Synthesis and multi-applications of conductive magnetic stable polypyrrole dispersion with phase-convertible characteristics

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HIGHLIGHTS

- Synthesis of highly stable conductive aqueous polypyrrole dispersion.
- Liquid colloidal dispersion with phase-convertible characteristics.
- 0-3D magnetic and conductive polymer composite nanostructures.
- Excellent processability and selective solubility of conductive polymer.
- Extremely selective and sensitive solution or solvent nanodetector.

GRAPHICAL ABSTRACT
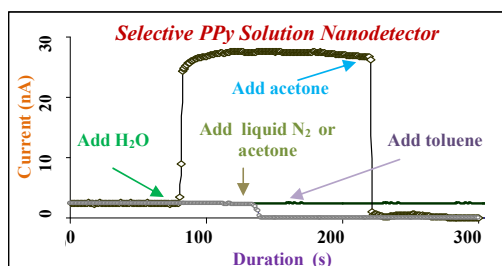
ABSTRACT

Due to the insoluble and non-thermoplastic properties, pure electroactive polymers are difficult to be processed into device nano features and thus their performances (e.g., sensitivity, selectivity, and miniaturization) are limited. Here we demonstrate an approach to synthesize highly stable colloidal polypyrrole dispersion or magnetic conductive fluid with excellent processability. Remarkably, the unique liquid dispersion possesses specific liquid-solid-liquid phase-convertible characteristics, a great improvement from the pure conductive polymers. Hence the dispersion can be readily converted to device structures of any scale sizes and shapes. Zero to three dimensional magnetic conductive polypyrrole nanostructures are fabricated via novel casting, injecting or coating of the dispersion. With the distinct selective solubility in different solutions and large surface-to-volume ratio, the smart polypyrrole nanostructures can be applied to extremely sensitive, selective, and rapid response nanosensors of solutions/solvents as well as in the detection of liquid N_2. This novel methodology introduces a facile way to enhance the processability and applications of insoluble conductive polymers by encapsulating them with small bi- or multi-surfactant molecules.

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1. Introduction

Since the discovery of conductive polymers in the last century, they have been intensively studied and widely used in various fields of electronics, optics, actuators, medicine and energy devices [1–3]. To further improve their performances, applications, and properties for catering to emerging or advanced technologies (e.g., miniature nanodevices, high-speed transistors, rapid response sensors), it is crucial to overcome the limits of their intrinsic

properties and processibility [4,5]. For instance, being synthesized from conventional chemical and electrochemical methods, conducting polymers have limited applications in highly selective and sensitive sensors as their common powder or bulk-film phases possess a low surface-to-volume ratio [6,7]. In addition, these polymers can only be made into simple architectures [2,4,8] and are difficult to achieve diverse morphologies and shapes (e.g., fine 0 to 3 dimensional (0-3D) nanostructures) for miniature nanodevices [9–11]. Hence simple processes to fabricate deformable polymer structures, particularly in fine nanoscales and solid-liquid-convertible phases are highly desirable. Many of the electroactive polymers of importance, such as polypyrrole (PPy), polyacetylene, polyaniline, polyphenylene, polythiophene, are not molten in nature and are generally insoluble in common solvents [1–4]. Thus, the processibility and performances of these conductive polymers are relatively poor due to this weakness [3,12,13]. Liquids and melts can be readily cast or processed into various shapes and sizes (including nanostructures). Therefore, to improve the processibility and performances, numerous studies [14–18] have been focusing on the preparation of stable dispersions as substitutes of liquids and melts, such as the mostly focused PPy dispersions. Among the electroactive polymers, PPy is more widely used in different technologies [2,19], as it possesses unique low-toxicity, excellent environment stability, high electrical conductivity and interesting redox properties [20,21]. However, despite some inspiring progresses achieved on the syntheses of PPy dispersions [17–19], the enhancement in processibility and functions (such as in the fabrications of nanostructures and devices) with the use of conductive PPy polymer are still limited [7,20,21]. Therefore, to further promote the greater applicability and better performance of the electroactive polymers, it is crucial to synthesize highly stable liquid colloidal dispersions with enhanced properties.

Herein, we adopt a molecule-encapsulated method to fabricate fairly stable colloidal PPy dispersion (colloidal emulsion) as a substitute of liquid polymer melts. In-situ oxidative polymerization of pyrrole by ferric chloride was carried out under carefully selected process parameters. Two simple surfactants were used as the steric stabilizers in the reaction. The as-synthesized aqueous dispersion possessed desirable conductivity, magnetic properties, excellent processibility, and specific liquid-solid-liquid phase-convertible characteristics. Therefore they could be readily converted to various 0-3D nanostructures via different novel processes. In particular, the as-synthesized 2D porous PPy nanofilm exhibited significantly improved sensitivity and selectivity to solutions/solvents, hence could be used as extremely selective and sensitive solution sensors/detectors with fast response. The unique microspheres with magnetic handles were also prepared from the PPy nanosphere film via the phase-convertible property. More applications may be explored for these stable PPy fluids, nanostructured colloids and metal/PPy features because of their scalable and deformable shapes as well as good conductive and magnetic properties.

2. Results and discussion

The highly stable liquid colloidal PPy dispersion with multifunctional applications was achieved via adsorbing or absorbing unique aqueous bi-surfactant molecules on PPy molecules and by carefully selecting reactant concentrations during the polymerization of pyrrole. The synthesis of 0-3D PPy-based nanostructures and nanosensor applications was based on the excellent processibility and selective solubility of the as-synthesized dispersion and colloids.

2.1. Theoretical proposal and synthesis of desirable stable aqueous colloidal PPy dispersion

To achieve highly stable liquid aqueous conductive PPy, based on its following chemical formula, two methods can be proposed to improve its solubility.
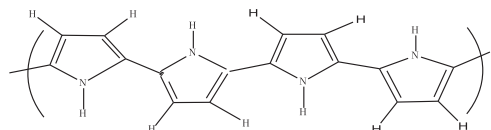
One method is to include hydrophilic functional groups by replacing −H bonds on the PPy molecule through chemical modification. However, previous works show that it remained difficult to produce stable modified liquid PPy solutions through this method [3,12,14]. Another method is to encapsulate PPy molecules by adsorbing or absorbing small surfactant molecules, which possess hydrophilic functional groups, for forming stable liquid PPy dispersions (depicted in Fig. 1A). Others' and our groups have earlier reported the successful syntheses of relatively stable PPy dispersions by using individual surfactant (e.g., ethylhydroxyethylcellulose [22], sodium benzoate [17], polyoxyethylene nonylphenyl ether sulfate [23], polyvinylpyrrolidone [24], sodium dodecylbenzene sulfonate (SDBS) [19,25], poly(vinyl alcohol) (PVA) [18,21], etc) or two surfactants (e.g., PVA and hyaluronic acid) [20]. Nevertheless, there remains challenges in the use of these synthesized aqueous and non-aqueous colloidal PPy dispersions in the fabrication of uniform sub-100 nm nanostructures, such as fast phase-conversion, etc [19,22,23]. In addition, it remains unclear if these synthesized dispersions are able to improve the polymer functions or applicability as many of them are not highly stable or do not possess the desirable processibility [20,26]. Thus in this work, in order to achieve PPy dispersion of greater stability, ease of processibility and much better performances, during the in-situ oxidative polymerization of pyrrole by $FeCl_3$, the two simple surfactants (SDBS and PVA) with two types of strong hydrophilic functional groups ($-OSO_3^-$ and $-OH$, respectively) were simultaneously selected as the steric stabilizers. The schematic illustration of the synthesis process is shown in Fig. 1B. The experiments revealed that the simultaneous utilization of both group functions of SDBS and PVA surfactants in the polymerization produced much highly stable PPy dispersions with excellent performance. Preliminary studies showed that if the PPy dispersion was prepared using either SDBS or PVA, the dispersion either was not highly stable with precipitation within minutes (min) or hours (h), or produced non-uniform and rough colloidal nano-/micro-particles [18,19] when added drop-wise into acetone under vigorous stirring. Along with the use of the two simple surfactants to synthesize highly stable PPy dispersion with better performances, all reactant concentrations and reaction procedure should be carefully controlled. Based on the structures of PPy and its dispersion colloid molecules (Fig. 1A), it should be noted that a smaller number of repeating monomer-molecular units (n) in PPy and a higher surfactant to PPy molecule ratio were desirable for the formation of encapsulated PPy molecules. Hence we adopted a lower molar ratio of pyrrole to the surfactants as well as oxidant in the synthesis of stable PPy dispersion. A larger concentration of pyrrole (e.g., $\geq FeCl_3$ molar concentration) would otherwise lead to the formation of some PPy precipitates (top image of Fig. 2a). In this work, the molar ratio of pyrrole to the surfactants and pyrrole to the $FeCl_3$ was limited to $\leq$1:2 and 0.01:1, respectively. Furthermore, concentrations of SDBS and PVA were controlled in the range of 0.03–0.05 M and 0.05–0.08 M, respectively. This minimized the electrostatic
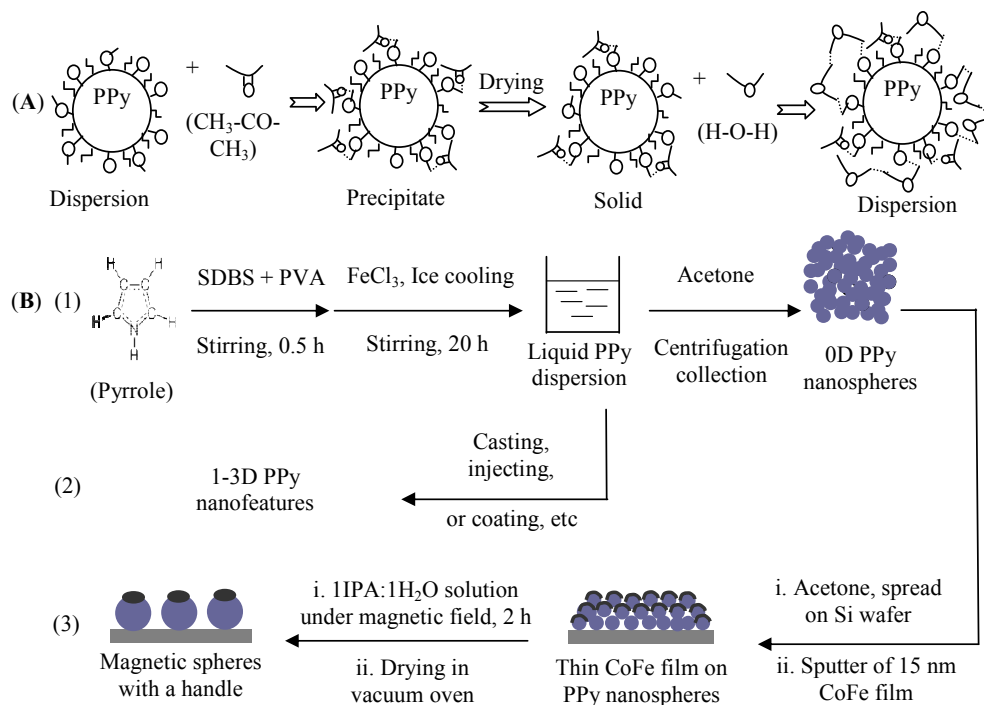
Fig. 1. Schematic illustrations of (A) the adsorption of PPy dispersion molecule in acetone and water, and (B) the fabrication of (1) liquid PPy dispersion and 0D solid PPy nanospheres by means of chemical oxidation of pyrrole, (2) 1–3D PPy nanofeatures from PPy dispersion, and (3) PPy microspheres with magnetic handles through magnetic film sputtering and solution treatment processes. In (A), "–O", "–O–" and "~" represent $-OSO_3^-$, –OH and alkyl function groups, respectively, while " O··· ⁻O " represents H-bond.
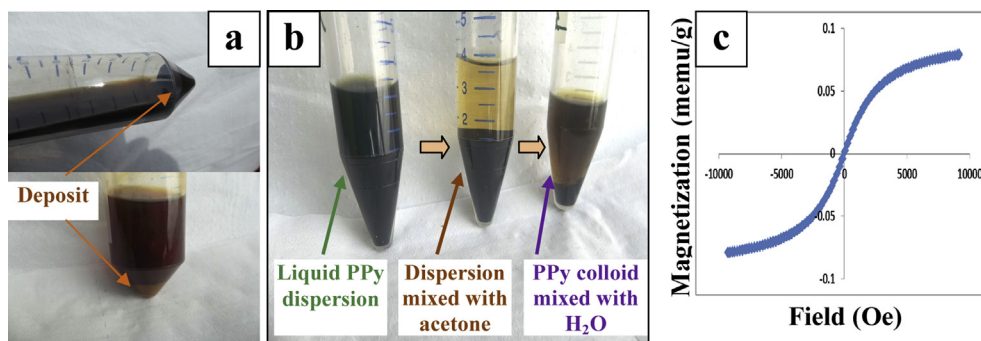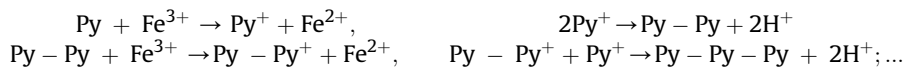

Fig. 2. (a) Optical images of PPy dispersion containing precipitates prepared from excess pyrrole (top) and excess SDBS (bottom). (b) Optical conversion images of the liquid PPy dispersion. From the left to middle, then middle to right, illustrating that PPy dispersion was mixed with acetone, then the deposit was mixed with distilled water after its drying. (c) *M-H* loop of the liquid PPy dispersion.

interaction among the reactant molecules, which would also lead to PPy precipitates (bottom image of Fig. 2a). In addition, PVA with the lower molecule weight (MW < 100,000) were used to improve the surfactant activity and solubility. After the polymerization under the vigorous stirring, it was interesting to note that the as-synthesized aqueous dark green dispersion(in web version) was very stable and showed no signs of liquid layer-separation and precipitation on long-term storage at room temperature for several years, as shown in Fig. 2b (left).

2.2. Specific properties and excellent processbility of the stable aqueous PPy dispersion

Since the as-synthesized PPy dispersion is highly stable liquid solutions with different functional groups, it is expected to display distinct characteristics in comparison to pure PPy or the commonly modified PPy. Thus, properties of the dispersion were studied in detailed. From the adopted additives and reaction for the pyrrole (Py) polymerization (illustrated as follows) by.

$$Py + Fe^{3+} \rightarrow Py^+ + Fe^{2+},$$
$$Py - Py + Fe^{3+} \rightarrow Py - Py^+ + Fe^{2+},$$
$$2Py^+ \rightarrow Py - Py + 2H^+$$
$$Py - Py^+ + Py^+ \rightarrow Py - Py - Py + 2H^+; \ldots$$

using $FeCl_3$ oxidizer [3], the stable PPy dispersion was known to contain PVA, SDBS, excess $FeCl_3$ and other products from the reaction, and should be aqueous magnetic and conductive colloidal fluid. The magnetic property was due to the hydrolyzes of the $FeCl_3$ reactant and reduced $FeCl_2$ to magnetic $Fe_2O_3 \cdot 3H_2O$ and $FeO \cdot H_2O$, respectively [17], which were retained in the colloidal PPy. The chemical reactions were described as follows. By means of the VSM

$$2FeCl_3 + 6H_2O \rightarrow Fe_2O_3 \cdot 3H_2O$$
$$+ 6HCl; \quad FeCl_2 + 2H_2O \rightarrow FeO \cdot H_2O + 2HCl.$$
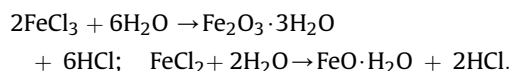
characterization of the fluid in a small sealed cell, the PPy dispersion was found to exhibit a saturation magnetization of $10^{-2} - 10^{-1}$ memu/g at an applied field of 5000 Oe (Fig. 2c). The magnetism of the colloidal PPy dispersion can be improved by increasing the $FeCl_3$ reactant concentration in the polymerization, where a higher $FeCl_3$ concentration would not lead to the precipitation of PPy. The 4-probe electrical measurement of the aqueous magnetic PPy dispersion revealed a high conductivity of up to 10^{-2} s cm^{-1} (Table 1). Thus, the PPy dispersion is a magnetic and electrically conductive fluid. Moreover, the aqueous PPy dispersion was found to quickly deposit out from some organic solvents like acetone and butanone (middle image of Fig. 2b). This was attributed to the adsorption and formation of H-bonds between the acetone molecules and −OH groups of the PVA in the encapsulated colloidal PPy molecules, which is shown in Fig. 1A. As the PPy dispersion incorporated the functional groups ($−OSO_3^-$ and −OH) from SDBS and PVA surfactants (Fig. 1A), which are hydrophilic (water affinity) and can form H-bonds (O···H−O) with water (H−O−H) molecules or−OH groups (e.g., from alcohols), the aqueous magnetic conductive PPy dispersion was found to be a distinct phase-convertible liquid, and the synthesized PPy colloids (middle image of Fig. 2b, deposited from the acetone) from it could be fully or partially dissolved in water and alcohols again through the linkage of H-bonds. The right image of Fig. 2b showed that such dried solid PPy-surfactant colloids were partially dissolved in water. Thus, the synthesized aqueous conductive PPy dispersion demonstrated liquid-solid-liquid convertibility with the use of acetone and water (or alcohols) as the transfer media. The phase-convertible mechanism was illustrated in Fig. 1A. To the best of our knowledge, it is the first time that such specific phase-convertible conductive colloidal PPy has been demonstrated even though PPy has been widely synthesized and studied.

Due to the unique phase-convertible property, the as-synthesized liquid colloidal PPy dispersion should possess excellent processibility and could be applied to the fabrications of diverse conductive magnetic structures of any shapes and sizes ranging from nano-to visual-scale. The FESEM images in Fig. 3 illustrate the diverse 0-3D nano-/micro-structures fabricated from the PPy dispersion using procedures described in Fig. 1B. Fig. 3a shows the FESEM image of colloidal PPy nanospheres (~80 nm), which were prepared via drop-wise addition of the PPy dispersion into acetone under vigorous stirring. Fig. 3b and c shows the FESEM images of the PPy nanowires with diameter of 250 and 150 nm, respectively, fabricated similarly using acetone treatment. As these nanowires were prepared by casting the aqueous PPy dispersion into alumina membrane with uniform straight-through nanopores of about 20−300 nm, the diameters of the PPy nanowires could be controlled by selecting the membrane with desirable pore sizes. In Fig. 3b, the alumina membrane had been etched away by using a 1:1 (v/v) unique mixture of 10% NaOH aqueous solution and acetone. To achieve long PPy nanowires, the aqueous PPy colloidal dispersion was injected into stationary acetone through the nano-porous membrane. Hence PPy nanowires of hundreds of micrometers (or longer) in length could be prepared. The FESEM image in Fig. 3c clearly depicts such long nanowires synthesized using this easy procedure. It is noted that the nanowires in Fig. 3c bent back on the side of the used porous alumina membrane after the injection into acetone solution. In addition to the 0D nanospheres and 1D nanowires, 2D mesoporous colloidal PPy nanofilms (Fig. 3d) could also be synthesized from the aqueous PPy dispersion via mixing with acetone and sprinkling on a Si wafer. The prepared 2D nanofilm has a thickness of about 3 μm and an average pore size of ~70 nm. Under drying at reduced pressure, the pores were formed due to the differential evaporation rates between acetone and water from the sprinkled film, while the remaining PPy along with adsorbed PVA, SDBS and partial acetone molecules formed the porous network structure. The EDX result in Fig. $4a_1$ illustrates the film composition.

Besides the above described process of rapid-phase-conversion through mixing with acetone, 2D and 3D PPy nanostructures could also be prepared from the liquid dispersion by means of drying the dispersion in air or vacuum [27,28]. Fig. 3e shows a thin 30 nm planar solid film fabricated on an atomically flat single crystal Si wafer. This was achieved by a high speed (3500 rpm) spin-coating process of the PPy dispersion, followed by a long drying time of 20 h in air to allow the slow evaporation of volatile components in the film. Due to the absence of acetone adsorption or absorption treatment, the composition of this planar film (inset of Fig. $4a_1$) slightly differed from the porous film (Fig. $4a_1$) even though the elemental components were the same.

As depicted in Fig. 3f, d nanoflowers were also prepared by sprinkling, cooling and drying process. The nanoflowers were 10−30 μm in size and had leaf thicknesses of down to about 20 nm. From the tilted side-view of the FESEM image, the nanoflower was ~3 μm in height. The 3D nanoflowers were formed individually, probably because the PPy colloids in the diluted dispersion shrank and coagulated into 3D aggregates under the cryogenic shock of liquid N_2. The EDX analyses on the nanoflower (Fig. $4a_2$) and the bottom substrate (inset of Fig. $4a_2$) affirmed that the flower consisted mainly of PPy polymer while the bottom regions beside the flower contained only inorganic salts.

To further examine the phase convertible property of the as-prepared colloidal PPy dispersion, conductive PPy microspheres with magnetic handles (Fig. 3h) were also fabricated from the thick colloidal PPy nanosphere film (~1.5 μm, Fig. 3g). Comparing the two figures, the PPy nanospheres swelled from 80 nm to about 2 μm in the solution. As shown in Fig. 1B(3), the fabrication was carried out

Table 1
Physicochemical properties of as-prepared PPy dispersion and structures.

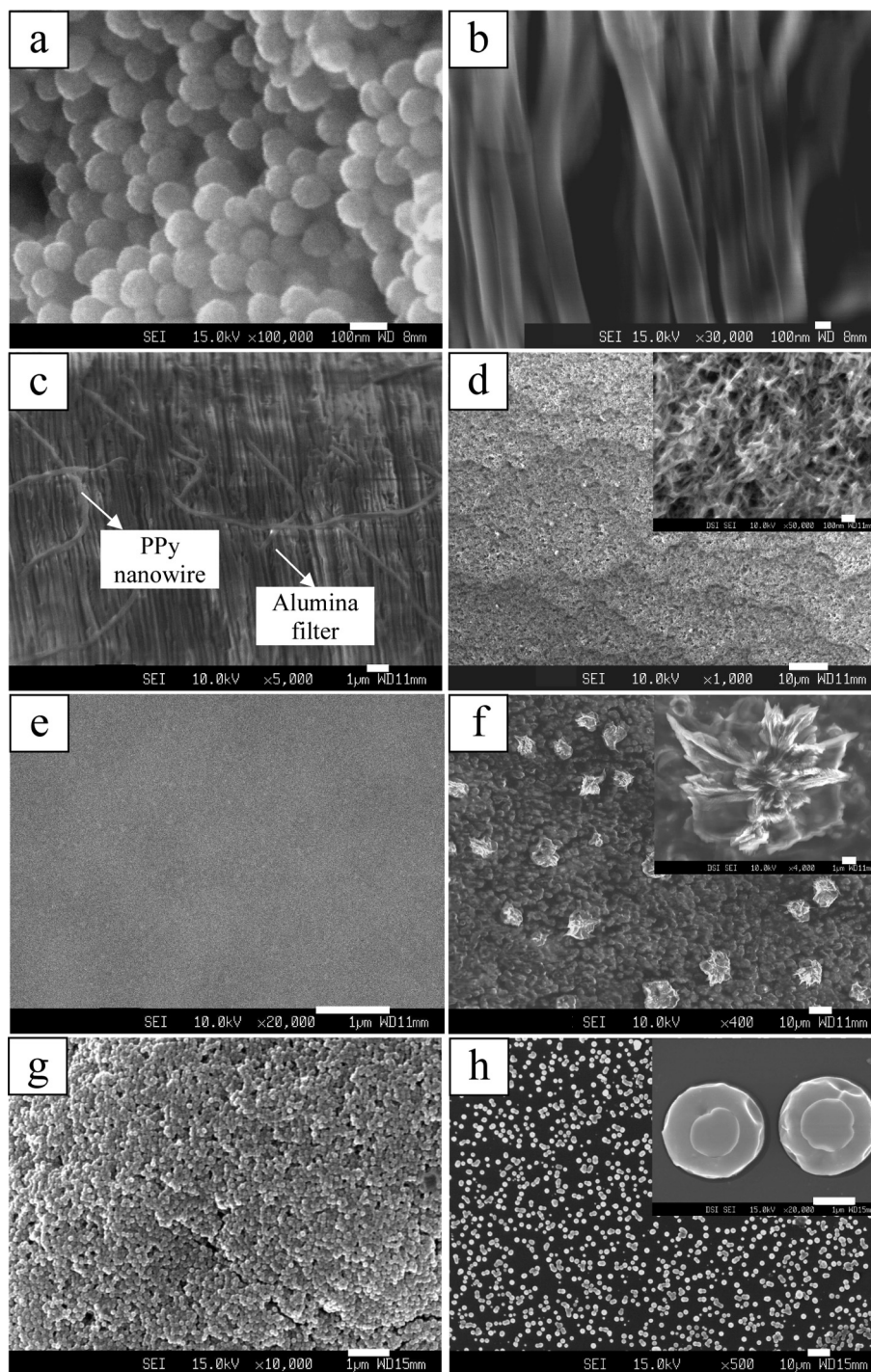|	Liquid dispersion	Planar solid film	Nano-spherical film	Porous film	Magnetic handle microsphere
Dissolvable media	H_2O, alcohol, dimethyl formamide				Acid, alcohol, dimethyl formamide
Non −dissolvable media	Acetone, butanone, CCl_4, $CHCl_3$, toluene, ethyl acetate, etc				
Conductivity σ (s.cm^{-1})	$10^{-2} - 10^{-4}$	$10^{-2} - 10^{-4}$	$10^{-3} - 10^{-5}$	$10^{-3} - 10^{-4}$	$10^{-3} - 10^{-4}$
Magnetization (memu/g, at 5 K Oe)	$10^{-2} - 10^{-1}$	$1 - 10$	$10^{-1} - 1$	$10^{-2} - 1$	$10 - 10^2$
Other properties	Dark green, pH 0.5 − 4.5	Brown	Black, sphere size: 20 −80 nm	High surface area	Size: 0.5 − 2 μm

Fig. 3. FESEM images of (a) PPy nanospheres synthesized via drop-wise addition of the dispersion into acetone at a stirring speed of 1000 rpm, (b) PPy nanowires prepared via casting PPy dispersion into porous alumina membrane, baking and dissolving the membrane, (c) long PPy nanowires synthesized via casting of liquid PPy dispersion into acetone through an alumina membrane with a pore size of 150 nm, (d) PPy porous film fabricated via sprinkling PPy and acetone solution onto Si wafer surface and drying under reduced pressure, (e) PPy planar solid film prepared via spin-coating PPy dispersion on Si wafer at speed of 3500 rpm and drying in air, and (f) PPy nanoflowers synthesized via sprinkling PPy and H_2O mixture on Si wafer, followed by cooling in liquid N_2 and drying under reduced pressure. (g) thick layer of PPy nanospheres laid on Si wafer surface from slow 500 rpm spin-coating and drying, and (h) magnetic handle microspheres converted from colloidal PPy nanospheres through aqueous IPA solution treatment. The scale bars in the images of (a), (b) and inset of (d) are 100 nm, (c), (e), (g), the insets of (f) and (h) are 1 μm, while (d), (f) and (h) are 10 μm.

by immersing the thick PPy nanosphere layer, sputtered with a thin ~15 nm CoFe film on the top surface, in IPA aqueous solution. During the synthesis, the vigorous ultrasonic agitation in the ultrasonic bath broke the thin 15 nm CoFe film into smaller pieces. Each CoFe piece, together with the tightly-bound top PPy nanospheres, behaved as a nucleus for the formation of the bigger spheres while in the stationary solution for the duration of 2 h. The nuclei grew larger by adsorbing the colloidal PPy molecules, which dissolved from the bottom PPy nanospheres under the vigorous vibration of the solution. The EDX analyses on different positions of
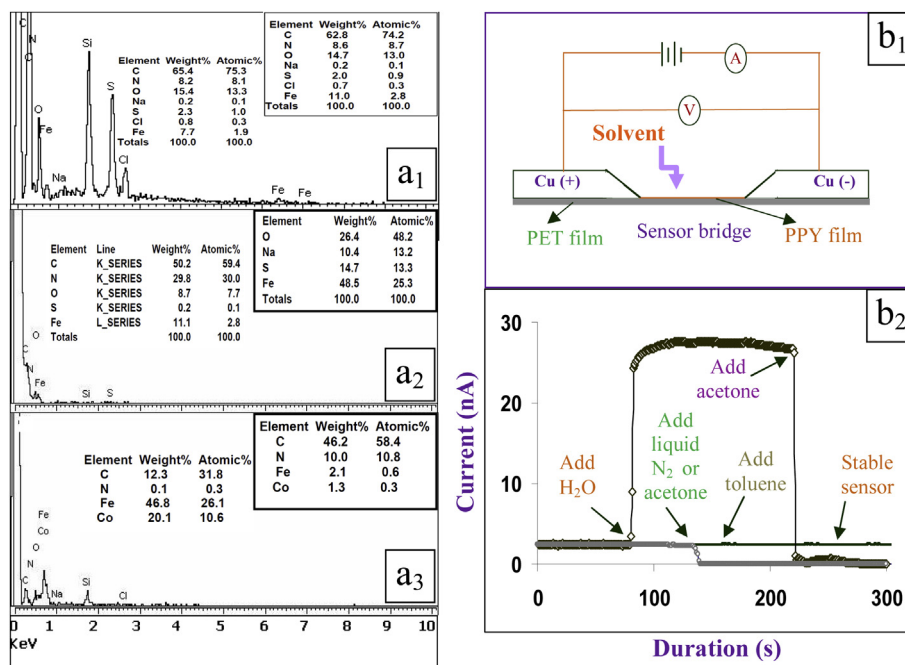
Fig. 4. (a) EDX results of (1) porous PPy film from acetone treatment and planar PPy film (inset) from drying the dispersion in air, (2) 3D PPy nanoflower and the substrate region (inset) beside the flowers. The Si peaks are from the Si substrates and (3) handle and bulk (inset) of magnetic PPy microsphere. (b$_1$) Measurement circuit and (b$_2$) results for PPy nanosensor. In (b$_2$), the solid line (−) represents the scenario without loading (before 150 s) and with the addition of toluene at 150 s) and]) stand for the addition of liquid N$_2$ or acetone, and water followed by acetone, respectively.

one PPy microsphere showed that the total Fe and Co content at the handle and bulk is 36.7 (Fig. 4(a$_3$)) and 0.9 (inset of Fig. 4(a$_3$)) in atom percentage, respectively, which indicates that the handle possesses much stronger magnetism (due to the CoFe film piece) than the bulk of the microsphere. In addition, the relatively uniform and smooth surface indicated that the PPy microspheres were result of the redeposition of PPy colloid molecules. This further confirmed that the converted colloid nanospheres from PPy dispersion could be dissolved in aqueous IPA solution again. Accordingly, we can conclude that these microspheres and the above achieved 0-3D PPy nanostructures validated the easy processibility and phase-convertible of the as-synthesized aqueous PPy dispersion.

2.3. Applications of the magnetic conductive PPy dispersion and nanostructures

Apart from converting to various 0-3D nano-/microstructures, the easy processibilty and unique solubility of the PPy dispersion enables it to fulfill other functions and applications. It is interesting to note that a thin uniform crack-free mesoporous PPy colloid nanofilm could be readily coated on an isolator substrate (e.g., SiO$_2$, PET). Therefore the film with high surface-to-volume ratio could serve as an extremely selective and sensitive nanosensor (Fig. 4b$_1$) to detect various solutions or solvents with a rapid response time. This was not achievable by PPy polymers synthesized via the commonly used methods [3,6,11,21]. Fig. 4b$_2$ illustrates the different quick responses of such quite sensitive PPy nano-sensor/-detector to water, acetone, toluene, etc. Since the sensor conductivity is proportional to the current passing through the sensor at a constant applied direct current (D. C.) voltage of 500 mV, the current vs. measuring time curves in Fig. 4b$_2$ clearly show that the sensor conductivity changed in an opposite manner when the sensor was wetted by distilled water and acetone. Water increased the sensor conductivity sharply while acetone decreased the

conductivity drastically to zero in all situations. It is because when water was used to wet the sensor bridge, which consisted of thin (~500 nm) mesoporous PPy nanofilm, some PPy colloid molecules dissolved in the water and filled up the pores of the film. This increased the conductive cross-section area of the sensor bridge greatly and as a result, the sensor current increased significantly. Similar results were also observed when the distilled water was replaced with ethanol or IPA, even though the level of sensitivity slightly differed. In contrast, acetone would shrink the PPy film with their absorption onto the PPy colloids, which resulted in a reduced conductive cross-section area and thus a decreased current. Furthermore, the thin PPy porous nanofilm in the nanosensor formed gaps after the shrinkage from the addition of acetone, which broke the contact of the PPy molecules at some locations. This caused the sensor bridge circuit to be fully opened and therefore the sensor current dropped to zero regardless of whether the sensor had been wetted by water previously. This was similar to the addition of liquid N$_2$ (Fig. 4b$_2$), which also led to the thermal shrinkage of thin PPy polymer under the cryogenic shock and the consequent open circuit of the sensor nano-bridge. Notably, if the PPy film was removed from the sensor bridge, the circuit current remained zero under the applied low voltage of 500 mV, even with the addition of distilled water on the bridge. Further investigation on the sensitivity of the PPy sensors to CCl$_4$, chloroform, toluene and their mixture solvents showed no changes in the conductivity. Fig. 4b$_2$ illustrates the scenario when toluene was added to the sensor, where the lack of change in conductivity was attributed to the as-synthesized colloidal PPy dispersion being immiscible with these solvents. Thus, these sensitivity results for the PPy nanosensors or -detectors revealed the selective solubility of PPy colloids to different solutions.

Since the as-synthesized PPy dispersion was a conductive magnetic fluid and able to readily form numerous nano-/microscale architectures, it should pose many other potential applications in industries, microelectronics, catalysis, nano- and bio-

technologies, such as magnetic fillers, electrical seepage-connectors, nano-linking channels, etc [1,9,13]. In addition, the 0-3D nano-/micro-structured PPy colloids converted from the dispersion are bio-degradable polymers and possess magnetic and electrically conductive properties as well (Table 1) [26]. They can also possess various functions or applications in numerous technical fields, such as the 0D nanospheres can be used for magnetic alignment tools and host for controlled-release of drugs in life-science [29,30], magnetic handle microspheres for stimuli-responsive tracers in bio-technology [28], and 1D PPy nanowires for gas sensors or active elements in optoelectronic devices [10,31]. The 2D porous PPy films have more applications in high performance super-capacitance or electrodes of batteries or fuel cells [7,32], and thin bulk PPy films for magnetoresistive or photovoltaic devices [5,33,34], while the 3D PPy flowers can be used as catalyst centers, nerve regeneration and neurotoxin sensors [4,26,35], etc.

3. Conclusions

In summary, using two specific simple surfactants as the steric stabilizers, we have devised a simple, controllable and novel approach to synthesize highly stable aqueous PPy dispersion with desirable conductive, magnetic and phase-convertible properties. Such highly desired characteristics were not achievable via common synthesis routes. The developed methodologies explored simple ways to modify and process insoluble polymers to variable nano-/micro-structures and multifunctional sensors or detectors, which can possibly be applied to other conductive polymers for the improvement of their performance. More functional nano-/micro-devices are also potentially fabricated using the devised approaches with some modifications [17,23].

4. Experimental section

4.1. Synthesis of stable PPy dispersion

Pyrrole monomer (>98%, C_4H_5N, Merck-Schuchardt, Schuchardt, Germany), polyvinyl alcohol (PVA, 88% $(C_2H_3OH)_x$, molecule weight ~25,000, Aldrich Chem. Company, USA), and sodium dodecylbenzene sulfonate (SDBS, 80% $C12H25OSO3Na$, SIGMA Chem. Co., USA) were used in the synthesis of aqueous PPy dispersion via $FeCl_3$ oxidization. The preparation of colloidal PPy dispersion was performed as reported previously [16] but with modifications. A mixture of 10 ml 0.005–0.03 M pyrrole, 0.03–0.05 M SDBS and 0.04–0.08 M PVA aqueous solutions was prepared under vigorous stirring (at speed of ≥1200 rpm). The reactant mixture was added gradually into 10 ml of 0.3 M (or higher) $FeCl_3$ solution in an ice-bath under vigorous stirring. After 2 h of stirring, the mixture was transferred into an ultrasonic bath for 20 min, and then continuously stirred for another 20 h. A dark green PPy dispersion was obtained.

4.2. Conversion of aqueous PPy dispersion into 0-3D nano-/micro-features

0D nanospheres were prepared by adding drop-wise the PPy dispersion into ketone solvent, such as acetone ($CH_3-CO-CH_3$), butanone, etc, under vigorous stirring in an ice-bath. The black solid PPy nanospheres were collected by centrifugation at a speed of 9000 rpm for 15 min, followed by acetone-rinsing and drying under reduced pressure. 1D nanowires were prepared by casting PPy dispersion into the nanopores of a alumina membrane filter (Whatman Anodisc 25, Maidstone, England), or injecting the PPy dispersion into a stationary acetone solution through the nanopores of the alumina membrane filter to obtain longer nanowires.

The membrane filter has uniform straight through nanoholes with diameters ranging from 20 to 250 nm and a maximum thickness of 60 μm. 2D PPy porous film was fabricated via sprinkling the mixture of acetone and PPy dispersion (at a ratio of 2:1, thoroughly mixed by vigorous shaking) on Si wafer, followed by drying under reduced pressure. The 2D planar solid film on Si was prepared via spin-coating the PPy dispersion on the Si wafer at speed of 200–4000 rpm for 30 s, followed by slow drying in air. The film thickness was controlled by the spinning speed. 3D nanoflowers were synthesized by sprinkling a mixture of PPy dispersion and water (at a ratio of 1:2) onto the Si wafer, followed by cooling in liquid N_2 and drying under reduced pressure. When fabricating PPy microspheres with magnetic handles, a suspension of PPy nanospheres in acetone was spread onto a Si wafer by spin-coating at a speed of 100 rpm for 20 s. The PPy nanospheres on Si wafer were dried under reduced pressure after the evaporation of acetone. A thin layer of CoFe (15 nm) was subsequently sputtered on the top of the PPy nanospheres via a magnetron sputtering system (ATC, AJA International, Inc.). The nanospheres on the Si wafer were covered with another Si wafer and immersed in an isopropanol (IPA) aqueous solution (IPA:H_2O = 1:1, v/v). The gap between the 2 wafers was kept at around 0.5 mm. When immersed in the solution, the sample was placed in an ultrasonic bath for 30 min, and an upward magnetic field (about 300 Oe) was continuously applied for 2 h. The solution was subsequently drained and the sample was dried in a vacuum oven.

4.3. Characterization of the PPy dispersion and structures

The morphology and thickness of PPy was studied with a VASE Ellipsometer (VB-250, J. A. Woollam Co., INC) and JEOL 6320 field emission scanning electron microscope (FESEM, JSM 7401F, Jeol Asia Ltd) at an accelerating voltage of 5–10 kV and a vacuum of ≤2.8×10^{-4} Pa. The conductivity and sensory property measurements of the conductive PPy polymer were carried out using a Keithley 238 electrometer (containing a 4-probe system) and a power supply. A constant D. C. current of 100 mA was set for the conductivity measurements using the 4-point probe method while a constant D. C. voltage of 500 mV was assigned for sensor measurements. The procedure for liquid PPy dispersion film was similar as that of its solid films. The PPy sensor, which was made of a thin layer of porous PPy nanofilm, was configured on a SiO_2 wafer or a polyethylene terephthalate (PET, 0.05 mm) film with deposited Cu films or Cu conductive tapes as the electrodes. The porous PPy layer was about 2×6 mm^2 in area and ~500 nm in thickness. Magnetic measurements of the samples were performed using a vibrating sample magnetometer (VSM, Lakeshore 735). The chemical composition of the conductive PPy nanospheres was analyzed using energy dispersive X-ray spectroscopy (EDX) attached to the FESEM. The pressure in the analysis chamber was maintained at ≤10^{-4} Pa during each measurement. Details of measurements were the same as previously reported [29,33].

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