doi:10.1246/cl.2010.138

Published on the web January 23, 2010

Dispersion Control of Surface-charged Prussian Blue Nanoparticles into Greener Solvents

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The insoluble Prussian blue pigment was dispersed into greener solvents as surface-charged nanoparticles via their surface modification using various alkylamines. The nanoparticles bore negative zeta potentials originated from the surface $[Fe^{III}–OH]^-$ moieties and their surrounding protonated alkylamines, $[R–NH_3]^+$, and their dispersible nature into solvents was controllable depending on the alkyl-chain lengths.

Over the course of three centuries,[1] the multifunctionalities of PB and its analogs (PBAs) have resulted in recently renewed scientific and industrial applications.[2–5] The importance of printed electronics has increased, realizing the direct formation of thin films and fine patterns of such functional materials on various substrates from usual printing techniques.[6] Nanoparticles are among the most promising printable materials, and fabrication of their dispersion solutions is a key technology in printed electronics.[6] In common reactions between $Fe^{3+/2+}$ and $[Fe^{II/III}(CN)_6]^{4-/3-}$ in an aqueous solution, initially suspended PB colloidal particles are immediately precipitated as an insoluble solid. Various attempts have been made in the last decade to provide stable dispersion solutions of PB nanoparticles.[7,8] We showed a renewed understanding that the insoluble PB solid was an aggregated form of ca. 10 nm nanoparticles, and we have proposed a potential for the insoluble PB solid to be transformed into dispersion solutions via surface modification of each nanoparticle.[9,10] The 3-D coordination bonding of Fe^{II}–CN–Fe^{III} of PB is discontinuous and two types of reaction sites, Fe^{II}–CN and Fe^{III}–OH_2, are inevitably exposed on the surface (Figure 1a). Surface modification using oleylamines was the first example for the direct transformation into toluene-dispersible PB nanoparticles; however, toluene is a hopeless solvent due to the global trend toward environmentally friendly industrial processes.[11]

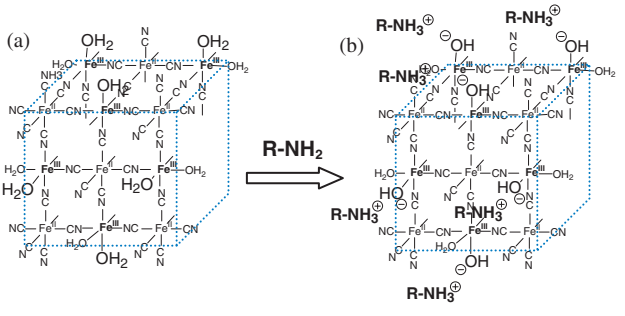

Figure 1. Synthetic strategy of surface-charged PB nanoparticles from their insoluble nanoparticle solid via the surface modification with alkylamines (R–NH_2). The PB nanoparticles are drawn as an ideal cubic shape (nanocube) consisting of a 3 × 3 metal arrangement.

A simple ligand-exchange mechanism between the surface H_2O and alkylamines has been speculated to occur in the surface modification of PB and PBA nanoparticles.[9,12] In this study, we reveal that alkylamines react with the surface Fe^{III}–OH_2 to generate negatively surface-charged PB nanoparticles via a proton-exchange mechanism (Figure 1b). The surface-charged PB nanoparticles are dispersible into environmentally friendly (greener) solvents, such as water and alcohols.[11] Various chain-length alkylamines (R–NH_2) have been investigated, and the dispersible nature of the surface-charged PB nanoparticles is controllable depending on the chain lengths.

An insoluble PB solid was isolated as $Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$ from a dense aqueous mixture of $Fe(NO_3)_3 \cdot 9H_2O$ and $Na_4[Fe(CN)_6] \cdot 10H_2O$, according to the literature,[9] in which the hydration number was determined by thermogravimetric (TG) analysis. The insoluble PB solid consists of 10.5-nm single-crystalline nanoparticles based on Scherrer's equation from the line broadening of powder X-ray diffraction (XRD) signals (Figure S1a).[13] The insoluble PB solid (0.600 g, 0.53 m mol) was stirred with water (1.0 mL) for 1 day, and into the resulting blue slurry, *n*-butanol (15 mL) and various alkylamines (20% based on total Fe ions) were added. The mixture was then stirred for 3 days, and the added quantity of alkylamines was more than 15%, as estimated by [the number of surface reaction sites of Fe^{III}–OH_2]/[the number of total Fe atoms of each nanoparticle] × 100 (%) in the case of an ideal 10-nm PB nanocube. After centrifugation at 6000 rpm (3540 G) for 10 min, the sediment was washed with diethyl ether two times to carefully remove unreacted alkylamines and dried under air for 30 min. The XRD patterns of the resulting solids were unaltered, indicating no significant change of the crystal structure and Scherrer's size from the original insoluble PB solid (Figure S1).[13] The resulting PB nanoparticle solids were dispersed into water and alcohols. The number-averaged dynamic light-scattering (DLS) particle sizes in possible high-concentration solutions are summarized in Table S1.[13] The dispersiblity of the PB nanoparticles depends on the chain lengths of alkylamines. Water-soluble *n*-propylamine and *n*-butylamine, along with water-insoluble *n*-hexylamine, assisted in the dispersion of the PB nanoparticles in water. Similar water-dispersible PB nanoparticles were unsuccessfully prepared using hydrophobic alkylamines with a longer aliphatic chain between C_8 and C_{18}. The PB nanoparticles reacted with alkylamines between C_3 and C_{12} could be dispersed into usual alcohols, methanol, ethanol, *n*-propanol, and/or *n*-butanol. In the case of *n*-hexadecylamine (C_{16}) and *n*-octadecylamine (C_{18}),

the PB nanoparticles were poorly dispersible even in such alcohols. In nanoparticles surface-protected by aliphatic molecules, their interparticulate aggregation is generally promoted by van der Waals attraction between the longer aliphatic chains. To obtain well-dispersible nanoparticles into nonpolar solvents, such as toluene and hexane, oleylamine has been preferably adopted because the bent C_{18}-*cis*-chain effectively inhibits the nanoparticles from such aggregation.[9,14] For the same reason, oleylamines drastically improved the dispersiblity of the PB nanoparticles into *n*-butanol, unlike the longer-chain *n*-hexadecyl- and *n*-octadecylamine.

Two types of surface modification using Fe^{III}–OH_2 sites with alkylamines (R–NH_2) are considered, i.e., the formation of coordination bonds, [Fe^{III}–NH_2–R], via a ligand exchange with H_2O, and the formation of ionic couples of $[Fe^{III}–OH]^-$ and $[R–NH_3]^+$ via an acid–base reaction (Figure 1b). To clarify the reaction mechanism, the surface charges of the water-dispersible PB nanoparticles were investigated. The water-dispersible PB nanoparticles showed negative zeta potentials in the case of *n*-propylamine (−47), *n*-butylamine (−38), and *n*-hexylamine (−57 mV). Triethylamine is a familiar alkylamine that is unable to attach to transition metals via a coordination bond because of steric hindrance. After a similar reaction with triethylamines, the insoluble PB solid was transformed into water-dispersible nanoparticles with a negative zeta potential (−44 mV). The negative surface charges suggest the formation of the ionic couples of $[Fe^{III}–OH]^-$ and liberated $[R–NH_3]^+$. Thus, the dispersiblity of the PB nanoparticles into water and alcohols will be controllable by adjustment of the hydrophilicity (polarity) due to the surface $[Fe^{III}–OH]^-$ moieties and hydrophobic aliphatic chains of their surrounding $[R–NH_3]^+$. As a typical example, an *n*-butanol dispersion solution of the PB nanoparticles reacted with *n*-dodecylamines exhibits highly transparent blue color due to the charge-transfer band of Fe^{II}–CN–Fe^{III} (Figure 2). The PB nanoparticles and their agglomerates were observed in individual diameters between 7 and 11 nm on a mica substrate from an atomic force microscopy (AFM) image (Figure S2).[13]

The PB nanoparticles reacted with alkylamines were preserved in the solid state. The FT-IR signals due to CH stretching of alkylamines could be observed at around 2950 cm^{-1} from a PB nanoparticle solid that was allowed to stand for 1 day under air, but the signal intensities due to shorter-chain alkylamines, *n*-propylamine and *n*-butylamine, were under the detection limit (Figure S3).[13] Nevertheless, a tendency was observed toward the gradual elimination of the shorter-chain alkylamines from the PB nanoparticle solid for its longtime

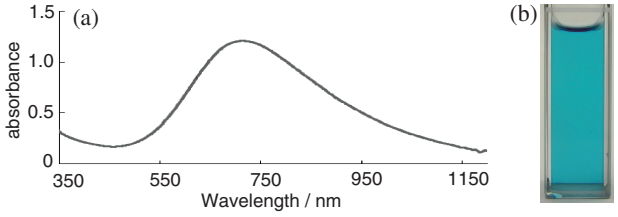

Figure 2. (a) UV–vis–near IR absorption spectrum of the *n*-dodecylamine-modified PB nanoparticles almost independently dispersed in *n*-butanol (78 μg mL^{-1}) and (b) a photograph of the blue dispersion solution with high transparency.

preservation. The attached numbers (%) of alkylamines based on the number of total Fe atoms of PB were calculated from the higher TG weights than that of the original insoluble PB solid. The attached number (13%, stood for 1 day) of *n*-propylamine decreased to 1.6% after 1-month preservation in a usual sample bottle. In contrast, the attached number (5.5%) of the long-chain oleylamine was maintained even after 1-month preservation.[15]

In conclusion, we have developed a simple procedure to obtain PB-nanoparticle dispersion solutions of greener solvents, such as water and alcohols, from the historically insoluble PB pigment by surface modification using alkylamines. The dispersion control of PB nanoparticles into greener solvents is realized via ionic combination between protonated alkylamines with various chain lengths and their surface $[Fe^{III}–OH]^-$ moieties formed by acid–base reaction.

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 21550055) of the Japan Society for the Promotion of Science (JSPS) and the Industrial Technology Research Grant Program (No. 06A22203a) in FY2006 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References and Notes

1 A. Kraft, *Bull. Hist. Chem.* **2008**, *33*, 61.
2 M. Kurihara, *Bull. Jpn. Soc. Coord. Chem.* **2007**, *49*, 34.
3 S. Hara, H. Shiozaki, A. Omura, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, M. Kurihara, M. Sakamoto, *Appl. Phys. Express* **2008**, *1*, 104002.
4 G. Selvarani, S. K. Prashant, A. K. Sahu, P. Sridhar, S. Pitchumani, A. K. Shukla, *J. Power Sources* **2008**, *178*, 86.
5 A. Eftekhari, *J. Power Sources* **2004**, *132*, 291.
6 K. Murata, J. Matsumoto, A. Tezuka, Y. Matsuba, H. Yokoyama, *Microsyst. Technol.* **2005**, *12*, 2.
7 S. Vaucher, M. Li, S. Mann, *Angew. Chem., Int. Ed.* **2000**, *39*, 1793.
8 T. Uemura, M. Ohba, S. Kitagawa, *Inorg. Chem.* **2004**, *43*, 7339.
9 A. Gotoh, H. Uchida, M. Ishizaki, T. Satoh, S. Kaga, S. Okamoto, M. Ohta, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Tokumoto, S. Hara, H. Shiozaki, M. Yamada, M. Miyake, M. Kurihara, *Nanotechnology* **2007**, *18*, 345609.
10 M. Ishizaki, Y. Sajima, S. Tsuruta, A. Gotoh, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Kurihara, *Chem. Lett.* **2009**, *38*, 1058.
11 I. T. Horváth, *Green Chem.* **2008**, *10*, 1024.
12 M. Yamada, M. Arai, M. Kurihara, M. Sakamoto, M. Miyake, *J. Am. Chem. Soc.* **2004**, *126*, 9482.
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
14 M. Itoh, T. Kakuta, M. Nagaoka, Y. Koyama, M. Sakamoto, S. Kawasaki, N. Umeda, M. Kurihara, *J. Nanosci. Nanotechnol.* **2009**, *9*, 6655.
15 The attached numbers after 1-month preservation; *n*-propylamine (1.6%), *n*-butylamine (3.6%), *n*-hexylamine (5.0%), *n*-octylamine (4.6%), *n*-dodecylamine (5.6%), *n*-hexadecylamine (4.6%), *n*-octadecylamine (7.2%), and oleylamine (5.5%).

