Processable stabilizer-free polyaniline nanofiber aqueous colloids

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Aqueous polyaniline colloids can be readily prepared by purifying polyaniline nanofibers and controlling the pH and self-stabilized *via* electrostatic repulsions without the need for any chemical modification or steric stabilizer, thus providing a simple and environmentally friendly way to process the conducting polymer in its conductive state both in bulk and at the nanometre level.

Processability is crucial to many applications of nanostructured materials. Consider the great amount of effort dedicated just to modifying carbon nanotubes to improve their solubility.[1,2] Our group[3,4] and others[5–7] have recently demonstrated that nanofibers of polyaniline, one of the most useful of the conducting polymers due to its environmental stability and simple acid–base doping–dedoping chemistry, can be readily prepared in bulk by the chemical oxidative polymerization of aniline under controlled conditions. Compared with their bulk counterparts, these nanostructures exhibit superior chemical sensing[8] and a unique photothermal effect.[9] To further the exploration of their fundamental properties including charge transport in the nanofibers and to exploit them in applications, the processability of these nanostructures in both bulk and thin film form needs to be addressed. Here we demonstrate the remarkable ability to form stable polyaniline nanofiber colloids without the need for any stabilizing agents. Thick films can be readily fabricated from colloidal dispersions through casting, while monolayers can be created by electrostatic self-assembly. The exceptional processability of these electroactive one-dimensional nanostructures could significantly impact both conventional uses of conducting polymers and emerging applications in nanotechnology.

In fact, one of the major goals in the field of conducting polymers since its inception has been to make them processable. Enormous effort has been directed towards functionalization, copolymerization and blending to enhance solubility.[10–12] However, there is a trade-off in terms of cost, purity, scalability and conductivity. For example, the solubility of polyaniline can be enhanced through chemical modifications, *e.g.* inserting substitutes either on the phenyl ring or on the nitrogen.[10,11] However, the resulting chain torsion generally causes significant decreases in conductivity. Solubility can also be improved with the use of compatible doping acids, but the counterion-induced processability is only suitable, so far, with organic solvents.[12] Another strategy to tackle the processability of conducting polymers is to form colloidal dispersions. This has been achieved through emulsion polymerization of aniline in the presence of steric stabilizers, such as surfactants, water-soluble polymers or silica colloids.[13–18] However, stabilizer-assisted dispersions are actually mixtures of polyaniline and other polymers/surfactants, which is disadvantageous for many applications. It is also tedious or impractical to remove by-products from the resultant mixtures. Additionally, the fabrication of nanoscale films from stabilizer-assisted dispersions has proven to be difficult.

According to the established theory for the stabilization of colloids,[19] both steric repulsion (by using a polymeric or surfactant as stabilizer) and electrostatic repulsion (by introducing charge to the particle surfaces) are often utilized to stabilize a colloid. However, most of the processes for preparing conducting polymer colloids so far have been based on steric repulsion with little attention paid to electrostatic stabilization.[13–18] Note that the backbone of the emeraldine form of polyaniline doped by a protonic acid (H^+A^-) is positively charged:
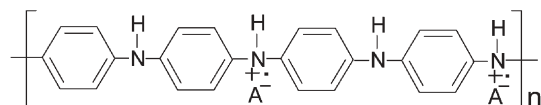
Therefore, in principle, a stable colloid could be formed through electrostatic repulsion without using steric stabilizers if the particle size is kept sufficiently small. Here we demonstrate that self-stabilized polyaniline aqueous colloids can be obtained by simply purifying chemically-prepared nanofibers and controlling the pH.

The formation of stable polyaniline nanofiber colloids is observed after centrifugation is employed to purify polyaniline nanofibers prepared from rapidly mixing a solution of aniline, ammonium peroxydisulfate and hydrochloric acid.[4] When as-prepared nanofibers are washed with water and separated by centrifugation to remove excess acid and other by-products, the supernatant becomes more intensely green as the nanofibers become more pure with an increasing number of washings (Fig. 1, vials a–c). After three cycles of washing–centrifugation, the supernatant remains dark green even with centrifugation at 3 000 rpm for 0.5 h or longer. These results clearly indicate that
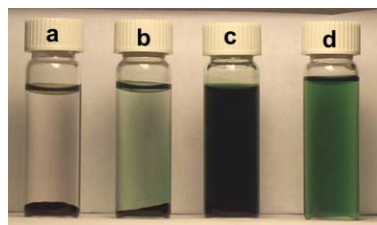

Fig. 1 As-polymerized polyaniline nanofibers after washing with water and centrifugation at 3 000 rpm for 0.5 h with different washing–centrifugation cycles: (a) 1; (b) 2; (c) 3. The green color of the dispersed emeraldine salt form of polyaniline is easier to see after diluting 1 ml of the supernatant from (c) with 4 ml of 0.005 M HCl to form (d).

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a stable polyaniline colloid has been created. This phenomenon may also be observable in some conventional processes of preparing polyaniline. However, the mechanism behind it and its potential applications have not until now been recognized.

Our experiments indicate that different doping acids such as hydrochloric, sulfuric and camphorsulfonic are all able to stabilize the colloids. The major parameters affecting the stability of the colloids are the pH and the concentration of electrolytes. As shown in Fig. 2, the optimal pH for stabilizing the colloid is around 2.6. When the pH is close to 4, the colloid turns blue and then changes to blue/violet as the pH increases to 7, indicating that dedoping occurs. Dedoping causes a loss of charge on the polymer chains, leading to flocculation of the colloid. This result suggests that it is crucial to keep the polymer chains positively charged for stabilizing the colloids. Adding an electrolyte such as a higher concentration of acid or a salt (e.g. NaCl), also results in the precipitation of the colloid. All these behaviors are characteristic of a lyophobic colloid stabilized through electrostatic repulsion and can be explained using the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.[19] Like other lyophobic colloids, the stability of the polyaniline colloid is also dependent on its concentration. A
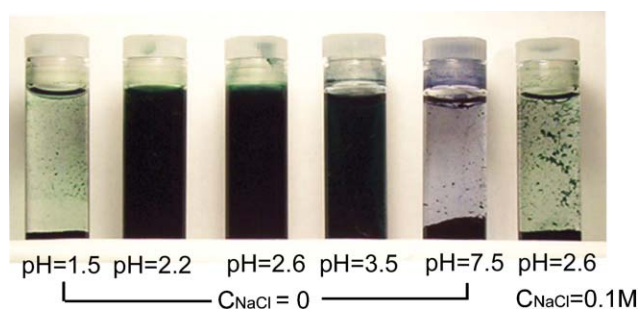
colloid of 10 mg ml^{-1} is generally stable for 1 day, while a colloid of 0.5 mg ml^{-1} appears to be stable for at least two months at the optimal pH of 2.6. Although concentrated dispersions do not exhibit long term stability, precipitated polyaniline nanofibers are still redispersable, with little affect on their processability.

The ability to form stable polyaniline colloids makes it very convenient to process this conducting polymer for practical applications including conducting polymer inks. Continuous films or coatings can be obtained simply through casting and evaporation, suggesting a simple and environmentally friendly method to process polyaniline for a variety of applications. Cast films exhibit a uniform green color and a relatively smooth surface as shown in Figs. 3a and b. The film is even smoother than films prepared from polymer-stabilized dispersions.[16,17]

Of potentially great interest is the adsorption behavior exhibited by the polyaniline colloids. When a glass slide or silicon wafer is immersed in a dilute stable colloid, an ultra-thin nanofiber layer can be spontaneously adsorbed onto the substrate surface. The scanning electron microscopy (SEM) image shown in Fig. 3c indicates the formation of a continuous nanofiber network. As-formed films exhibit a slight green color and the transmittance in the visible region is higher than 90% (see Fig. 3d). Although the amount of the absorbed polyaniline is very small, a continuous conducting network of nanofibers has been formed across the entire substrate as confirmed by conductivity measurements. This result indicates a simple way to integrate polyaniline nanofibers into a device.

The spontaneous adsorption of positively-charged polyaniline nanofibers on glass or silicon surfaces is likely to involve the following mechanism. It is well known that silica and silicate glass surfaces immersed in water are negatively charged.[20] When glass or silicon wafers are immersed in a cationic polyelectrolyte solution, a monolayer of this polyelectrolyte can be deposited on these surfaces through electrostatic self-assembly.[21] This can also account for our observation that the amount of adsorbed

Fig. 2 Polyaniline nanofiber colloids (1 mg ml^{-1}) with different pHs and with 0.1 M NaCl added after standing for 15 h at room temperature.
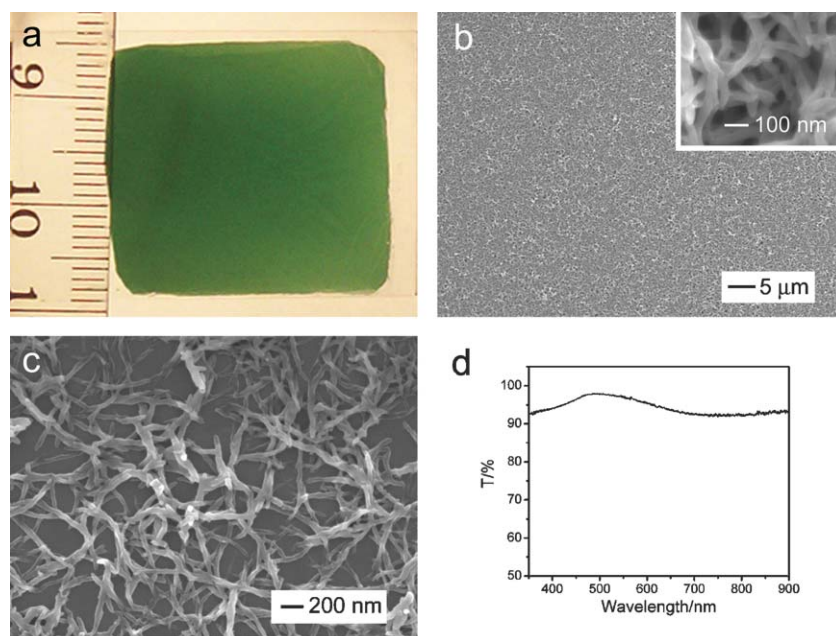

Fig. 3 Optical (a) and SEM (b) images of films cast on a glass slide (a) and a silicon wafer (b) from a polyaniline nanofiber colloid. SEM image (c) and transmission spectrum (d) of a monolayer of nanofibers spontaneously adsorbed on a silicon wafer and a glass slide, respectively, from the colloid.

nanofibers increases initially but then remains essentially constant. Thicker (or multilayered) films can be prepared by alternatively immersing films into the colloid and a polystyrene-sulfonic acid solution. These results suggest that the positively-charged colloids are a good source for fabricating composite multilayered films consisting of polyaniline and other negatively-charged materials using a layer-by-layer electrostatic self-assembly process.[21–23]

In summary, we have demonstrated that stable, pure aqueous polyaniline colloids can be readily prepared by purifying polyaniline nanofibers and controlling the pH without the need for any chemical modification or steric stabilizers. Electrostatic repulsive forces between nanofibers enable the long-term stability of the colloids. This work indicates that nanostructuring conducting polymers provides new possibilities to tackle the issue of processability. We expect that other conducting polymers such as polypyrrole and polythiophene could be made more processable through nanostructuring and tailoring the charge on their polymer chains. In addition to enhancing the conventional applications of conducting polymers in chemical sensing, actuators, lightweight battery electrodes, light-emitting devices and anticorrosion coatings, the remarkable processability as well as ease of synthesis of the conducting nanofibers make these electroactive one-dimensional nanostructures promising for use as a new class of functional building blocks for fabricating nanoscale electronic devices together with carbon nanotubes and other metallic or inorganic nanowires.[24] These well-dispersed nanofibers are also good sources or templates for fabricating other functional nanostructures and composites.

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