zhu, W. Li, X. Zhang, Y. Peng and Q. Huang, *Biomaterials*, 2010, **31**, 8410-8418.

205.E. Gullotti, J. Park and Y. Yeo, *Pharm. Res.*, 2013, **30**, 1956-1967.

206.D. Chang, Y. Gao, L. Wang, G. Liu, Y. Chen, T. Wang, W. Tao, L. Mei, L. Huang and X. Zeng, *J. Colloid Interf. Sci.*, 2016, **463**, 279-287.

207.L.-S. Lin, Z.-X. Cong, J.-B. Cao, K.-M. Ke, Q.-L. Peng, J. Gao, H.-H. Yang, G. Liu and X. Chen, *ACS nano*, 2014, **8**, 3876-3883.

208.J. Zhou, P. Wang, C. Wang, Y. T. Goh, Z. Fang, P. B. Messersmith and H. Duan, *ACS nano*, 2015, **9**, 6951-6960.

209.F. Liu, X. He, J. Zhang, H. Chen, H. Zhang and Z. Wang, *J. mater. Chem. B*, 2015, **3**, 6731-6739.

210.C. Wu, W. Fan, J. Chang and Y. Xiao, *J. Mater. Chem.*, 2011, **21**, 18300-18307.

211.R. Liu, Y. Guo, G. Odusote, F. Qu and R. D. Priestley, *ACS Appl. Mater. Interf.*, 2013, **5**, 9167-9171.

212.K. C. Black, J. Yi, J. G. Rivera, D. C. Zelasko-Leon and P. B. Messersmith, *Nanomedicine*, 2013, **8**, 17-28.

213.J. Cui, Y. Wang, A. Postma, J. Hao, L. Hosta-Rigau and F. Caruso, *Adv. Funct. Mater.*, 2010, **20**, 1625-1631.

214.Q. Liu, B. Yu, W. Ye and F. Zhou, *Macromol. Biosci.*, 2011, **11**, 1227-1234.

215.L. Zhang, J. Shi, Z. Jiang, Y. Jiang, S. Qiao, J. Li, R. Wang, R. Meng, Y. Zhu and Y. Zheng, *Green Chem.*, 2011, **13**, 300-306.

216.A. Postma, Y. Yan, Y. Wang, A. N. Zelikin, E. Tjipto and F. Caruso, *Chem. Mater.*, 2009, **21**, 3042-3044.

217.H. Xu, X. Liu and D. Wang, *Chem. Mater.*, 2011, **23**, 5105-5110.

218.C. J. Ochs, T. Hong, G. K. Such, J. Cui, A. Postma and F. Caruso, *Chem. Mater.*, 2011, **23**, 3141-3143.

219.J. Shi, C. Yang, S. Zhang, X. Wang, Z. Jiang, W. Zhang, X. Song, Q. Ai and C. Tian, *ACS Appl. Mater. Interf.*, 2011, **5**, 9991-9997.

220.M. S. Lee, J. E. Lee, E. Byun, N. W. Kim, K. Lee, H. Lee, S. J. Sim, D. S. Lee and J. H. Jeong, *J. Control. Release*, 2015, **192**, 122-130.

221.M. Lee, K. Yang, Y. H. Hwang, Y. Byun, D. Y. Lee, S.-W. Cho and H. Lee, *Adv. Healthcare Mater.*, 2015, **4**, 511-515.

222.B. Joddar, A. Albayrak, J. Kang, M. Nishihara, H. Abe and Y. Ito, *Acta Biomater.*, 2013, **9**, 6753-6761.

223.W. Hu, C. Peng, W. Luo, M. Lv, X. Li, D. Li, Q. Huang and C. Fan, *ACS nano*, 2010, **4**, 4317-4323.

224.Y. Cong, T. Xia, M. Zou, Z. Li, B. Peng, D. Guo and Z. Deng, *J. Mater. Chem. B*, 2014, **2**, 3450-3461.

225.H. Xu, X. Shi, H. Ma, Y. Lv, L. Zhang and Z. Mao, *Appl. Surf. Sci.*, 2011, **257**, 6799-6803.

226.H. Zhou, Y. Liu, W. Chi, C. Yu and Y. Yu, *Appl. Surf. Sci.*, 2013, **282**, 181-185.

227.Y. Dong, T. Liu, S. Sun, X. Chang and N. Guo, *Ceram. Int.*, 2014, **40**, 5605-5609.

228.H. Luo, C. Gu, W. Zheng, F. Dai, X. Wang and Z. Zheng, *RSC Adv.*, 2015, **5**, 13470-13477.

229.T. Shalev, A. Gopin, M. Bauer, R. W. Stark and S. Rahimipour, *J. Mater. Chem.*, 2012, **22**, 2026-2032.

230.G. Yeroslavsky, O. Girshevitz, J. Foster-Frey, D. M. Donovan and S. Rahimipour, *Langmuir*, 2013, **31**, 1064-1073.

231.C. Wu, G. Zhang, T. Xia, Z. Li, K. Zhao, Z. Deng, D. Guo and B. Peng, *Mater. Sci. Eng. C-Mater.*, 2013, **55**, 155-165.

232.Z. Shi, J. Tang, L. Chen, C. Yan, S. Tanvir, W. A. Anderson, R. M. Berry and K. C. Tam, *J. Mater. Chem. B*, 2015, **3**, 603-611.

233.L. Guo, Q. Liu, G. Li, J. Shi, J. Liu, T. Wang and G. Jiang, *Nanoscale*, 2012, **4**, 5864-5867.

234.C. Yang, X. Ding, R. J. Ono, H. Lee, L. Y. Hsu, Y. W. Tong, J. Hedrick and Y. Y. Yang, *Adv. Mater.*, 2015, **26**, 7346-7351.

235.Z. Zhang, J. Zhang, B. Zhang and J. Tang, *Nanoscale*, 2013, **5**, 118-123.

236.K. C. Black, T. S. Sileika, J. Yi, R. Zhang, J. G. Rivera and P. B. Messersmith, *Small*, 2014, **10**, 169-178.

237.C.-T. Kao, C.-C. Lin, Y.-W. Chen, C.-H. Yeh, H.-Y. Fang and M.-Y. Shie, *Mater. Sci. Eng-C Mater.*, 2015, **56**, 165-173.

238.S. K. Madhurakkat Perikamana, J. Lee, Y. B. Lee, Y. M. Shin, E. J. Lee, A. G. Mikos and H. Shin, *Biomacromolecules*, 2015, **16**, 2541-2555.

239.H.-J. Park, K. Yang, M.-J. Kim, J. Jang, M. Lee, D.-W. Kim, H. Lee and S.-W. Cho, *Biomaterials*, 2015, **50**, 127-139.

240.J. M. Lee, J. H. Ryu, E. A. Kim, S. Jo, B.-S. Kim, H. Lee and G.-I. Im, *Biomaterials*, 2015, **39**, 173-181.

241.J. Ryu, S. H. Ku, H. Lee and C. B. Park, *Adv. Funct. Mater.*, 2010, **20**, 2132-2139.

242.C.-C. Lin and S.-J. Fu, *Mater. Sci. Eng-C Mater.*, 2016, **58**, 254-263.

243.L. Ge, Q. Li, Y. Huang, S. Yang, J. Ouyang, S. Bu, W. Zhong, Z. Liu and M. M. Xing, *J. mater. Chem. B*, 2014, **2**, 6917-6923.

244.H.-j. Cho, S. K. Madhurakkat Perikamana, J.-h. Lee, J. Lee, K.-M. Lee, C. S. Shin and H. Shin, *ACS Appl. Mater. Interf.*, 2014, **6**, 11225-11235.

245.K. Yang, J. S. Lee, J. Kim, Y. B. Lee, H. Shin, S. H. Um, J. B. Kim, K. I. Park, H. Lee and S.-W. Cho, *Biomaterials*, 2012, **33**, 6952-6964.

246.C.-Y. Chien and W.-B. Tsai, *ACS Appl. Mater. Interf.*, 2013, **5**, 6975-6983.

247.E. Ko, K. Yang, J. Shin and S.-W. Cho, *Biomacromolecules*, 2013, **14**, 3202-3213.

248.Y. B. Lee, Y. M. Shin, J.-h. Lee, I. Jun, J. K. Kang, J.-C. Park and H. Shin, *Biomaterials*, 2012, **33**, 8343-8352.

249.K. Kang, I. S. Choi and Y. Nam, *Biomaterials*, 2012, **32**, 6374-6380.

250.M. Liu, J. Zhou, Y. Yang, M. Zheng, J. Yang and J. Tan, *Colloids Surf. B Biointerfaces*, 2015, **136**, 74-83.

251.Y. Cai, X. Wang, C. K. Poh, H. C. Tan, M. T. Soe, S. Zhang and W. Wang, *Colloids Surf. B Biointerfaces*, 2014, **116**, 681-686.

252.Z. Wang, K. Wang, Y. Zhang, Y. Jiang, X. Lu, L. Fang, D. Gan, C. Lv, H. Zhang and S. Qu, *Part. Part. Syst. Char.*, 2016, **33**, 89-100.

253.E. Van De Walle, I. Van Nieuwenhove, E. Vanderleyden, H. Declercq, K. Gellynck, D. Schaubroeck, H. Ottevaere, H. Thienpont, W. H. De Vos and M. Cornelissen, *Biomacromolecules*, 2016, **17**, 56-68.

254.S. H. Ku and C. B. Park, *Biomaterials*, 2010, **31**, 9431-9437.

255.T. E. Douglas, P. B. Messersmith, S. Chasan, A. G. Mikos, E. L. de Mulder, G. Dickson, D. Schaubroeck, L. Balcaen, F. Vanhaecke and P. Dubruel, *Macromol. Biosci.*, 2012, **12**, 1077-1089.

256.M. Vert, K.-H. Hellwich, M. Hess, P. Hodge, P. Kubisa, M. Rinaudo and F. Schué, *Pure Appl. Chem.*, 2012, **84**, 377-410.

257.L. Ma, H. Qin, C. Cheng, Y. Xia, C. He, C. Nie, L. Wang and C. Zhao, *J. Mater. Chem. B*, 2014, **2**, 363-375.

258.C. Cheng, S. Sun and C. Zhao, *J. Mater. Chem. B*, 2014, **2**, 7649-7672.

259.S. Hong, K. Y. Kim, H. J. Wook, S. Y. Park, K. D. Lee, D. Y. Lee and H. Lee, *Nanomedicine*, 2011, **6**, 793-801.

260.X. Liu, J. Cao, H. Li, J. Li, Q. Jin, K. Ren and J. Ji, *ACS Nano*, 2013, **7**, 9384-9395.

261.J. Chen, C. Glaus, R. Laforest, Q. Zhang, M. Yang, M. Gidding, M. J. Welch and Y. Xia, *Small*, 2010, **6**, 811-817.

262.H. K. Moon, S. H. Lee and H. C. Choi, *ACS nano*, 2009, **3**, 3707-3713.

263.J. T. Robinson, S. M. Tabakman, Y. Liang, H. Wang, H. Sanchez Casalongue, D. Vinh and H. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 6825-6831.

264.W. Yin, L. Yan, J. Yu, G. Tian, L. Zhou, X. Zheng, X. Zhang, Y. Yong, J. Li and Z. Gu, *ACS nano*, 2014, **8**, 6922-6933.

265.X. Huang, I. H. El-Sayed, W. Qian and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2006, **128**, 2115-2120.

266.K. Yang, H. Xu, L. Cheng, C. Sun, J. Wang and Z. Liu, *Adv. Mater.*, 2012, **24**, 5586-5592.

267.X. Song, Q. Chen and Z. Liu, *Nano Res.*, 2015, **8**, 340-354.

268.R. Zhang, S. Su, K. Hu, L. Shao, X. Deng, W. Sheng and Y. Wu, *Nanoscale*, 2015, **7**, 19722-19731.

269.M. Wu, D. Zhang, Y. Zeng, L. Wu, X. Liu and J. Liu, *Nanotechnology*, 2015, **26**, 115102.

270.K. Y. Choi, G. Liu, S. Lee and X. Chen, *Nanoscale*, 2012, **4**, 330-342.

271.A. K. A. Silva, R. Di Corato, T. Pellegrino, S. Chat, G. Pugliese, N. Luciani, F. Gazeau and C. Wilhelm, *Nanoscale*, 2013, **5**, 11374-11384.

272.J. Chen, M. Yang, Q. Zhang, E. C. Cho, C. M. Cobley, C. Kim, C. Glaus, L. V. Wang, M. J. Welch and Y. Xia, *Adv. Funct. Mater.*, 2010, **20**, 3684-3694.

273.A. Wang, M. Guo, N. Wang, J. Zhao, W. Qi, F. Muhammad, L. Chen, Y. Guo, N.-T. Nguyen and G. Zhu, *Nanoscale*, 2014, **6**, 5270-5278.

274.J. Liu, J. Han, Z. Kang, R. Golamaully, N. Xu, H. Li and X. Han, *Nanoscale*, 2014, **6**, 5770-5776.

275.M. Zhou, G. Ku, L. Pageon and C. Li, *Nanoscale*, 2014, **6**, 15228-15235.

276.B. E. Smith, P. B. Roder, X. Zhou and P. J. Pauzauskie, *Nanoscale*, 2015, **7**, 7115-7126.

277.G. Huang, X. Zhu, H. Li, L. Wang, X. Chi, J. Chen, X. Wang, Z. Chen and J. Gao, *Nanoscale*, 2015, **7**, 2667-2675.

278.P. Rong, P. Huang, Z. Liu, J. Lin, A. Jin, Y. Ma, G. Niu, L. Yu, W. Zeng and W. Wang, *Nanoscale*, 2015, **7**, 16330-16336.

279.Y. Yong, L. Zhou, Z. Gu, L. Yan, G. Tian, X. Zheng, X. Liu, X. Zhang, J. Shi and W. Cong, *Nanoscale*, 2014, **6**, 10394-10403.

280.J. Qin, Z. Peng, B. Li, K. Ye, Y. Zhang, F. Yuan, X. Yang, L. Huang, J. Hu and X. Lu, *Nanoscale*, 2015, **7**, 13991-14001.

281.L. Zeng, L. Luo, Y. Pan, S. Luo, G. Lu and A. Wu, *Nanoscale*, 2015, **7**, 8946-8954.

282.W. Li, W. Bing, S. Huang, J. Ren and X. Qu, *Adv. Funct. Mater.*, 2015, **25**, 3775-3784.

283.Y. Chen, K. Ai, J. Liu, X. Ren, C. Jiang and L. Lu, *Biomaterials*, 2016, **77**, 198-206.

284.X. Zhong, K. Yang, Z. Dong, X. Yi, Y. Wang, C. Ge, Y. Zhao and Z. Liu, *Adv. Funct. Mater.*, 2016, DOI: 10.1002/adfm.201503587.