Preparation of Yellow Core–Blue Shell Coordination Polymer Nanoparticles Using Active Surface Coordination Sites on a Prussian-blue Analog

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Yellow core–blue shell coordination polymer nanoparticles were prepared through the combination of Fe^{2+} to the surface Fe^{III}–CN sites exposed on the yellow core nanoparticles of nickel hexacyanoferrate, $K_{0.12}Ni_{3.0}[Fe(CN)_6]_{2.04}\cdot 14H_2O$. The Fe^{2+}-attached surface shell layer, Fe^{II}–NC–Fe^{III}, changed into the Prussian blue-like valence state, Fe^{III}–NC–Fe^{II}, via single-electron transfer.

Prussian blue (PB) pigment, with its three-century history, is recognized as the first synthetic coordination polymer.[1] The multifunctionalities of PB and its analogs (PBAs) have recently renewed scientific as well as industrial applications,[2] such as electrochromic displays,[3] electrocatalysts,[4] fuel cell electrodes,[5] secondary batteries,[6] ion- and biosensors,[7] photomagnets,[8] and hydrogen storage.[9] In common syntheses, $M^{3+/2+}$ and $[Fe^{II/III}(CN)_6]^{4-/3-}$ are reacted in an aqueous solution, and the as-formed PB and PBAs are initially suspended as colloidal particles but immediately precipitated as an insoluble solid. Various attempts have been made in the last decade to provide PB and PBA nanoparticles and their dispersion solution by reversed micelle,[10] polymer protection,[11] and template[12] techniques. In 2007, we showed a renewed understanding that the PB, nickel hexacyanoferrate (Ni–PBA), and cobalt hexacyanoferrate (Co–PBA) insoluble solids were a physically aggregated form of 10–20-nm nanoparticles,[13] i.e., historically so-called "colloidal particles," from their consistency between Scherrer's and transmission electron microscope sizes. Based on the insoluble PB and PBAs as nanoparticles, we have focused on their active surface coordination sites, where the three-dimensional cyano-bridged coordination bonding of Fe–CN–M is discontinued and two types of active coordination sites, Fe–CN and M–H_2O, are exposed on the surface (Figure 1a). Through surface modification with alkylamines and $[Fe^{II}(CN)_6]^{4-}$ using the surface Fe^{III}–H_2O sites, we achieved the simple transformation of the PB-insoluble solid into toluene- and water-dispersible nanoparticles, respectively.[13] In an ideal PB nanocube, the 10-nm nanocubes bear 15% surface Fe^{III}–H_2O sites, numerically, of all Fe ions.[14] The surface coverage was experimentally saturated by ca. 15% surface modification using $[Fe^{II}(CN)_6]^{4-}$.

In this study, we will propose a pioneering nanoarchitecture using such surface coordination space on the coordination polymer nanoparticles. In the first attempt, we adopted the formation of the surface PB-like layer of Fe–CN–Fe on Ni–PBA yellow nanoparticles, in which Fe^{II} ions could be combined with the Fe^{III}–CN sites exposed on the surface (Figure 1b).

Ni–PBA was isolated as a yellow insoluble nanoparticle solid of $K_{0.12}Ni_{3.0}[Fe(CN)_6]_{2.04}\cdot 14H_2O$ from a dense aqueous mixture of $Ni(NO_3)_2\cdot 6H_2O$ and $K_3[Fe(CN)_6]$, according to the literature,[13] where the metal composition and hydration number were determined by wavelength-dispersive X-ray spectroscopy (WDX) and thermogravimetric analyses, respectively. As already reported, the Scherrer's particle size of the insoluble Ni–PBA is estimated as 11.6 nm from the line broadening of powder X-ray diffraction (XRD) signals (Figure 1a). The surface modification with Fe^{2+} to Fe(III)–CN sites was investigated on the addition number of $FeSO_4$ between 1 and 40% to Ni–PBA, numerically, of all transition-metal ions of Fe and Ni.[14] Into an aqueous suspension (4 mL) of Ni–PBA (1.00 g, 1.17×10^{-3} mol), an aqueous solution (3 mL) of $FeSO_4\cdot 7H_2O$ (16.2–648 mg, 5.83×10^{-5}–2.33×10^{-3} mol) was added and stirred for 1 day. After centrifugation at 15000 rpm (22140 G), the sediment was washed with water six times to carefully remove unreacted $FeSO_4$ and then dried under reduced pressure. The powdery solids exhibited color gradation from yellow to green depending on the addition number of Fe^{2+}. The XRD patterns of the solids were unaltered after the reaction with Fe^{2+}, indicating that no significant change of the crystal structure or size (11.3 nm) occurred (Figure S1b).[15] The metal ratios of Fe/Ni (mole/mole) of the yellow-to-green solids were estimated from the WDX analyses (Figure 2). The Fe content corresponds to the addition numbers of $FeSO_4$ between 1 and 15% and deviates from them above 15%. The Fe/Ni ratios are almost independent of an addition number of more than 15%, but there is a gradual increase of the ratio. The initial yellow color of Ni–PBA changed to green up to addition numbers of 15%, but the green color was visually maintained with the addition of more than 15%. These facts suggest the limited sites of the insoluble Ni–PBA solid to bind Fe^{2+} in number, which is ca. 15%. When the insoluble Ni–PBA is a

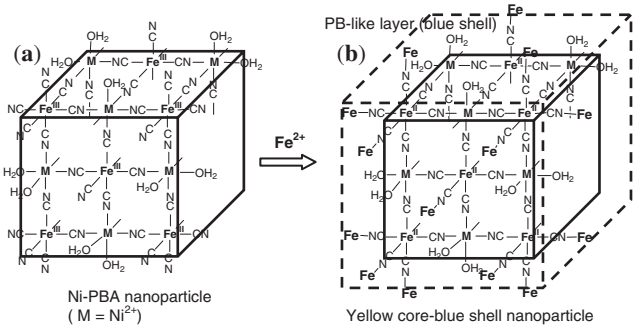

Figure 1. Synthetic strategy of yellow core–blue shell nanoparticles from the insoluble Ni–PBA nanoparticle solid via the surface modification with Fe^{2+} to Fe–CN sites. The Ni–PBA nanoparticles are drawn as an ideal cubic shape (nanocube) surrounded by six {100} surfaces and consisting of a 3×3 metal arrangement with a 0.5 nm $\times$ 2 dimension.

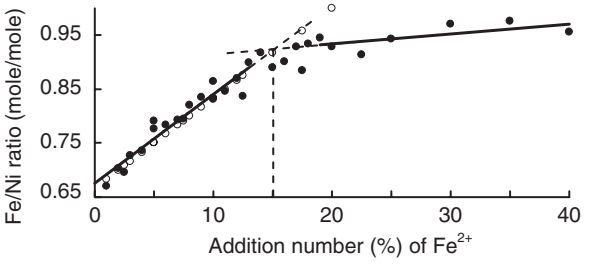

Figure 2. Metal ratios (solid circles) of Fe/Ni (mole/mole) of the yellow core–blue shell nanoparticles estimated by the WDX analyses. Open circles show the case in which all of Fe^{2+} is chemisorbed on Ni–PBA.

physically aggregated nanoparticle solid of 10-nm Scherrer's size, each nanoparticle bears the surface Fe^{III}–CN sites occupying 15%, numerically, of all transition-metal ions as an ideal nanocube (Figure 1a).[13,14] The experimentally valid number is consistent with that of the size-dependent surface Fe–CN sites on the individual 10-nm Ni–PBA nanoparticles. In a possible reaction mechanism to afford the greenish solids, the surface Fe^{III}–CN sites of Ni–PBA predominantly capture Fe^{2+}, but the surface Ni^{2+} ions may be partially displaced with Fe^{2+} based on the gradual increase in the Fe/Ni ratio on more than a 15% addition. In the FT-IR spectrum, a new absorption band at 2063 cm^{-1} beside the CN stretching bands at 2097 and 2166 cm^{-1} of Ni–PBA appears and intensifies as the addition number of Fe^{2+} increases (Figure 3a). According to the consistency of the new band with that of insoluble PB at 2063 cm^{-1}, the Fe^{2+}-attached surface layer, Fe^{II}–NC–Fe^{III}, changes into PB-like valence state, Fe^{III}–NC–Fe^{II}, via single-electron transfer to generate yellow core–blue shell coordination polymer nanoparticles, whose color visually depends on the coverage of the PB-like layer.

In the second attempt to fabricate water-dispersible nanoparticles, the surface modification of $[Fe^{II}(CN)_6]^{4-}$ was performed via the ligand exchange of the surface Ni^{II}–OH_2 sites of the initial Ni–PBA and/or Fe^{III}–OH_2 sites of the PB-like layer of the yellow core–blue shell PBA nanoparticles to produce the charged surface layer, Ni^{II}–$[NC–Fe^{II}(CN)_5]^{4-}$ and/or Fe^{III}–$[NC–Fe^{II}(CN)_5]^{4-}$ (Figure S2).[15] According to a previous report of surface-charged water-dispersible PB nanoparticles,[13] the core–shell PBA nanoparticle solids (0.20 g) were stirred for 3 days in water (2 mL) with $Na_4[Fe(CN)_6]\cdot 10H_2O$ (30%, numerically, of all transition-metal ions). After centrifugation at 15000 rpm (22140 G) to remove unreacted $Na_4[Fe(CN)_6]$, the sediment was stirred with water and almost dispersed into water in the same way as the core–shell PBA nanoparticles to exhibit yellow-to-green color with high transparency (Figure S3)[15] on the basis of the UV–vis–near IR absorption spectra (Figure 3b). The absorption band ($\lambda_{max} = 767$ nm) is ascribable to the charge-transfer band of the PB-like layer, based on a similar absorption band due to the mixed-valence state of Fe^{II}–CN–Fe^{III} at around 700 nm of the water-dispersible PB nanoparticles,[13] and intensifies as the coverage of the PB-like layer increases (Figure 3b). In the typical dispersion solution at 15% coverage, the number-averaged dynamic light-scattering (DLS) particle size is 22 ± 4 nm in a high-concentration dispersion solution (0.1 g mL^{-1}) (Figure S4),[15] and the zeta potential of the nanoparticles is -26 mV in the dilute dispersion solution. The core–shell PBA nanoparticles are stably dispersed in water through electrostatic repulsion of the surface negative charges. The water-dispersible core–shell PBA nanoparticles were observed as the averaged diameter of 9.1 nm on a mica substrate from the atomic force microscopy (AFM) images (Figure S5).[15]

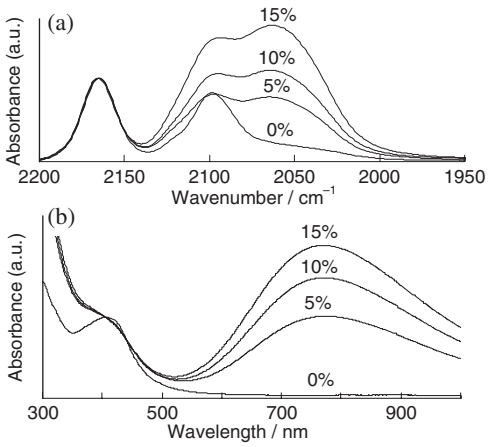

Figure 3. FT-IR (a) and UV–vis–near IR absorption spectra (b) of the yellow core–blue shell nanoparticles. The absorption intensity is normalized by that of Ni–PBA.

In conclusion, we have developed surface nanoarchitecture of coordination polymer nanoparticles using their specific unsaturated surface coordination sites. The surface Fe^{III}–CN site chemisorbs Fe^{2+} on Ni–PBA, and the as-formed Fe^{III}–CN–Fe^{II} layer changes into the PB-like valence state, Fe^{II}–CN–Fe^{III}, via single-electron transfer to generate yellow core–blue shell coordination polymer nanoparticles.

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14 The nanoparticles bear size-dependent surface metals whose number is defined by [the number of surface metal atoms]/[the number of total metal atoms of each nanoparticle] × 100 (%).
15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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