

Assembling of Prussian Blue Nanoclusters Along Single Polyelectrolyte Molecules

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INTRODUCTION

Molecular electronics is attracting considerable interest of scientists because of physical and economic limitations expected for existing bottom down lithographic technologies. The use of various biological templates to assemble nanoscale nonbiological building blocks into well-defined meso- and macroscopic objects¹ is an attractive alternative for the lithographic procedures. DNA is a highly promising material to develop such a strategy. Both naturally occurring and synthetic DNA have been used as templates for metalization to create nanowires.² At the same time, polymer chemistry offers a fascinating world of various molecular architectures. It would be a challenging task to utilize those structures as a templates for the generation of nanoparticles with a particular shape and desired composition. In our research we use *synthetic polyelectrolytes* (PE) exploiting the range of advantages: (a) variety and availability of PE of different architectures, composition, charge, and functionality; (b) PE are highly functionalized and reactive polymers and can be easily modified; (c) variety of PE conformations (size of PE molecules can be changed in the range of several orders of magnitude by changing of the environment).³ Recently, we have described an approach to produce *wire-shaped* Pd nanoparticles via metalization of flexible synthetic PE of linear architecture deposited onto the Si-wafer.⁴ Metalization is based on ion exchange reaction between positively charged polymers and bivalent PdCl_4^{2-} anion. It was also shown that metalization of star shaped polystyrene-poly(2-vinylpyridine) block copolymer ($\text{PS}_7\text{-P2VP}_7$) deposited in conformation with extended P2VP arms leads to star shaped organic-inorganic NP.⁵ Thus, most of researchers are focused on fabrication of metallic wires and less attention has been paid to the deposition of semiconductive NP along single polymer molecules.⁶

Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot z\text{H}_2\text{O}$, PB) and related mixed valence hexacyanometalate inorganic coordination polymers are well-known due to their interesting electrochemical, electrochromic, photophysical, and magnetic properties.⁷ Among them photoinduced reversible magnetization is one of the most important properties of PB. Such stimuli-responsive materials can be, in principle, used for creation of high-density information data storage devices and for quantum-computing applications. Although synthesis of PB and study of its properties are extensively studied, the fabrication of PB nanoparticles and their positioning onto the surface are considerably less explored areas. Here we report on the synthesis of water soluble negatively charged PB nanoclusters with adjustable diameter, and on the method to selectively deposit them along polycation poly(methacryloyloxyethyl dimethylbenzyl ammonium chloride) (PMB) molecules.

EXPERIMENTAL

Materials. Synthesis of poly(methacryloyloxyethyl dimethylbenzyl ammonium) chloride (PMB) ($M_w = 6130$ Kg/mol, polydispersity index (PDI) = 1.6) was described elsewhere.⁸

Substrates. Si-wafer (obtained from Wacker-Chemitronics), were first cleaned in an ultrasonic bath three times for 5 min with dichloromethane (DCM), placed in the cleaning solution prepared from NH_4OH and H_2O_2 at 60°C for one hour. (Note: the $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ solution reacts violently with organic compounds. Caution should be used when handling this solution). Samples were finally exposed to 50% sulfuric acid for 15 min and then rinsed several times with Millipore water (18 MQxcm).

Samples preparation. PMB was deposited onto the substrate from the 0.0005 g/l acid water (pH 2, HCl, Aldrich) solution by the dipping of the substrate into the solution or by drop casting. To deposit PC chains in stretched conformation we placed several drops of the solution onto the substrate rotating at 10000 rpm. The dry samples were investigated with AFM.

Deposition of PB clusters. To prepare a dispersion of PB clusters, the solution of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (0.5 g/l, 1.18 mMol/l) in acid water (HCl, pH 2.0) and equal volume of the FeCl_3 solution (0.048 g/l, 0.296 mMol/l) in acid water (HCl, pH 2.0) were intensively mixed for several minutes. The substrate with deposited PC was then dipped into the freshly prepared dispersion of PB clusters for 3 min at ambient temperature and afterward rinsed in water. Finally, the substrate was dried with the Argon flux.

AFM measurements. Multimode AFM instrument or NanoScope IV-D3100 (Digital Instruments, Santa Barbara) were operating in the tapping mode. Silicon tips with radius of 10-20 nm, spring constant of 30 N/m and resonance frequency of 250-300 KHz were used after the calibration with gold nanoparticles (5 nm in diameter). The dimensions of structures obtained from AFM images were corrected (decreased) by the tip radius.⁹

UV-vis measurements were carried out using Perkin Elmer UV-vis Spectrometer Lambda 19.

X-ray diffraction (XRD) diagrams were recorded using Siemens P4-System diffractometer at Cu K α radiation.

DISCUSSION

It is well known that mixing of stoichiometric amounts of $\text{K}_4\text{Fe}(\text{CN})_6$ and FeCl_3 leads to microscopic particles of PB ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) which precipitate from solution: $3\text{K}_4\text{Fe}(\text{CN})_6 + 4\text{FeCl}_3 = \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$. Several methods to fabricate well-defined surfactant- or polymer-protected PB nanoclusters have been recently reported.¹⁰ Here we described a simple method to produce surfactant-free water-soluble negatively charged PB nanoclusters stabilized by excess of HCF-anions.¹¹ Specifically, we found out that mixing of a diluted solution of FeCl_3 with excess of $\text{K}_4\text{Fe}(\text{CN})_6$ solution in acid conditions (pH 2) leads to a clear deep-blue dispersion stable during several months. We prepared and studied a range of PB dispersions at different mixing ratios and stirring time. The characteristic blue color and broad band in the UV-vis spectra with λ_{max} at 695 nm for all dispersions are consistent with an intermetal charge-transfer band from Fe^{2+} to Fe^{3+} and reflects the formation of PB (Figure 1).¹²

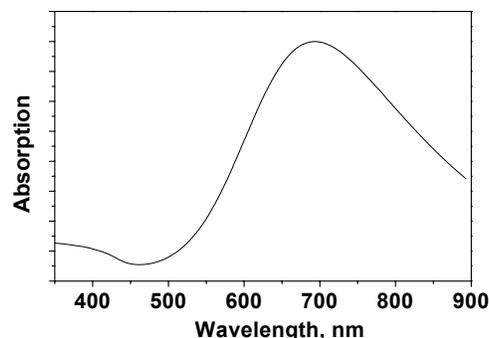


Figure 1. UV-vis spectra of Prussian Blue dispersion (prepared at molar ratio $\text{K}_4\text{Fe}(\text{CN})_6/\text{FeCl}_3 = 4/1$).

To characterize the size of PB clusters we set a drop of the dispersion onto the Si-wafer with the pre-adsorbed PMB molecules and washed out an excess of unattached materials. In that case polycation molecules are necessary to bind PB to the Si-wafer. In the reference experiment we found no adsorption of PB clusters onto bare substrates (without pre-adsorbed PMB molecules) neither at neutral pH nor in acid conditions, as confirmed by AFM and ellipsometry. After washing and drying the samples were investigated with AFM in tapping

mode. Figure 2 shows typical AFM images of PMB-PB nanoparticles with beads-on-string morphology obtained upon the deposition of PB clusters onto the spin-stretched PMB molecules. We made cross-sections of all clusters observed on images and defined their height. Finally, we performed a statistical treatment of the data. Figures 2i-j present histograms of height distribution of PB clusters for 1/4 $K_4Fe(CN)_6/FeCl_3$ mixing ratio at different time of the stirring. We assume near spherical geometry of PB clusters and hence their height corresponds to the diameter. As seen from Figure 2, the average diameter of PB clusters is about 5 nm (PDI = 1.1-1.25).

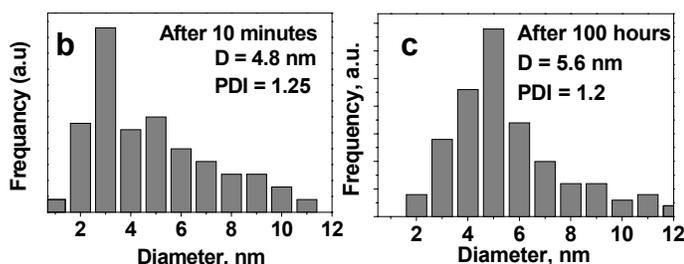
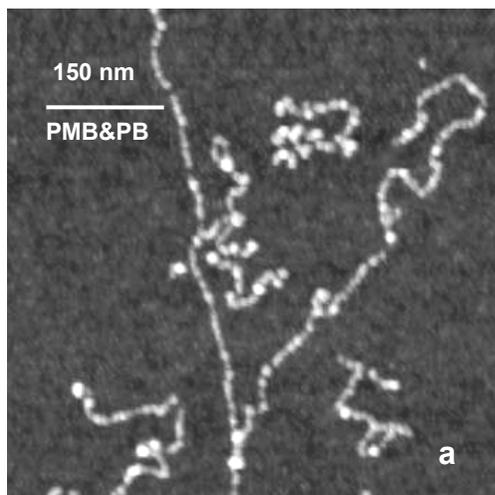


Figure 2. AFM topography image (Z-range 10nm) of the PB nanoclusters (prepared at molar ratio $(K_4Fe(CN)_6)/FeCl_3$ - 4/1) deposited along PMB molecules (a). Histograms presents the size distribution of the PB clusters stirred before the deposition during following time: 10 minutes, $D = 4.8$ nm (b); 100 hours, $D = 5.6$ nm (c).

To further characterize obtained dispersions we performed X-ray investigation. $K_4Fe(CN)_6$ and $FeCl_3$ solutions have been mixed at 4/1 ratio and dried at room temperature. Addition of water (as well as acid water) to resulting solids leads to clear deep-blue solutions without any insoluble solids. These redissolved dispersion has been again investigated with AFM. We found that partial aggregation of PB clusters occurred (the average size increased from 5 nm to about 15 nm) as indicated AFM data. For the reference experiment we also prepared a water insoluble PB powder by mixing of stoichiometric amounts of $K_4Fe(CN)_6$ and $FeCl_3$. A powder X-ray diffraction pattern for soluble PB NP (Figure 3) corresponds to superposition of following patterns: bulk PB (peaks at 17.5° (200), 24.8° (220), 35.2° (400)), $K_3Fe(CN)_6$ and KCl,

In summary, mixing of solution of $FeCl_3$ with excess of $K_4Fe(CN)_6$ solution results in a stable dispersion of Prussian Blue nanoclusters which can be selectively deposited along pre-adsorbed isolated polycation molecules.

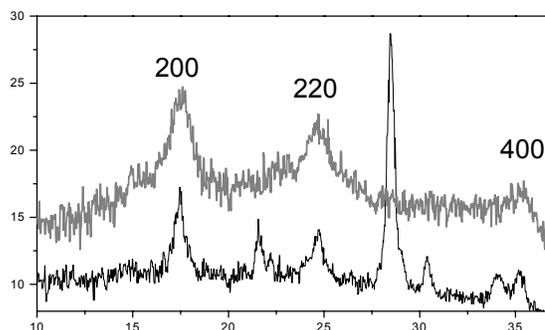


Figure 3. X-ray diffraction patterns of Prussian Blue bulk and PB nanoclusters (prepared at molar ratio $(K_4Fe(CN)_6)/FeCl_3$ - 4/1).

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REFERENCES

1. Storhoff, J.; Mirkin, C. *Chem. Rev.* **1999**, *99*, 1849. Shipway, A.; Katz, E.; Willner, I. *ChemPhysChem* **2000**, *1*, 18.
2. Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. *Nature* **1998**, *391*, 775. Richter, J.; Seidel, R.; Kirsch, R.; Mertig, M.; Pompe, W.; Plaschke, J.; Schackert, H. K. *Adv. Mater.* **2000**, *12*, 507. Ford, W. E.; Harnack, O.; Yasuda, A.; Wessels, J. M. *Adv. Mater.* **2001**, *13*, 1793.
3. Minko, S.; Kiriya, A.; Gorodyska, G.; Stamm M. *J. Am. Chem. Soc.* **2002**, *124*, 3218. Kiriya, A.; Gorodyska, A.; Minko, S.; Jaeger, W., Štěpánek, P.; Stamm, M. *J. Am. Chem. Soc.*, **2002**, *124*, 13454.
4. Kiriya, A.; Minko, S.; Gorodyska, A.; Stamm, M. *J. Am. Chem. Soc.* **2002**, *124*, 10192. Kiriya, A.; Minko, S.; Gorodyska, A.; Stamm, M.; Jaeger, W. *Nano Letters* **2002**, *2*, 881.
5. Gorodyska, A.; Kiriya, A.; Minko, S.; Tsitsilianis, C.; Stamm, M. *Nano Letters* **2003**, *3*, 365. Gorodyska, A.; Kiriya, A.; Minko, S.; Tsitsilianis, C.; Stamm, M. *Macromolecules* **2003**, ASAP.
6. Coffey, J. L.; Bigham, S. R.; Pinizzotto, R. F.; Yang, H. *Nanotechnology* **1992**, *3*, 69.
7. Sato, O.; Lyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *271*, 49. Ferlay, S.; Mallah, T.; Quahes, R.; Veillet, P. Verdaguer, M. *Nature* **1995**, *378*, 701.
8. Jaeger, W.; Paulke, B.-R.; Zimmermann, A.; Lieske, A.; Wendler, U.; Bohrisch, J. *Polymer Prepr.* **1999**, *40*, 980.
9. Xu, S.; Arnsdorf, M. F. *J. Microscopy* **1994**, *173*, 199-210. Vesenka, J.; Manne, S.; Giberson, R.; Marsh, T.; Henderson, E. *Biophys. J.* **1993**, *65*, 992.
10. Vaucher, S.; Li, M.; Mann, S. *Angew. Chem.* **2000**, *112*, 1863. Catala, L.; Gacoin, J.-P. B.; Rivere, E.; Paulsen, C.; Lhotel, E.; Mallah, T. *Adv. Mater.* **2003**, *15*, 826. Uemura T.; Kitagawa S. *J. Am. Chem. Soc.* **2003**, *125*, 7814.
11. Kiriya, A.; Gorodyska, A.; Minko, S.; Tsitsilianis, C.; Jaeger, W., Stamm, M. *J. Am. Chem. Soc.*, **2003**, *125*, 11202.
12. Robin, M. B. *Inorg. Chem.* **1962**, *1*, 337.