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Organic Semiconductor Nanoparticle Film: Preparation and Application

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1. Introduction

Organic semiconductors usually comprising π -conjugated structure in their molecules can exhibit excellent optical and electronic properties. They have advantages of simple fabrication and ease of tuning the chemical structure to give desired features. So they can serve as attractive candidates for applications in bio/chemical sensors and optoelectronic devices.^{1,2} To meet the requirement of domains including information, energy and healthcare, nanoscale materials have emerged as new building blocks for optoelectronic devices, bioimaging agents, and drug delivery carriers in recent years.³⁻⁵ These nanomaterials especially nanoparticles have already shown great potential to offer exciting opportunities in these areas.

Currently, most of the relevant works have been focused on inorganic semiconductor nanoparticles. Besides inorganic ones, organic semiconductor nanoparticles (OSNs) are desirable for a number of reasons. Their properties can be easily tuned for desired applications through the choice of functional molecules and surface modification. Additionally, their facile synthesis, good processability, high photoluminescence (PL) efficiency, high reaction activity, tunable properties, low toxicity and good biocompatibility further make them complementary to the inorganic nanomaterials and highly attractive in the material choice. As a result, OSNs have captured more and more interests. These OSNs can exhibit unique optical and electrical properties different from both the bulk solid samples and their molecular precursors. In comparison with molecule dispersed systems, OSNs are expected to show improved photostability and enhanced emission in various media.^{6,7} These properties are essentially important in fluorescent labeling applications, such as fluorescence bioimaging and single molecular spectroscopy. For example, single molecules of most commercial dyes undergo photo-bleaching in a few milliseconds under typical excitation conditions under the radiation of a laser beam. On the contrary, because large numbers of chromophores are incorporated in single nanoparticles, they can show bright fluorescence even at a low excitation power. Thus, the fluorescent nanoparticles do not undergo rapid photo-bleaching and give less emission blinking which are generally observed in single molecule experiment.⁸

Up to now, most of the OSNs are used in aqueous solutions to serve as biological labels,^{9,10} chemical sensors,¹¹ and photocatalysis materials.¹² To expand the application area of OSNs, there is an increasing effort to prepare OSNs as an active solid film in chemo/biosensors and optical and electronic devices.^{13–16} Compared with bulk solid samples, nanoparticle films provide larger contact interface area, which is highly desired for chemical and biological sensing in sensors. So OSN based functional films tend to become a promising research area for applications in biosensing, energy conversion, photonic and optoelectronic devices.

In this review, after a brief introduction of organic semiconductor materials, we will summarize the methods for preparation OSN films. Then, its application in optical/electronic devices and chemo-/biosensors will be described. We hope this review can cast light on the advances and main problems in the research field of nanoparticle-based devices and sensors.

2. Organic semiconductor materials

Organic semiconductor materials are mainly classified into two categories. One is small molecules and the other is polymers made from repeated small conjugated monomer units.

2.1 Small molecule semiconductors

Polyphenyl derivatives (**1–3**),^{17,18} fused aromatic rings (**4–8**),^{19,20} porphyrin derivatives (**9,10**),^{21,22} metal phthalocyanines (**11**),²³ fullerenes (**12**),²⁴ and some fluorescent dyes (**13,14**) have been made into nanoparticles.^{25,26} Their molecular structures are illustrated in Figure 1. Small molecules are more easily packed to form crystals than polymers, so in some cases the nanoparticles of small-molecule semiconductors can transform to nanorods, nanotubes and nanoflakes.

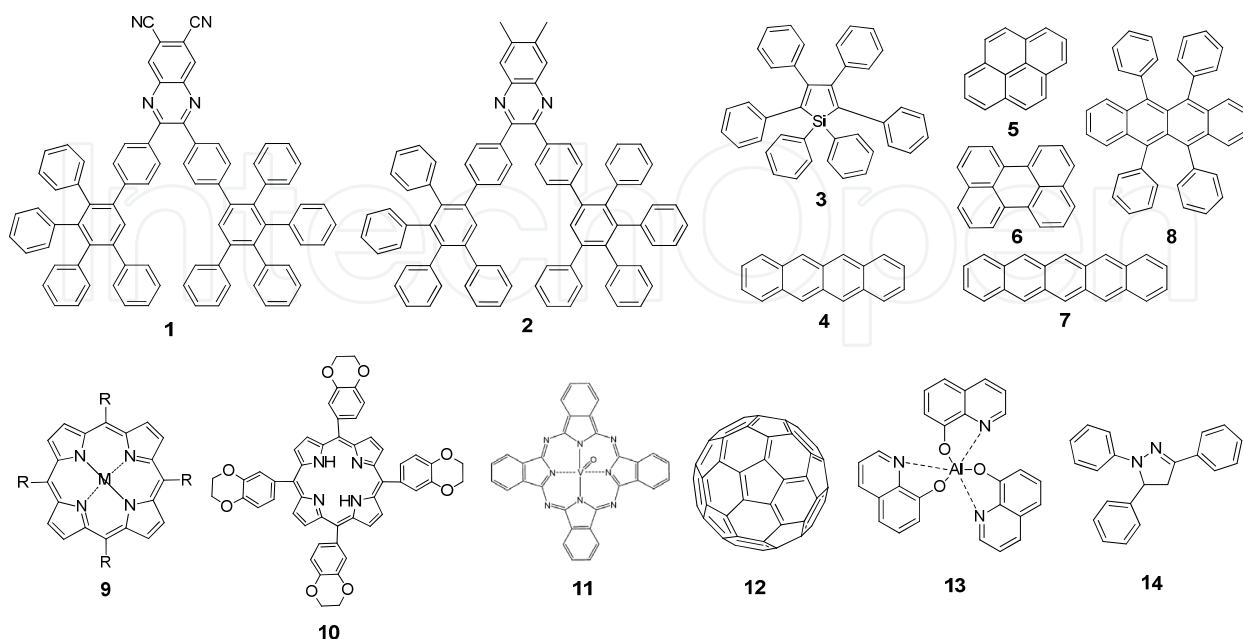


Fig. 1. Molecular structures of some small molecule semiconductors for synthesizing OSNs.

2.2 Polymer semiconductors

Poly(phenylene vinylene)s (**15**),²⁷ polyfluorenes (**16–18**),^{28–30} polythiophenes (**19**),³¹ ladder-type poly(para-phenylene)s (LPPP) (**20**),³² poly(phenylene ethynylene)s (PPEs) (**21,22**),³³ polyanilines (PANIs) (**23**),³⁴ and some copolymers (**24,25**) have been utilized to prepare nanoparticles.^{35,36} Their molecular structures are shown in Figure 2. Polymers have longer chains than small molecules, so it is possible for polymers to form nanoparticles even with a single molecule, which is advantageous for researches on single molecule behavior.

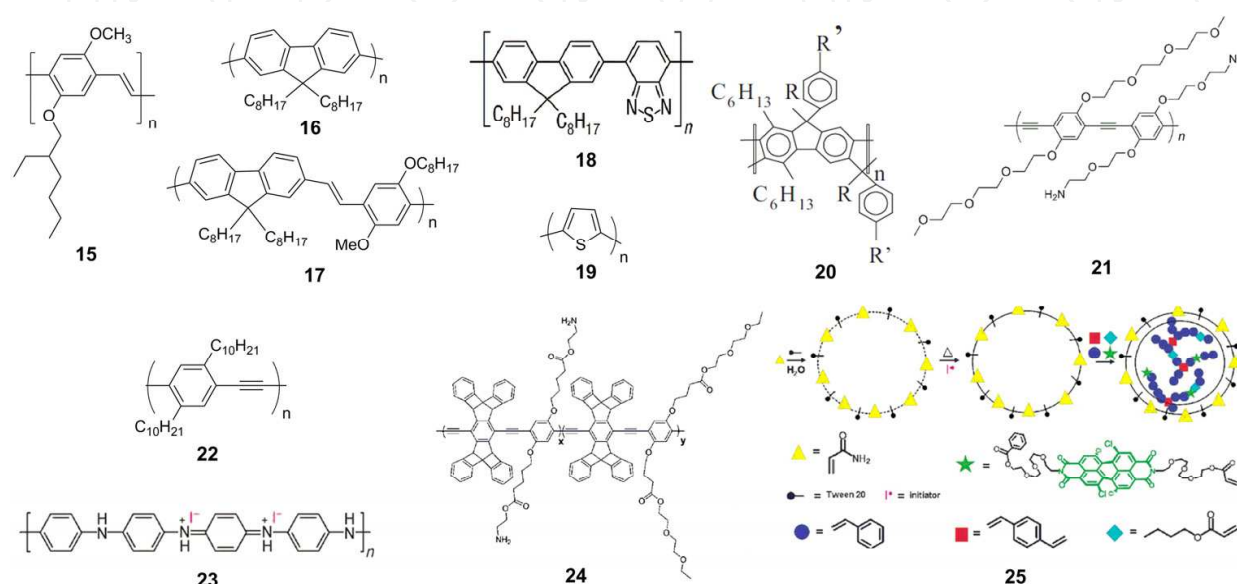


Fig. 2. Molecular structures of some polymer semiconductors for synthesizing OSNs.

3. Methods for synthesizing organic semiconductor nanoparticles

3.1 Reprecipitation

In 1992, Nakanishi and co-workers proposed the reprecipitation method and demonstrated the nanoparticles with the particle size less than 100 nm dispersed in water.³⁷ Since then, this method has been widely used in nanoparticle preparation for various kinds of molecules. In this method, a hydrophobic organic semiconductor material is dissolved in a good solvent (e.g., THF) for it and poured into a poor solvent (e.g., water), which is miscible with the good solvent. The resulting mixture is stirred vigorously using a magnetic stir bar or a sonicator to assist the formation of nanoparticles. After the nanoparticle formation the organic solvent is removed either by partial vacuum evaporation or by repeated dialysis process to leave behind water-dispersible nanoparticles. The main driving force for the formation of nanoparticles is the hydrophobic effect. When the solution of an organic semiconductor material in organic solvent is added to water, the compound molecules tend to avoid contacting with water. Consequently, in order to achieve minimum exposure they fold or packed into spherical shapes. The preparation does not involve the use of any additives such as surfactants and can be applied to a wide variety of organic semiconductors including both polymers and small molecules given that they are soluble in organic solvents. Moreover, using this method, it is possible to tune the size of nanoparticles by adjusting the concentration and the temperature of the solutions.

3.2 Miniemulsion

This is another commonly used method in the synthesis of OSNs. Using this method, Landfester and co-workers prepared nanoparticles from various polymers.³⁸ To prepare OSNs, the compound is dissolved in a water immiscible organic solvent and then the resulting solution is injected into an aqueous solution of an appropriate surfactant. The mixture is stirred vigorously by ultrasonication to form stable miniemulsions containing small droplets of the polymer solution. The organic solvent is then evaporated to obtain a stable dispersion of polymer nanoparticles in water. The size of nanoparticles could vary from 30 nm to 500 nm depending on the concentration of the polymer solution. However, the droplets could also be destabilized by Ostwald ripening as well as the flocculation caused by the coalescence of droplets. To prevent flocculation appropriate surfactants are needed, while Ostwald ripening can be suppressed by addition of a hydrophobic agent (hydrophobe) to the dispersed phase. The hydrophobic agent promotes the formation of an osmotic pressure inside the droplets that counteracts the Laplace pressure (the pressure difference between the inside and the outside of a droplet) preventing diffusion from one droplet to the surrounding aqueous medium.

3.3 Pulsed-laser ablation

In this method, OSNs are formed by pulsed-laser ablation of large, several-micrometer-sized, organic crystals suspended in a liquid.^{39,40} The powder of organic semiconductors was added to an aqueous solution containing surfactants such as sodium dodecyl sulfate (SDS). Then, the suspension was sonicated for a while. The mixture was put into a quartz cuvette, stirred vigorously with a magnetic stirrer, and then simultaneously exposed to the second harmonic of a nanosecond YAG laser. The spot area was approximately tens of mm², and the laser intensity was adjusted using a polarizer. The laser ablation mechanism for nanosecond laser ablation is based on photothermalization. The organic crystals in solutions absorb the laser light leading to a local increase in temperature and evaporation of a small amount of material from the crystal surface. The vaporized material is rapidly cooled by the surrounding liquid to form nanoparticles.

For nanosecond photothermal ablation in a solvent, rapid temperature elevation upon pulse excitation is compensated by a cooling process due to thermal diffusion to the solvent, and its balance gives the transient temperature determining the nanoparticle size. Higher fluence gives higher effective transient temperature, leading to efficient fragmentation to smaller particles. One advantage of the laser ablation method is its high controllability of size and phase of nanoparticles by tuning laser pulse width, wavelength, fluence, and shot number. However, this method is limited to fabricate OSNs based on small molecules only.

3.4 Direct condensation of organic vapor

Due to the fact that in the reprecipitation or miniemulsion process a solution of organic material (of typically about millimolar concentration) is added to a large excess of non-solvent, only very dilute particle dispersions can be obtained. That is one main disadvantage of these methods. The second one is that the reprecipitation or miniemulsion method is not applicable for organic materials that are poorly soluble in organic solvents (such as pentacene). As for laser ablation, more concentrated nanoparticle dispersions can be

prepared compared to the reprecipitation and miniemulsion method. However, as particle formation only occurs within the narrow laser beam, only small amounts of these nanoparticle dispersions can be prepared. Furthermore, the intense laser light may cause severe photochemical damage especially in the case of rather sensitive organic materials.

To overcome the above mentioned drawbacks, an approach for preparation of concentrated dispersions of organic nanoparticles by direct condensation the vapor of an organic semiconductor material into a liquid dispersion medium has been developed.¹⁹ This approach combines elements from the physical vapor deposition (PVD) technique with cooling and condensation of the vapor directly inside a liquid. An illustration of the apparatus used in the direct condensation method is shown in Figure 3. The apparatus consists of four main parts: a tube furnace, a double-walled heated-vapor injection tube, a condensation and receiving vessel, and a vacuum pumping system. Temperatures in the different zones are adjusted according to the organic material to be evaporated, and were maintained such that no condensation of the organic materials occurred in the tubes. The evaporated organic material will be carried by the inert gas flow to the vapor-injection tube, which guides the organic material into a liquid condensation medium. The condensation liquid typically consists of an aqueous solution containing surfactants or polymeric stabilizers. It rapidly cools down the gas leading to condensation of the organic vapor and formation of nanoparticles. These nanoparticles are subsequently stabilized in situ by the surfactant or polymeric additive at the bubble/liquid interface to form a stable dispersion. The size of OSNs prepared by this method is in the range of 100–200 nm for fused aromatic hydrocarbons such as pentacene, rubrene, and tetracene.

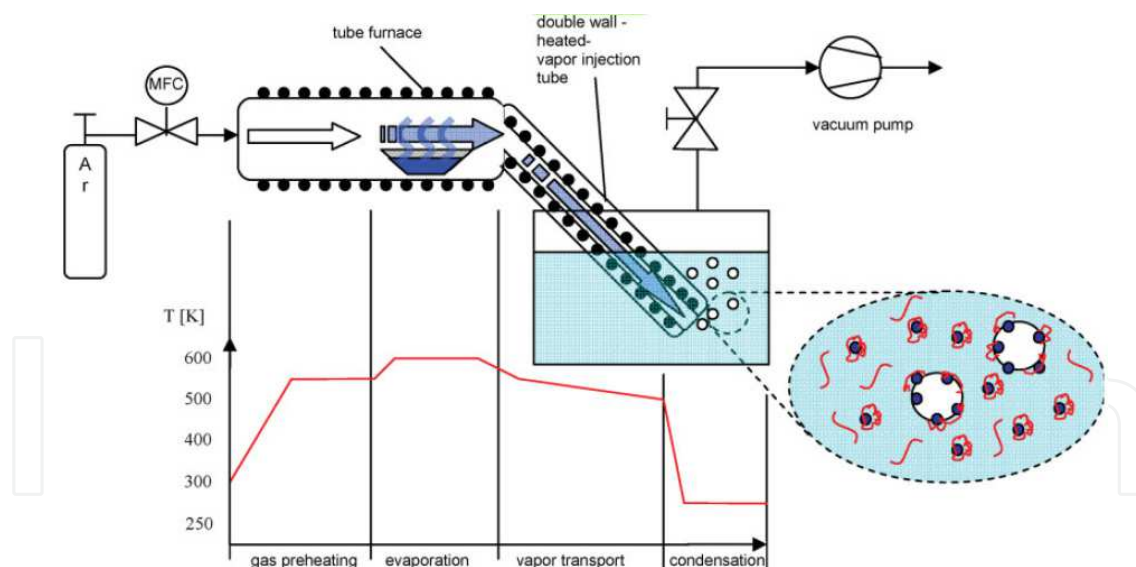


Fig. 3. Apparatus for direct condensation of organic vapor (Reproduced from Ref. 19, Copyright 2009 Wiley-VCH Verlag GmbH & Co.)

3.5 Template-based approaches

3.5.1 Soft templates

Micelles can be used as soft templates to conduct the polymerization in the aqueous heterophase system. By dispersing the appropriate monomers, surfactant, solvent, and

catalysts in an aqueous medium, the Glaser coupling reaction can be carried out exclusively within the hydrophobic interior of surfactant micelles to produce the poly(arylene diethynylenes) nanoparticles.⁴¹ Similarly, poly(p-phenyleneethynylene) nanoparticles can also be prepared by this method.⁴²

The molecular structure of surfactant used in the aqueous heterophase system has a big influence on the shape of the formed nanoparticles. Using dodecylbenzene sulfonic acid as a surfactant and doping agent for poly(3,4-ethylenedioxythiophene) (PEDOT) yielded amorphous and polydisperse particles with diameters in the range of 35–100 nm.⁴³ Short chain alcohol ethoxylate surfactants yielded more spherical particles, but significant amounts of surfactant residue were trapped on the PEDOT latex, and secondary nucleation could not be completely suppressed.⁴⁴

These examples show that the soft template approach has been a versatile method for preparing conjugated polymer nanoparticles. However, control over important parameters such as particle diameter and polydispersity by this method is often not easy. Many of these issues can be addressed by the use of a hard template.

3.5.2 Hard templates

Due to the shape persistence of hard templates, they typically offer a more reliable way of directing the shape of conjugated polymer nanostructures. Monodisperse nanoparticles such as silica and polystyrene particles can be used as a hard template for preparing core-shell structures. Conjugated polymers such as polypyrrole, PANI and PEDOT, highly fluorescent polymers such as PPE have also been attached to the surface of colloidal particles.⁴⁵ The conjugated polymers can either be polymerized in situ from monomers absorbed on the surface of the particle templates or be deposited from a layer-by-layer technique through electrostatic interactions.⁴⁶

4. Methods for preparing nanoparticles film

Since OSNs are usually synthesized in solution with a low concentration, conventional thin film forming processes such as spin-coating or dip-casting are not appropriate for preparing OSN films. So other methods have been developed to prepare good OSN films.

4.1 Electrophoresis deposition

Electrophoretic deposition, which is based on the electrical collection of small, charged particles dispersed in dielectric liquids, is one of the most widely used coating methods capable of patterning. It has been reported that the phosphors for a cathode ray tube,⁴⁷ the oxide superconductors,⁴⁸ and the carbon nanotubes for a cold cathode have been successfully coated by electrophoretic deposition.⁴⁹ As for OSNs in solutions, they often carried charges on their surface. Such surface charges are generated according to Coehn's empirical rule. That is, the electrostatic charge separation may occur when two dielectrics are in intimate contact. The substance with the higher dielectric constant will receive the positive charge, while the other one will receive the negative charge. As illustrated in Figure 4, a DC voltage (usually hundreds of volts) was applied between two ITO-coated glass plates soaked in the nanoparticle suspension. Then nanoparticles will move towards the

corresponding electrode under the driving of electric field force.⁵⁰ The films thus obtained were washed with clean solvent and dried in air.

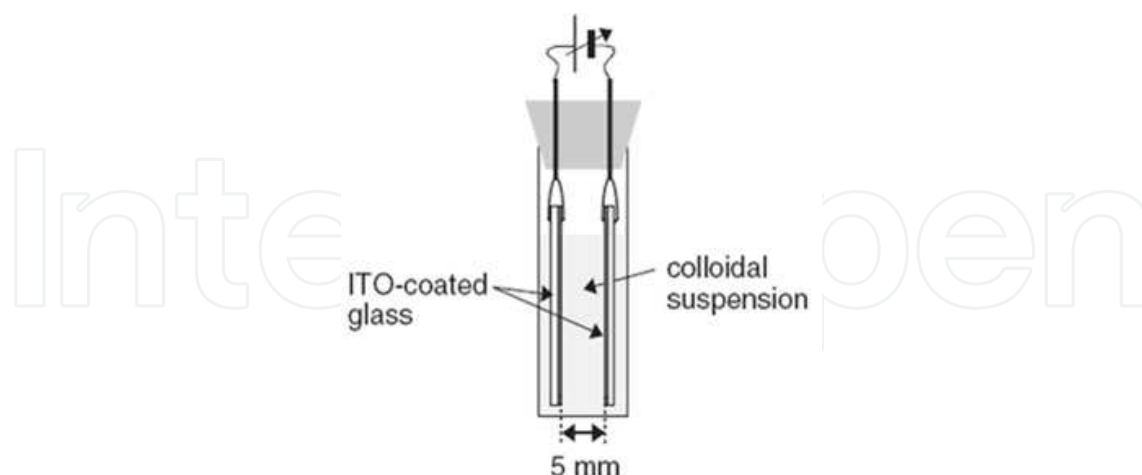


Fig. 4. Apparatus for electrophoretic deposition of OSNs

4.2 Rapid expansion of supercritical solution (RESS) technique

This technique for prepare OSN film is based on a rapid expansion process of supercritical solution (e.g. CO₂) which contains dissolved organic semiconductors.⁵¹ By using an apparatus illustrated in Figure 5, organic semiconductors dispersed in supercritical CO₂ solution can be sprayed on the substrate through a long stainless steel capillary tube attached to the chamber. After the rapid evaporation of CO₂, OSNs are precipitated on the surface of substrates. Using process conditions of compressed-fluid precipitation and formulation, it appears possible to produce organic nanoparticles with tunable sizes and optical properties. This capability opens up avenues to create devices and functional films using organic nanoparticles as building blocks, which may be tailored for the application.

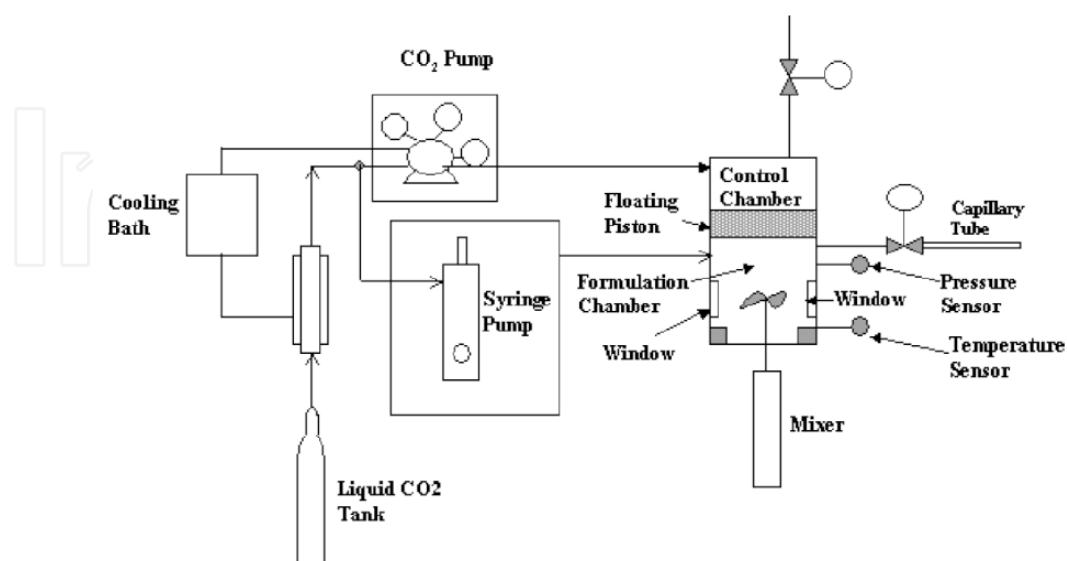


Fig. 5. Apparatus for preparation of OSN films by RESS technique (Reproduced from Ref. 51, Copyright 2006 Wiley-VCH Verlag GmbH & Co.)

Additionally, it is possible to mix building blocks of organic nanoparticles or combine different molecules within a building block. However, the limitation of this technique is that only small molecule based OSN film can be prepared while preparation of polymer based OSN films by this technique is not available. Also, surfactants such as the ammonium-exchanged Fluorolink 7004 ($\text{Cl}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_n\text{CF}_2\text{COO}-\text{NH}_4^+$) need to be introduced into the supercritical solution to adjust the size of ultimate nanoparticles.⁵¹

4.3 Solvent-evaporation induced self-assembly

The evaporation behavior during the drying process of a solution plays a vital role in controlling the film morphology and the distribution of solute in the final films. It is well known that when a liquid drop containing dispersed solids evaporates on a surface, it commonly leaves a dense, ring-like deposit along the perimeter. The reason is that the contact line is pinned during the drying process, leading to a fixed contact area on the substrate. Therefore, a capillary flow of the solvent occurs from the center of the drop to the contact line to replenish the evaporation loss, and this flow transports the solutes to its periphery.⁵² As far as the OSNs solution is concerned, such phenomenon will result in an undesirably uneven distribution of nanoparticles across the deposited films. However, if another flow which has an opposite direction to the capillary flow is introduced into the OSNs solutions during the drying process, the transportation of nanoparticles towards the contact line by the capillary flow is expected to be counteracted. Marangoni effect is usually observed in a solution containing two kinds of solvents with different surface tensions and boiling points, and a flow is induced by the surface tension gradient existed in the solution caused by solvent evaporation. Such a flow is named as the Marangoni flow, and its direction can be controlled to be the same as the spreading of a drop on a solid surface (outward) or opposite to the spreading (inward), depending on the boiling points and surface tensions of the two solvents to be mixed. Consequently, by proper introduction of a second solvent into the solution, a Marangoni flow with an opposite direction to the capillary flow can be achieved.

The solvent-evaporation induced self-assembly method for preparing the thin nanoparticles films from their OSNs solutions is illustrated in Figure 6.⁵³ By using ethylene glycol (EG) as the second solvent with a high boiling point but a low surface tension, the capillary flow in the solution can be counterbalanced by the Marangoni flow. The self-assembly of nanoparticles on the substrate can thus be achieved through the nanoparticle-substrate and nanoparticle-nanoparticle van der Waals interactions.

4.4 Vapor-driven self-assembly

The vapor-driven self-assembly process is based on the selective phase demixing and self-assembled aggregate formation. Such behaviors occur from a molecularly dispersed solid solution of specific fluorescent molecules in a polymer matrix when it is exposed to volatile organic solvent vapors.⁵⁴ After solvent exposure, the supramolecular self-assembly of organic semiconductor materials leads to the formation of spherical nanoparticles (see Figure 7). The advantage of this method is to form nanoparticles films *in situ* on the substrate. Nevertheless, this kind of method is only appropriate for small-molecule

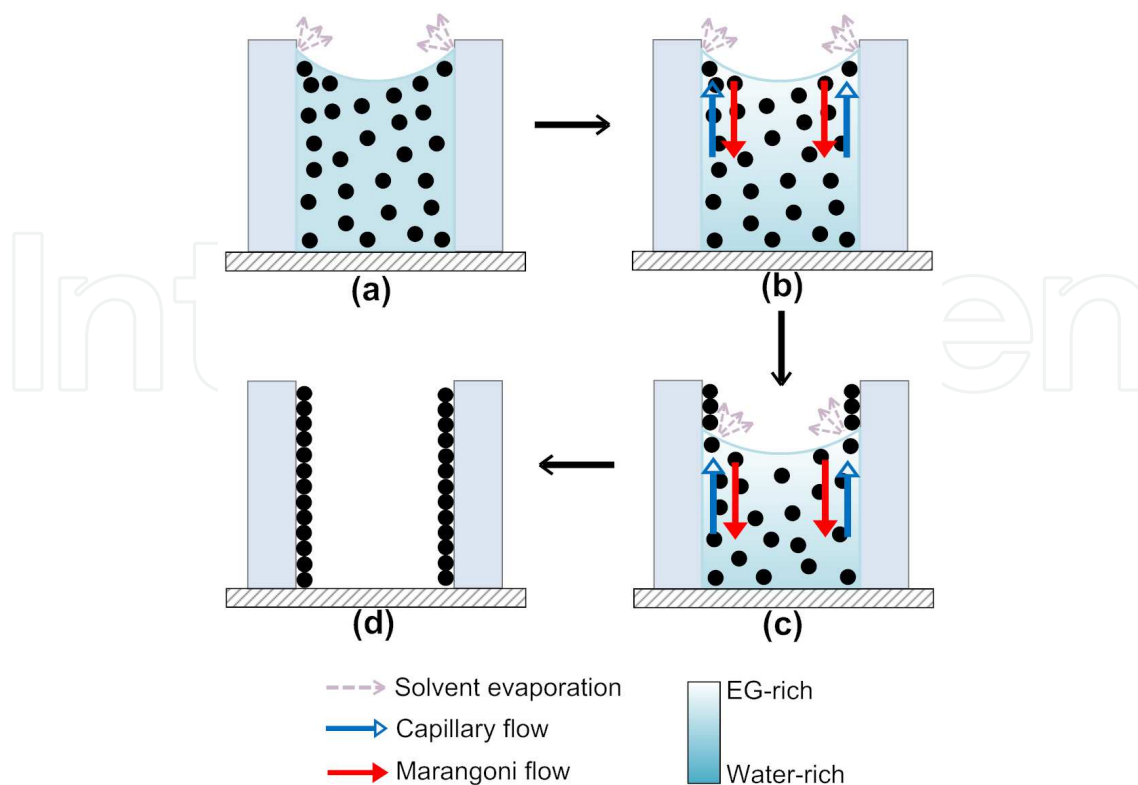


Fig. 6. Scheme for the solvent-evaporation-induced self-assembly of OSNs on the substrates to form films. (Reproduced from Ref. 53, Copyright 2010 The American Chemical Society)

compounds with certain structures and is not a universal method for most polymer semiconducting materials. In addition, OSNs formed by this method are discrete and continuous OSNs films can not be obtained.

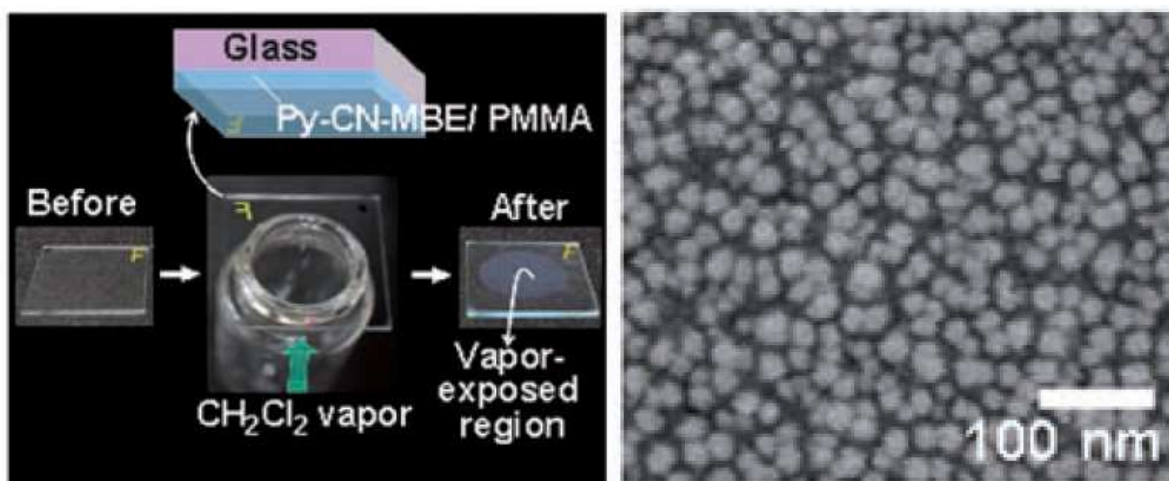


Fig. 7. Photograph of the 1-cyano-trans-1-(4'-methylbiphenyl)-2-[4'-(2'-pyridyl)phenyl]ethylene (Py-CN-MBE)/poly(methyl methacrylate) (PMMA) film before and after exposure to dichloromethane vapor (Left panel) and the SEM image of the Py-CN-MBE nanoparticles formed by the vapor-driven self-assembly process (Right panel). (Reproduced from Ref. 54, Copyright 2007 Wiley-VCH Verlag GmbH & Co.)

4.5 Inkjet printing

As mentioned above, when a droplet of OSN solution is dripped on the surface of a substrate, the OSNs tend to form coffee-stains after the evaporation of the solvent. So direct inkjet printing of OSN solutions can not provide good film morphology. To avoid this drawback, an aqueous dispersion of semiconducting polymer nanospheres is deposited by inkjet printing onto a polymer surface patterned by soft embossing.⁵⁵ By interaction between the spheres and the undulated surface a self assembly process is triggered, resulting in the formation of OSN nanostructures determined by the template.

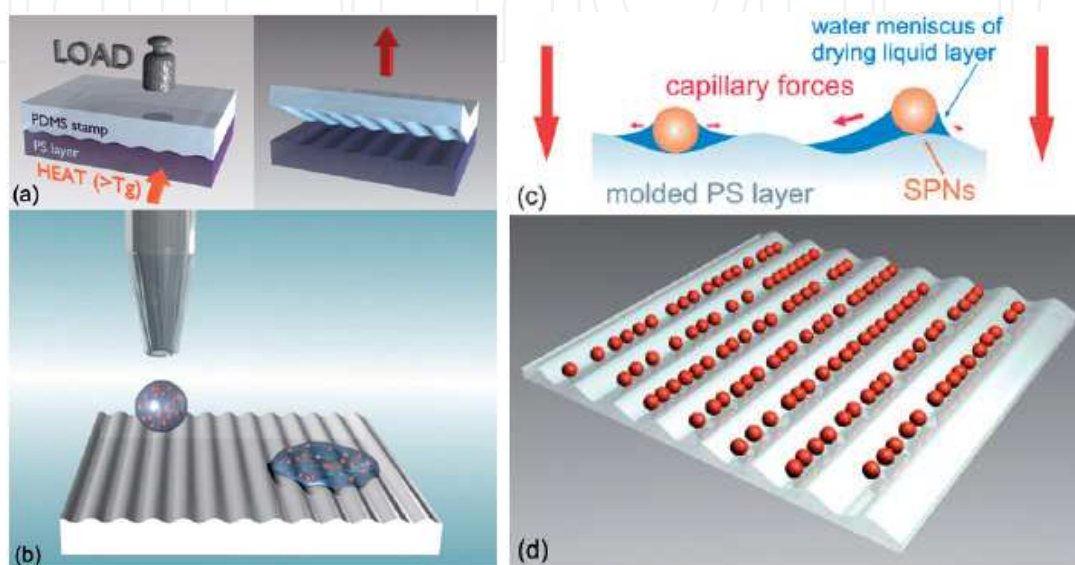


Fig. 8. The fabrication process for functional nanostructures from inkjet printing. Reproduced from Ref. 55 (Copyright 2008 The Royal Society of Chemistry).

As shown in Figure 8, after a droplet of the OSN solution was printed on the surface of the structured polymeric template layer, OSNs assemble in the grooves of the embossed surface. This method relies on the application of a polymer template layer, so that the patterned structure that is formed with the OSNs can be incorporated into a device.

4.6 Spin-coating

Due to the very low concentration of OSN solutions, good film can hardly be formed by spin-coating or dip-coating method without any additives. As a result, auxiliary underlayers or additives such as surfactants or polymer matrix have to be introduced to assist the deposition of nanoparticle films. As mentioned above, nanoparticles usually carry charges on their surfaces when they are dispersed in solutions. Therefore, negatively charged nanoparticles can be formed on polycationic films with the help of electrostatic interactions via spin-coating and vice versa. Layers of LPPP nanoparticles were spin-coated on poly(allylamine hydrochloride) (PAH) can exhibit a homogeneous fluorescence over large areas.³⁸ Similarly, conjugated polymer nanoparticles such as polyfluorene derivatives and LPPP spin-coated on poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) film can also exhibit a good film morphology.^{32,56} Besides auxiliary underlayers, polymer matrix can also be utilized to act as a binder to improve the film quality deposited from OSN solutions. This kind of binder for the nanoparticles can also assist in the reduction of electric field

singularities around the particles that may result in regions of pinhole formation in electronic devices. Poly(vinyl alcohol),⁵⁷ hexadecyl-modified poly(ethylene oxide) (PEO),⁵⁵ and PEDOT:PSS⁵⁸⁻⁶⁰ are polymer matrixes used for this purpose. These binders have virtually no effect on the color characteristics of the electroluminescence spectrum since PVA, PEO, and PEDOT:PSS have a negligible absorption in the luminance regime of OSNs. Although by this means the film quality is improved, the additives remained in the nanoparticles films will be disadvantages to the optical and electrical properties of OSNs. For example, when using PEDOT:PSS as an additive to the OSNs aqueous solution for preparing thin nanoparticles films by spin-coating, the acidity of PEDOT:PSS will deteriorate the luminescent properties of the conjugated compounds largely.

5. Applications of OSN film in optical and electronic devices

5.1 Organic light-emitting diodes

LPPP, poly(9-vinylcarbazole) (PVK), 2-(4-tert-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (tBu-PBD), coumarins, nile red, nanoparticles prepared by miniemulsion method, core-shell nanoparticles with perylene as the core and poly[methyl methacrylate-co-vinylcarbazole-co-2-(3'-nitrophenyl)-5-(4'-acryloylphenyl)-1,3,4-oxadiazole] as the shell formed by emulsion copolymerization, poly(3-octadecylthiophene) nanoparticles prepared by reprecipitation method, multi-component nanoparticles prepared by RESS process or miniemulsion method have been reported to serve as an active layer in organic light-emitting diodes.⁶¹ For nanoparticles synthesized by both miniemulsion and RESS methods, surfactants, stabilizing agents or hydrophobes are necessary and can hardly be removed. Such additives will be disadvantageous to the native optoelectronic properties of OSNs in devices. It would be still interesting to fabricate optoelectronic devices from OSNs prepared via the reprecipitation method in which there would be no additives including surfactants, stabilizing agents and hydrophobes. Electrophoretic deposition of OSN films from reprecipitation-processed nanoparticle solutions has been employed in fabricating OLEDs.⁶² Although an electroluminescent emission from the device could be observed, the emission is not uniform because the nanoporosity of the OSN film prepared by electrophoretic deposition probably causes fatal pin-holes. As a result, an approach for preparing high-quality OSN films from reprecipitation-processed nanoparticle solutions is highly desired. Fortunately, the solvent-evaporation induced self-assembly method introduced above can meet this requirement. Currently, the main drawback of this method for fabricating OLEDs is that the solvent evaporation period is time-consuming. If there are some ways are found to overcome this drawback, this method is very promising for fabricating OSN based OLEDs.

5.2 Organic field-effect transistors

Organic field-effect transistors (OFETs) fabricated using solution-deposition techniques are particularly well-suited for large-area electronic devices. For meaningful practical applications, the organic semiconductors need to provide FET mobilities close to that of amorphous silicon. This will necessitate establishment of proper molecular order in the semiconductors to achieve high mobilities, since charge-carrier transport in organic semiconductors is dominated by hopping and disordered materials are not efficient charge-transporting media. In nanoparticles, molecules are closely packed and they are usually

highly ordered. For example, both poly(3-hexylthiophene) (P3HT) and poly(9,9'-dioctylfluorene) (PFO) nanoparticles can exhibit highly ordered structures and can be distinguished from the UV absorption spectrum with occurrence of a new peak.^{31,63} Poly(3,3''-dialkylquarterthiophene)s (PQTs) nanoparticles have been explored for using in OFETs.⁶⁴ As expected, the presence of lamellar π -stacking order in the nanoparticles can be verified by XRD and UV spectrum data. OFETs based on PQT nanoparticles show a 50 % improvement in mobility on bare SiO₂ dielectric layer and an order of magnitude improvement in mobility on surface modified SiO₂ dielectric layer relative to those based on normal films.

5.3 Organic solar cells

It is well known that excitons formed in the active layer of organic solar cells usually have a migration distance less than 20 nm.⁶⁵ So in organic solar cells, the distance for excitons diffused to the interface of electron donors and acceptors should be smaller than 20 nm to ensure good light conversion efficiency. However, because the entropy of mixing is generally low for polymers, solid polymer blends tend to phase-separate at the macroscopic scale. Moreover, when a thin layer of immiscible polymers is deposited from solution, the resulting morphology strongly depends on various parameters, such as the individual solubility of the polymers in the solvent used, the interaction with the substrate surface, the layer thickness and the method of deposition, drying and annealing. Therefore, controlling of the lengths of phase separation in thin layers is important for organic solar cells to avoid large-scale phase separation. Kietzke et al. have reported that by using the blend of poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9'-dioctylfluorene-co-N,N-bis(4-butylphenyl)-N,N'-diphenyl-1,4-phenylenediamine) (PFB) nanoparticles as the active layer the phase separation in organic solar cells can be controlled on the nanoscale.^{29,56}

5.4 Photonic crystals

If a photonic crystal is constructed from a material with sufficiently high refractive index, it can exhibit a photonic bandgap, a frequency range in which the mode density is zero and photons cannot propagate in any direction. Although this property is desirable since it would allow the inhibition of spontaneous emission and the ability to manipulate the flow of light, it is difficult to be achieved with organic semiconductors due to their relatively low refractive index. Instead, an organic photonic crystal would more likely have a partial bandgap, a frequency range where light can propagate in a limited number of directions. However, even in this case, the mode density for forbidden directions can be strongly modified by the photonic crystal. For frequencies just outside the partial bandgap, the mode density along these directions can be higher than in free space. This increase indicates that more optical modes are available to interact with electronic excitations. Thus, by combining organic semiconductors with photonic crystals, this enhanced interaction with light can be used to further improve optoelectronic properties.

One of the simplest ways of preparing photonic crystals is by the self assembly of monodisperse spheres, for instance, by the self-assembly of colloidal silica or polystyrene microspheres widely reported in the literatures. These spheres can then act as secondary

templates for the fabrication of conjugated polymer inverse photonic crystals, where the interstitial voids of the sphere template have been filled with conjugated polymer. This approach has been successfully used in the preparation of poly(p-phenylenevinylene) (PPV) inverse photonic crystal films.⁶⁶

6. Applications of OSN film in chemo-/biosensors

Although lots of applications of organic nanoparticles in chemo-/biosensors have been explored in recent year, most of them are carried out in solutions. Compared with solutions, solid-state samples can be more convenient for storage and transport which are highly desired for off-site laboratory analysis. Here we will introduce some applications of OSN film in chemical and biosensors.

6.1 Chemical sensors

Hydroxyl radical is one of the most important reactive oxygen species, which is recognized to play an important role in physiological and pathological processes of the organisms. In addition, hydroxyl radical is also involved in many chemical, environmental, and pharmaceutical processes such as semiconductor photocatalysis in aqueous solution, wastewater treatment, and tumor cell killing. By using a binary nanoparticle system combining PFO nanoparticles and MEH-PPV nanoparticles, a linear relationship between the concentration of hydroxyl radical and the intensity ratio (Band I to Band III) of PFO nanoparticles can be found in the deposited nanoparticle film.⁶⁷ The synergy between MEH-PPV NPs and PFO NPs are crucial to the response of free radicals in this kind of binary NP system. When exposed to free radicals, MEH-PPV NPs undergo molecular structure changes in the outer shell. As a result, a broad-sense polarity vector across the whole NP pointing from the weak-polarity core to the strong-polarity shell is established. Such a polarity vector will influence on the vibronic coupling among different electronic states of PFO molecules when the core-shell MEH-PPV NPs are adjacent to PFO NPs, which will change the relative PL emission intensity between bands I and III of PFO.

6.2 Biosensors

In general, conducting polymer nanoparticles are dispersed on the surface of the electrode to increase the area/volume ratio and to favor the adsorption of bio-molecules. By this means, uniform electrostatic adsorption of protein was enabled, thereby exhibiting higher signal-to-background ratios and shorter response times than electrochemically prepared films.⁶⁸ Taking advantage of conducting polymer nanoparticles, sufficient amounts of enzyme were firmly immobilized during the fabrication of a phosphate biosensor. The response time of the biosensors was about 6 s. A linear response was observed between 1.0 μM and 100 μM and the detection limit was determined to be about 0.3 μM .⁶⁹ Besides, an ascorbic acid sensor has been fabricated via the drop-casting of PANI nanoparticles onto a screen-printed carbon-paste electrode.⁷⁰ The PANI nanoparticles not only enhanced the catalytic reaction, but also allowed the detection of ascorbate at the reduced applied potential of 0 V and operation at neutral pH, avoiding the problem of sample interference.

7. Conclusions and prospects

Most of the organic semiconductors including both small molecules and conjugated polymers can be utilized for preparing OSNs, thus ensuring a very wide material selectivity for their applications. Various approaches have been reported for synthesizing OSNs. Besides reprecipitation method, additives such as surfactants are usually employed in other methods, which may be disadvantageous to the optical and electronic properties of OSNs. When depositing the OSN solution onto the substrate to form nanoparticle films, auxiliary underlayer and binders such as polymer matrix or surfactants are often used to improve the film quality. An exception is the vapor-driven self-assembly and solvent-evaporation induced self-assembly methods, which can prepare clean nanoparticle films and is highly desired for the optical and electronic applications.

Although OSNs have been proved to be effective building blocks in both optoelectronic devices and chemo/biosensors, a number of challenges and avenues of exploration remain. The interface between nanoparticles and the surroundings is crucial to its optical, electrical, and catalytic properties. So surface modification of OSNs can not only improve their contact properties but also endow them with a new function. However, the surface modification of OSNs is seldom reported yet.

The field of photonic crystals has recently provided a number of novel insights into the manipulation of light. These photonic properties have yet to be fully combined with the optoelectronic properties of OSNs, and the development of this area remains a very active area of research. Additionally, the ability to precisely control the morphology and alignment of OSNs is of importance to all fields of organic electronics.

In the field of electronic devices, OSN based OLEDs have been widely explored. However, OSN based OFETs still need to be paid more attention. By appropriate design, OFETs using OSNs as an active layer may be served as multifunctional optoelectronic devices.

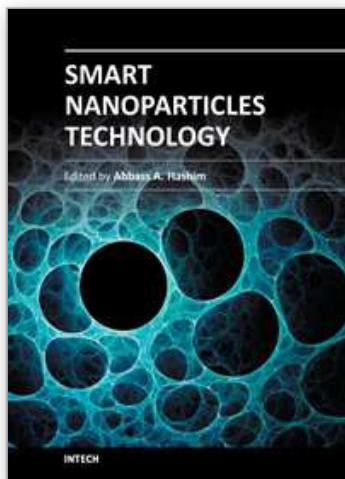
With the great advantages of OSNs, they are believed to play an important role in more and more application fields and will provide new scientific insights in the coming years.

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