# Nano-Architecture by Molecular Structure-Directing Agent

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Currently, highly ordered structures of nanoparticles exhibit attractive physical properties for future nanoelectronics.[1] The availability of colloidal particles that are monodisperse in size and shape is crucial in the elucidation and control of the electronic, optomagnetic, and mechanical properties associated with this class of materials.[2] Self-assembly is the current effective way for organizing nanoparticles into densely packed and ordered arrays.[3] For example, colloidal nanoparticles can be spontaneously organized into one-, two-, and three-dimensional (1D, 2D, and 3D) arrays that are close-packed and highly ordered by simply controlling the evaporation of solvents.[4] Such self-assembly is the hallmark of supramolecular chemistry, by which constituent molecular components may be spontaneously connected and integrated using both specific and noncovalent interactions such as hydrogen-bonding,[5] electrostatic interactions,[6] and van der Waals versus electrostatic interactions.[7] The building and patterning of both inorganic and organic nanoparticles into two- and three-dimensional well-ordered structures has attracted a great deal of interest.[8] However, reports describing the assembly of ordered polymer nanoparticle structures (for all polymers excluding polystyrene (PS), poly(methyl methacrylate) (PMMA) and silica) are scarce, which may be due to the difficulty in the organization of polymer nanoparticles.[9] Recently, by employing Allure Red AC, Xia and co-workers[10] reported their observation on the ordered array formation of oriented PANI nanoparticle−nanorods (NPNR) which have two hydrophilic ends. In line with previously reported work, it was found that two hydrophilic ends were crucial to the formation of nanoparticle arrays. This new finding prompted us to explore the function of two hydrophilic ends in structure-directing agents in the synthesis of ordered arrays of nanostructures through self-assembly. Self-assembly has demonstrated an immense flexibility for the construction of supramolecular architectures with high levels of complexity over microscopic and macroscopic length scales due to the deliberate design of the constituent molecules.[11] The defined structure of supramolecules also results in a well-defined structure at the molecular level. However, the current challenge is that strong attraction particles rapidly and irreviseibly stich to each other and form gel-like aggregates.[12] Recently, it was demonstrated that the role of electrostatics in the formation of nanoparticle crystal can be controlled as parameter to assemble various crystals of new symmetry and composition.[12]

In this communication, we will report the successful synthesis of ordered hexagonal arrays of uniform PANI nanoparticles in terms of the structure-directing agent (DHNSAE)[13] and show the usefulness of electrostatic self-assembly in generating such a novel material. The hexagonally ordered arrangement of PANI particles was achieved by precise adjustment of the Van der Waals force and electrostatic force among particles. The preparation procedure is as follows: the first stage is the formation of individual primary PANI nanoparticles doped with different amounts of DHNSAE (Scheme 1a); in the second stage, the individual primary PANI nanoparticles will form different nanostructures by self-assembly upon continued polymerization (Scheme 1b−d). When the ratio of aniline to DHNSAE (presented as [An]/[DHNSAE]) is 40, spherical aggregates with an average

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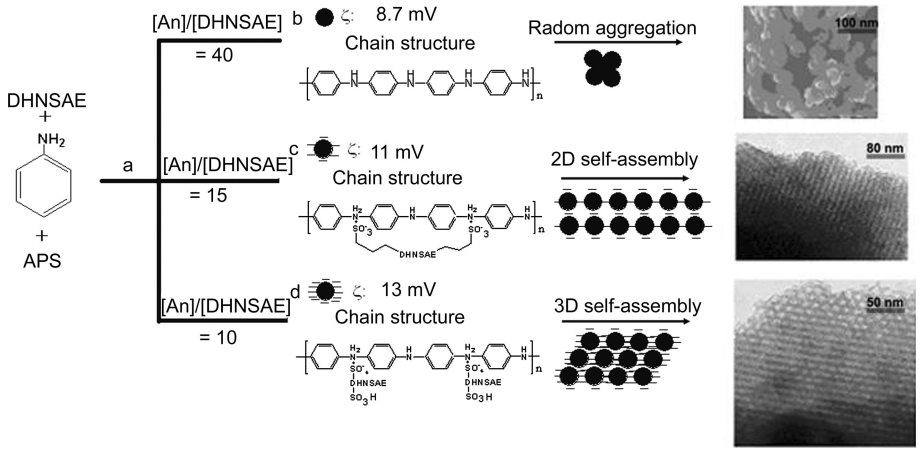
**Scheme 1. Schematic Presentation of Different Arrays of PANI Nanoparticles Produced at [An]/[DHNSAE] Values of 40, 15, and 10 ([An] = 0.14 M, [An]/[APS] = 1, reaction time = 24 h, temperature = 2.5 °C)**




diameter of 55 nm were observed (shown in Scheme 1b). The ordered arrangements of PANI particles occurs (Scheme 1c,d and Figure S1, Supporting Information) when [An]/[DHNSAE] is lowered. The characterization of PANI nanoparticle arrangements was performed by transmission electron microscopy (TEM). When [An]/[DHNSAE] is 15, oriented PANI nanoparticle−nanowires made up of PANI particles of diameter of about 12 ± 0.5 nm were observed (Scheme 1c). When [An]/[DHNSAE] was decreased to 10, PANI nanoparticles were found in the hexagonally ordered arrangements up to a few micrometers (Scheme 1d and Figure S1, Supporting Information). The hexagonal form, the one most expected for an ordered arrangement, is made up of uniformly distributed nanoparticles with an average diameter of 12 ± 0.5 nm, as can be seen from the TEM images (polydispersity < 5%, by counting a total of 500 nanoparticles to calculate the polydispersity).

Interparticle interactions are the governing factor in controlling the structure of the nanoparticle assembly. For an ordered assembly, both the attactive and the repulsive interactions should be present among particles to maintain the equilibrium structure. In the dispersion of PANI particles, the attractive force is mainly attributed to van der Waals force, which is dispersed in a solvent with dielectric contrast; the repulsive force from the electric double layers of the nanoparticles originates from the surface charge on the PANI particles.[14] When a small amount of SDA was added to the reaction system, the surface charge density or the zeta potential of the particles was reduced due to fewer $-SO_3H$ groups suspended on the surface of the PANI particles. Consequently, the repulsion between the particles was also weakened. In such a case, the attractive force becomes dominant. When two particles approach each other, they can be trapped at the energy minimum. It is very difficult or impossible to separate them.[14] Under such a case, aggregates are formed (Scheme S1a, Supporting Information). When the surface charge density of PANI particles is enhanced by the addition of more SDA, the thickness of the electric double layer increases, which gives rise to a larger repulsive force between PANI particles. This will allow the "aggregated" PANI particles to rearrange[15] so that some ordered structures can be formed eventually (Scheme S1b, Supporting Information).

In our case, each of these primary PANI particles includes $-SO_3H$ groups from our synthesized SDA. These $-SO_3H$ groups can be divided into two parts according to their functions.[16] Some of them are used for internanoparticle doping, including interchain and intrachain doping in primary PANI nanoparticles; the others are suspended on the surfaces of the primary PANI nanoparticles. These primary PANI particles were functionalized with different amounts of strong acid groups ($-SO_3H$) which resulted in different surface charges[13] in aqueous solution when the different concentrations of SDA were used. The zeta potential of the colloidal PANI particles changes with the pH of the reaction system (see Figure S2, Supporting Information). The zeta potential of the colloidal PANI particles with small amounts of $-SO_3H$ groups on their surfaces remained at the same level (see Figure S2a, Supporting Information); however, the zeta potential of those with a high amount of $-SO_3H$ groups on their surfaces was remarkably decreased (see Figure S2b, Supporting Information). Therefore, the surface charge of PANI particles is dependent on the density of the $-SO_3H$ group on their surfaces which can be controlled by the concentration of the structure-directing agent. No ordered arrays of PANI nanoparticles were observed when the pH of reaction system was over 1.5.

From the perspective of energy landscapes, highly monodisperse collections of ordered structures are useful for a quantitative analysis of the physical properties of the nanoparticles. By tracking the relative positions of particles through the imaging equipment, one can measure the pair distribution function, $g(r)$, for the PANI particle array.[17] The analysis of a representative ordered PANI particle assembly is depicted in Figure 1. This example presents a highly ordered hexagonal crystal, which consists of the monodisperse PANI particles [Figure 1a]. A close view of the first

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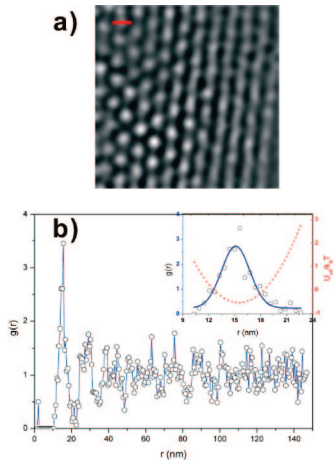


**Figure 1.** Calculated interaction energy between the particles. (a) A typical array of PANI particles. The scale bar is 15 nm. (b) The pair distribution correlation $g(r)$. The inset shows the Gaussian fit of the first peak in $g(r)$. The dotted red line is a parabolic fit of the logarithm of the first $g(r)$ peak, which is the effective potential of the mean force, $w(r)$.

peak in the $g(r)$ distribution (Figure 1b, inset) reveals a Gaussian distribution of the interparticle separation distances, which indicates an average interparticle distance (∼15 nm) of the PANI particle array. The interparticle distance is slightly larger than the diameter of the particles, which was measured from the TEM pictures. The nonclose packed structure excludes the possibility of interaction between the hydrogen bonds present between the particles. Furthermore, $g(r)$ provides a measure of the mean interparticle potential $\{w(r) = -k_BT \ln[g(r)]\}$.[18] The red curve in the inset of Figure 1b shows the pair interaction versus the interparticle distance. The minimum pair energy is about –0.5 $k_BT$, which corresponds to the separations between the nearest neighbors. Therefore it is suggested that a strong and long-range attraction exists between the similarly charged PANI particles, which is contrary to the prediction of the Derjaguin−Landau−Verwey−Overbeek (DLVO) theory.[19,20] The discrepancy with the DLVO potential indicates that the like-charge interaction could dominate the ordered assembly of PANI particles.[19,20] As well-known, the electrostatic repulsive force occurring between colloidal/nanoparticles keeps the particles from aggregation. However, van der Waals attractive interaction appears when the spheres' ion clouds interact strongly. In balancing the repulsive and attactive forces, the ordered 3D structures of nanoparticles were formed. In our previous work,[21] the driving forces of self-assembled ordered PANI nanotubes come mainly from intermolecular interactions (H-bonding and $\pi-\pi$ interactions) when another structure-directing agent[13] (crown ether derivative, CE) is used. This reduces the amount of $-SO_3H$ groups suspended on the surfaces of the primary PANI nanoparticles and, consequently, their surface charge. When the ratio of aniline to CE is high ([An]/[CE] = 50), PANI nanoparticles are formed, an effect similar to our current work. When the ratio is low, ordered arrays of oriented PANI nanotubes ([An]/[CE] = 25) and disordered PANI nanotubes ([An]/[CE] = 15) were obtained. There is no ordered array of PANI particles. Therefore, the main driving force behind the self-assembly of 3D arrays of PANI particles in our present work is the electrostatic force due to the surface charges on the primary PANI nanoparticles. Hence, the self-assembled morphology of polymer nanoparticles can be controlled by selective use of SDAs. This work demonstrates the potential to exploit the relationship between building blocks and assembled phase morphology. It will help us to develop heuristics and principles to assemble building blocks into useful 1D, 2D, and 3D structures. The fundamental achievements will certainly enhance technological progress in this rapidly evolving area.

In summary, the results can be considered as a successful first step in 3D arrangements of polymer nanoparticles by a self-assembly approach. The TEM image exhibited a highly ordered hexagonal orientation, which would be attributed to electrostatic forces due to surface charge on the primary PANI nanoparticles. The assembled morphology of nanoparticles can be controlled by the concentration and type of structure-directing agents. Although further investigations are necessary to optimize these procedures to generate a well-defined system in long-range order, these preliminary results are promising for applications in nanoelectronics and photonic crystals. This route can be extended to the preparation of 3D arrays of various functionalized metal dots.

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**Supporting Information Available:** Experimental details, TEM images, self-assembly behavior of PANI, zeta potential data, surface charge or zeta potential on primary PANI nanoparticles details, and structure-directing agent structure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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