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Yonglan Luo[a]
[a] School of Chemistry and Chemical Engineering, China West Normal University, Nanchong, P.R. China

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Controlled formation of novel supramolecular microbelts or microprisms from aniline and H_2PdCl_4 driven by coordination and $\pi-\pi$ interactions

Yonglan Luo*

School of Chemistry and Chemical Engineering, China West Normal University, Nanchong, P.R. China

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In this communication, I report the formation of novel supramolecular one-dimensional (1D) structures including microbelts and microprisms by a direct mix of aniline and H_2PdCl_4 aqueous solutions at room temperature. As-formed supramolecular structures were characterised by scanning electron microscopy, X-ray photoelectron spectra and X-ray diffraction techniques. Both coordination and $\pi-\pi$ interactions are expected to be responsible for these 1D microstructures. It suggests that the molar ratio of the reactants is crucial to the formation of such 1D structures.

Keywords: supramolecular assembly; one-dimensional structures; aniline; H_2PdCl_4

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Self-assembly refers to the spontaneous organisation of molecules, molecular clusters and aggregate structures into two-dimensional (2D) arrays and three-dimensional (3D) networks by attractive forces or chemical bond formation. This technique offers an effective and versatile approach for constructing a structured system at a molecular level and leads to new materials and devices, and therefore is considered to have a great potential in nanoelectronics (*1*). Although the most often studied involves self-assembled monolayers formed on planar solid substrates, monolayer-protected clusters, self-assembly into 3D networks on planar solid substrates, layer-by-layer self-assembly of ultrathin films on planar solid substrates or colloidal particles, etc. (*2*), increasing attention has also been paid to the study of the self-assembly in solution because it provides a means for the integration of molecular systems into functional mesoscopic devices and macroscopic materials, and recent years have witnessed the rapid development of such solution-based assembly technique (*3*).

During the past few years, research into one-dimensional (1D) structures has developed largely since the discovery of carbon nanotubes (*4*), and the study on the oxidative polymerisation of aniline into polyaniline (PANI) conducting polymer 1D structures has always been a hot research topic and various useful methods have been developed to prepare such 1D structures (*5*). For all these cases, only aniline molecules are used as precursors and building blocks to construct the final structures. More recently, Sun et al. (*6*) have demonstrated the coordination-induced formation of submicrometre-scale, monodisperse, spherical colloids of organic–inorganic hybrid materials, carried out by mixing H_2PtCl_6 and *p*-phenylenediamine (PPD) aqueous solutions at room temperature. However, to the best of my knowledge, until now, no attention has been paid to the controlled formation of supramolecular structures of aniline and metal salts. In this communication, I report for the first time on the formation of novel supramolecular 1D structures including microbelts or microprisms generated by a direct mix of aniline and H_2PdCl_4 aqueous solutions at room temperature. It suggests that the molar ratio of the reactants is crucial to the formation of such 1D structures. Both coordination and $\pi-\pi$ interactions are expected to be responsible for the formation of these assemblies.

The H_2PdCl_4 aqueous solution was prepared by dissolving $PdCl_2$ powder in H_2O acidified with an appropriate amount of 0.1 M HCl aqueous solution. A typical protocol for the preparation experiment is described as follows. In brief, 10 μl of aniline was introduced into 10 ml of 0.0024 M H_2PdCl_4 aqueous solution at room temperature under rapid stir with the molar ratios 1:2, 1:1, 2:1 and 4:1 of aniline to Pd corresponding to samples 1, 2, 3 and 4, respectively. Immediately, a large amount of the precipitate was observed for each sample. The resulting precipitate was then washed three times with water and used for further characterisation. Scanning electron microscopy (SEM) measurements were made on a Zeiss CrossBeam 1540XB microscopy at an accelerating voltage of 5 kV. The samples for the SEM examination were made by placing a drop of the dispersion of the precipitate in water on a glass slide and air-dried at room temperature. The X-ray photoelectron spectra (XPS) were collected on an ESCLAB MKII using Mg as the exciting source. The X-ray diffraction (XRD)

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*Email: luo.yonglan@hotmail.com

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analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation.

Figure 1 shows the typical SEM images of the precipitate of these four samples thus formed. At the molar ratio 1:2, the precipitate consists of irregular aggregates as shown in Figure 1(a). However, when the molar ratio is increased up to 1:1, it is clearly seen that the precipitate consists of transparent microbelts with several ten micrometres in length and several micrometres in width, as shown in Figure 1(b). When the molar ratio is further increased up to 2:1, microbelts are also obtained, but their width decreases (Figure 1(c)). However, when a higher molar ratio 4:1 is applied in this synthesis, microprisms with smaller size are obtained, as can be supported by the corresponding SEM image of the precipitate obtained as shown in Figure 1(d). These observations demonstrate that the molar ratio of the reactants plays an important role in the formation of the structures and the use of sufficient aniline is key to generating belts and prisms. It is also worthwhile mentioning that all these belts and prisms are very straight, indicating their rigid nature.

The chemical composition of the resulting precipitate was determined by the energy-dispersed spectrum (EDS) and the X-ray map analysis. Figure 2 shows the corresponding results of the precipitate of sample 2. Figure 2(a) and (b) shows the SEM image and the EDS data of these belts, respectively. The peaks of C, N, Cl and Pd are found (other peaks originated from the substrate), which indicate that these belts contain four elements: C, N, Cl and Pd. The X-ray maps shown in Figure 2(c)–(f) further reveal that each element is relatively uniformly distributed in the 1D structures. These observations clearly confirm that such belts are the products formed from aniline and H_2PdCl_4. A quantity analysis indicates that the atom number ratio of N:Cl:Pd for samples 1, 2, 3 and 4 is 20.03:59.96:20.02, 40.02:39.40:20.00, 40.72:39.60:19.32 and 40.23:39.87:20.21, respectively, demonstrating that the molar ratios 1:1, 2:1 and 4:1 of aniline to Pd lead to structures with the same atom number ratio, N:Cl:Pd = 2:2:1, but the use of insufficient aniline, which is the case of the 1:2 molar ratio, produces structures with different atom number ratios, N:Cl:Pd = 1:3:1.

It is well established that aniline can be oxidised by oxidants to form 1D structures (*5*). On the other hand, another reactant Pd(II) used is an oxidant, and, therefore, it is possible that aniline molecules might be oxidatively polymerised by Pd(II) to form PANI structures with the occurrence of the reduction of Pd(II) to form metallic Pd in our present study. However, Sun et al. (*6*) have recently reported the formation of colloidal spheres of coordination polymers from a solution containing H_2PtCl_6 and PPD due to the coordination interactions between the nitrogen atoms of PPD and the Pt centre and no redox reaction between these two reactants occurred. To get further insight into the oxidation state of Pd species contained in the belts, the XPS of the belts was also acquired. It is well known that the metallic state of the Pd 3d region is characterised by the two spin–orbital components 3d5/2 (335.2 eV) and 3d3/2 (340.5 eV) (*7*). However, the XPS of the belts thus formed (Figure 3(a)) shows two binding energy peaks centred at 337.8 eV (3d5/2) and 343.4 eV (3d3/2), indicating that the Pd species contained therein

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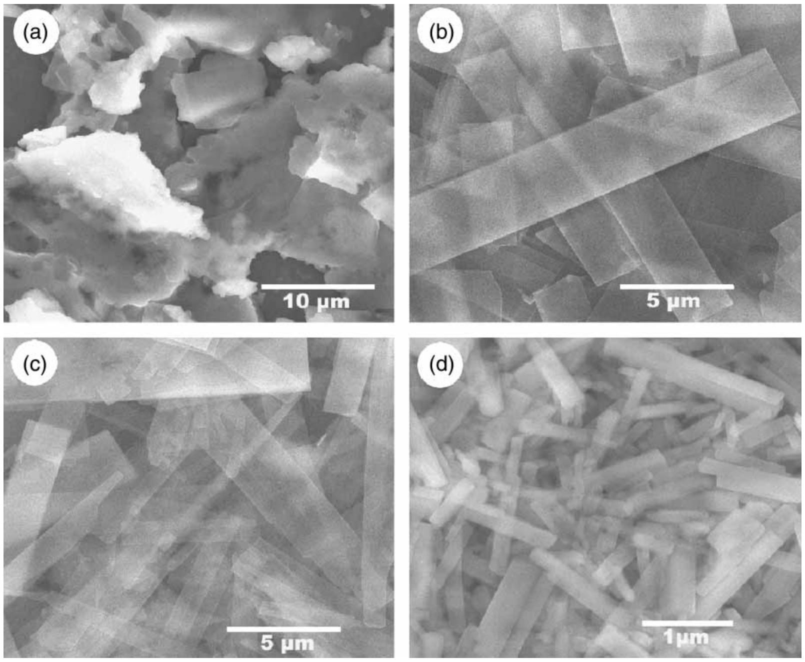

Figure 1. The typical SEM images of the precipitate obtained at the molar ratios (a) 1:2, (b) 1:1, (c) 2:1 and (d) 4:1 of aniline to Pd.

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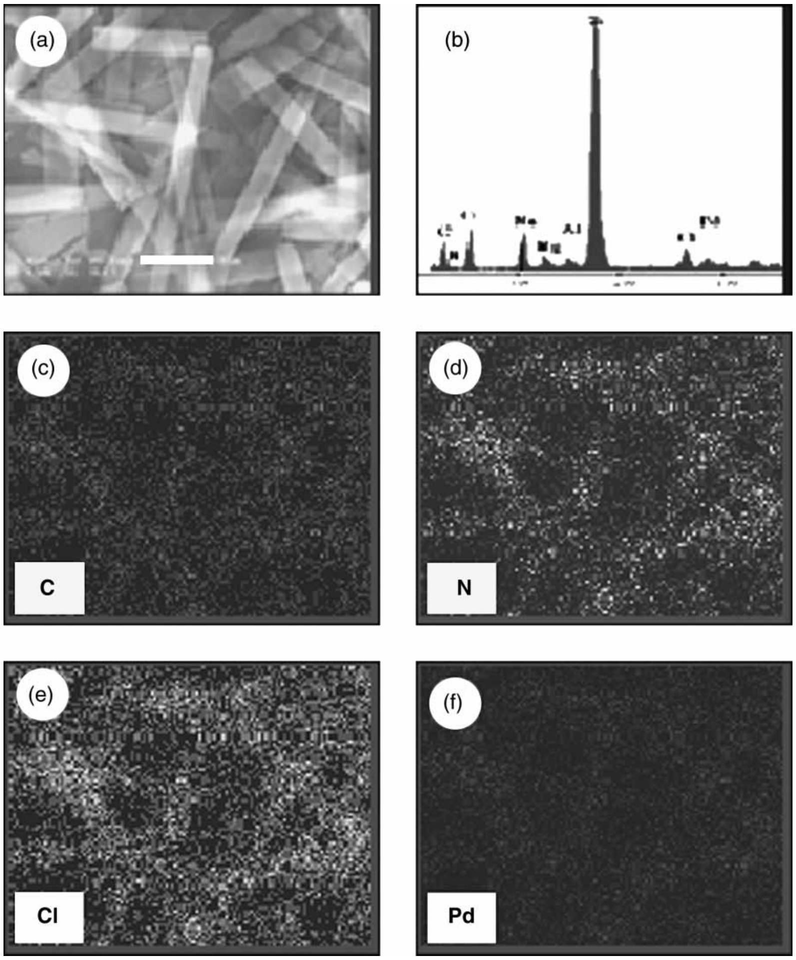

Figure 2. (a) The SEM image, (b) the EDS and (c)–(f) the X-ray maps of the precipitate for sample 2.

only exist in the Pd(II) form, not in the metallic form (*8*). Figure 3(b) shows the corresponding XRD pattern of the belts. No peak corresponding to metallic Pd is observed at the expected position (*9*). Although it is possible that if the metallic Pd was present as nanoparticles, they may not diffract well and hence the relevant peaks may be absent[1]; the XPS shown above clearly proves that no metallic Pd species were observed. It should be noted that several distinct peaks are observed at a low Bragg angle (inset), which may be attributed to the formation of crystalline belts; however, owing to a lack of standard or referenced XRD data on this kind of new structures, at present, the

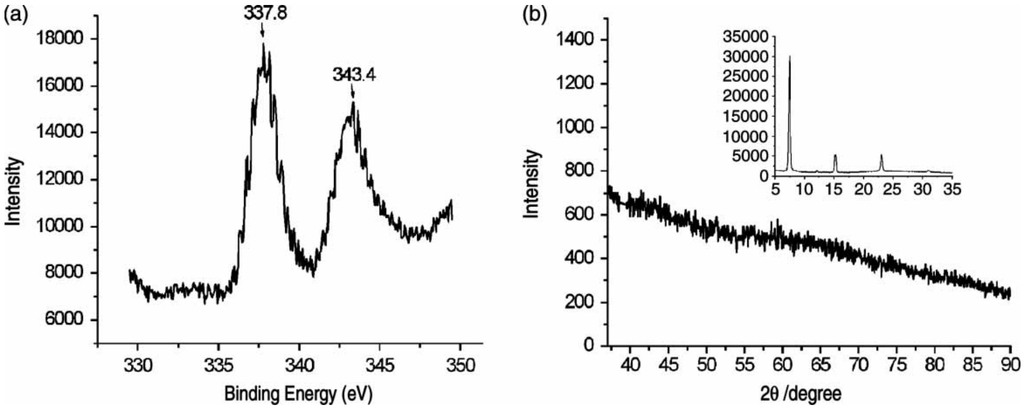

Figure 3. (a) The XPS and (b) XRD patterns of the precipitate for sample 2.

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detailed information on the crystal nature of the structures obtained cannot be proposed.

It is well known that Pd(II) species can react easily with a number of nitrogen-containing organic compounds such as amines and imines, leading to complexes in which nitrogen atoms are coordinatively bonded to the Pd centre (*10*). When aniline is mixed with the H_2PdCl_4 aqueous solution, it is expected that a coordination bond is formed between the nitrogen atom of aniline and Pd(II) centre. Given the fact that one aniline molecule only contains one amine group and thus one nitrogen atom, one aniline molecule can only coordinate to one Pd(II) centre; that is, one aniline molecule cannot coordinate to two or more different Pd(II) centres to give aniline-bridged structures (*6*).

It should be noted again that the atom number ratio of N:Cl:Pd is 2:2:1 for all these three 1D samples, although different molar ratios of the reactants are applied. Considering that each $PdCl_4^{2-}$ complex contains four Cl coordination atoms, it is reasonable to conclude that two Cl atoms are replaced by two aniline molecules when aniline is introduced into the H_2PdCl_4 aqueous solution, i.e. a ligand replacement reaction takes place and two weakly coordinated Cl atoms are exchanged with two nitrogen atoms with a stronger coordination ability leading to a new complex $PdCl_2(AN)_2$. It is widely accepted that the $\pi-\pi$ interactions often exist in π-conjugated materials (*11*). In water, the stacking interaction between aromatic molecules is mainly caused by the hydrophobic effect. Because water molecules solvating the aromatic surface have a higher energy than bulk water, the aromatic surfaces are stacked together to reduce the total surface exposed to the water. Given the fact that the $PdCl_2(AN)_2$ complexes formed due to the coordination interaction are rich in π-type bonds, it is reasonable to conclude that the $\pi-\pi$ interactions between different complexes cause them to further assemble into the final 1D structures (*12*).

Finally, I have performed one control experiment by mixing H_2PdCl_4 and PPD aqueous solutions at room temperature and obtained aggregated microspheres as shown in Figure 4. The formation of such assemblies could be attributed to the fact that only the coordination interactions are involved in the formation of the spheres, which are quite consistent with Sun's report (*6*).

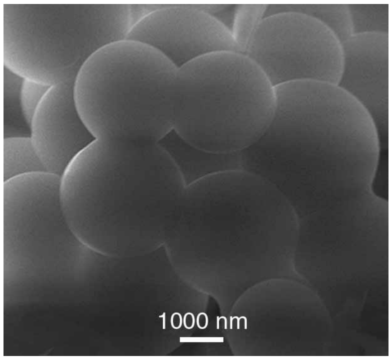

Figure 4. An SEM image of the precipitate formed by mixing H_2PdCl_4 and PPD aqueous solutions at the molar ratio 2:1 of PPD to Pd at room temperature.

In summary, the mix of aniline and H_2PdCl_4 aqueous solutions leads to the rapid formation of novel 1D supramolecular microbelts or microprisms. It may suggest that the formation of such assemblies involves the following two stages: (1) two Cl ligands of the $PdCl_4^{2-}$ complex are exchanged with two aniline molecules driven by the coordination interactions between the nitrogen atom of aniline and the Pd(II) centre to form a new complex $PdCl_2(AN)_2$; and (2) the $\pi-\pi$ interactions between the complexes thus formed further drive the self-assembly of these complexes into the final 1D structures. Our observations are important for the following two reasons. (1) It is the first example of the self-assembly formation of aniline-containing 1D supramolecular microstructures driven by the coordination and $\pi-\pi$ interactions. (2) Such Pd(II)-containing 1D structures may provide a refinement matrix for the generation of Pd nanostructures.

Note

1. Comments of one reviewer.

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