Preferential Evolution of Prussian Blue’s Morphology from Cube to Hexapod†

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Prussian blue (PB), Fe₄⁺[Fe²⁺(CN)₆]₃·xH₂O, has been used as a pigment for three centuries.¹ It has a prototypical hexacyanometalllic face centered cubic structure, with the Fe³⁺ coordinating the nitrogen atoms and the Fe²⁺ to the carbon, resulting in Fe³⁺–NC–Fe²⁺–CN–Fe³⁺ linkage.² The separation between the Fe³⁺ ions corresponds to an a = 1.031 nm. A similar compound, soluble Prussian blue, (KFe⁴⁺[Fe²⁺(CN)₆]) contains potassium ions in alternate interstitial sites (Scheme 1).

PB analogues have unique and potentially useful magnetic, optical, and structural properties. Photoinduced magnetization has been observed in K₀.₂Co₁.₄[Fe(CN)₆]·₉H₂O, a PB analogue.³ Incident light can induce electrons to transfer from Fe²⁺(S=0) to Co³⁺(S=0) in the Fe²⁺–CN–Co³⁺ linkage, yielding a long-lived metastable Fe³⁺–CN–Co²⁺ linkage with Fe³⁺(S=1/2) to Co³⁺(S=3/2), resulting in photo-induced magnetization. Therefore, PB analogues have been studied as photoinduced magnets and molecular magnets and photomagnetic switches.⁴⁻⁹ They have porous frameworks and contain water molecules at the incomplete coordination sites at the surfaces of their frameworks. The coordinated water molecules can be removed by moderate heating and hydrogen gas can be stored in the resulting spaces, making PB analogues potential useful for hydrogen storage.¹⁰⁻¹² They can also act as electrocatalysts for both the reduction and oxidation of hydrogen peroxide and as sensors of hydrogen peroxide and biological glucose.¹³⁻¹⁵

Controlling PB analogues' morphology during their synthesis is important as it affect their properties.¹⁶⁻²⁰ PB analogues have face centered cubic structures, leading to most PB analogues showing cubic morphologies.²¹⁻²³ Most synthetic methods have aimed to prepare a single final morphology and relatively little is known about the morphology evolution of PB analogues with respect to the synthetic conditions. To the best of authors’ knowledge, this is the first report of the evolution of PB’s morphology from cube to hexapod.

Figure 1 shows X-ray diffraction (XRD) patterns of PB products prepared by microwave-assisted reactions from aqueous K₀.₂[Fe²⁺(CN)₆] using different concentrations of HNO₃. When 8.0 × 10⁻² M HNO₃ was used, XRD patterns resulted in peaks attributable to only KFe⁴⁺[Fe²⁺(CN)₆],

Scheme 1. The crystal structures of (a) Fe₄⁺[Fe²⁺(CN)₆]₃·xH₂O (insoluble Prussian blue) and (b) KFe⁴⁺[Fe²⁺(CN)₆] (soluble Prussian blue).

†This paper is to commemorate Professor Kook Joe Shin's honourable retirement.
soluble PB. XRD data of KFe\textsuperscript{3+}[Fe\textsuperscript{3+}(CN)_6] are not available and results were compared to the similar structure of monoclinic K\textsuperscript{2+}Mn\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6] (JCPDS 51-1896, \textit{a} = 1.0108 nm, \textit{b} = 1.0104 nm, \textit{c} = 1.0114 nm, \(\beta = 92.93^\circ\)). Since the ionic radius of Fe\textsuperscript{3+} (0.64 Å) is slightly smaller than that of Mn\textsuperscript{2+} (0.66 Å), the XRD peaks of KFe\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6] appeared at slightly higher angles than those of K\textsuperscript{2+}Mn\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6].\(^{23}\) Increasing the use of HNO\textsubscript{3} decreased that attributable to soluble PB at 17.62° (Figure 1), and results were compared to the similar structure of KFe\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6]xH\textsubscript{2}O. The energy-dispersive X-ray spectroscopy (EDS) was also used to further characterize the PB products prepared with local thermal heating under microwave irradiation from aqueous K\textsuperscript{4+}[Fe\textsuperscript{3+}(CN)_6]. XRD data of KFe\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6]xH\textsubscript{2}O (JCPDS 73-0687, \textit{a} = 1.031 nm). Using HNO\textsubscript{3} at 1.6 × 10\textsuperscript{-3} M led to XRD peaks attributable to both PB and soluble PB. Increasing use of HNO\textsubscript{3} increased the intensity of the peak attributable to insoluble PB at 17.46° and decreased that attributable to soluble PB at 17.62° (Figure 1). This indicates that soluble PB was converted to insoluble PB as the concentration of HNO\textsubscript{3} increased. The FT-IR spectra of soluble PB and insoluble PB showed the very strong peaks at 2065 cm\textsuperscript{-1}, which are corresponded stretching vibration of CN. The energy-dispersive X-ray spectroscopy (EDS) was also used to further characterize the compositions of soluble PB and insoluble PB. The EDX data within experimental errors also confirmed that the soluble PB and insoluble PB had been synthesized. [Analysis observed (calculated) for soluble PB: C, 31.6 (40.0%); N, 42.4 (40.0%); K, 12.3 (6.7%); Fe, 13.7 (13.3%); O, 0.0 (0.0%) and for insoluble PB of Fe\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6]xH\textsubscript{2}O: C, 35.4 (30.0%); N, 38.7 (30.0%); K, 3.0 (0.0%); Fe, 9.1 (11.7%); O, 13.8 (28.3%)].

Aqueous K\textsubscript{4+}[Fe\textsuperscript{3+}(CN)_6] was used with HNO\textsubscript{3} to prepare soluble PB and insoluble PB under microwave irradiation. The formation constant of [Fe\textsuperscript{3+}(CN)_6]\textsuperscript{4+} at 25 °C is ca. 1 × 10\textsuperscript{37}. Under microwave irradiation, [Fe\textsuperscript{3+}(CN)_6]\textsuperscript{4+} dissociated slowly into Fe\textsuperscript{3+} ions. [Fe\textsuperscript{3+}(CN)_6]\textsuperscript{4+} was also partially oxidized by HNO\textsubscript{3} and then Fe\textsuperscript{3+} ions were released. The Fe\textsuperscript{3+} ions reacted with [Fe\textsuperscript{3+}(CN)_6]\textsuperscript{4+} to produce soluble PB, KFe\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6]. K\textsuperscript{+} ions were further substituted by Fe\textsuperscript{3+} ions to form insoluble PB, Fe\textsuperscript{3+}[Fe\textsuperscript{2+}(CN)_6]xH\textsubscript{2}O.

The PB products prepared with local thermal heating under microwave irradiation from aqueous K\textsubscript{4+}[Fe\textsuperscript{3+}(CN)_6] and different concentrations of HNO\textsubscript{3} were characterized by scanning electron microscopy (SEM), as shown in Figure 2. 8.0 × 10\textsuperscript{-2} M HNO\textsubscript{3} led to the formation of soluble PB. 1.6 × 10\textsuperscript{-1} M and 2.0 × 10\textsuperscript{-1} M HNO\textsubscript{3} resulted in truncated cubes, the corners of which were etched by the acid. Increasing the concentration of HNO\textsubscript{3} transformed the truncated cubes to cuboctahedrons and then to truncated octahedrons. 3.9 × 10\textsuperscript{-1} M HNO\textsubscript{3} resulted in hexapods with six arms. Further increases of HNO\textsubscript{3} to 4.8 × 10\textsuperscript{-1} M and 5.7 × 10\textsuperscript{-1} M etched the arms of hexapods to form star-like hexapods.

PB's morphological evolution with increasing HNO\textsubscript{3} concentration is outlined in Figure 3. As increasing HNO\textsubscript{3} concentration, the particles evolved from cubes, through truncated cubes, cuboctahedrons, truncated octahedrons, and hexapods with arms, to star-like hexapods. This indicates that the oxidation reaction started at the cubes' corners, suggesting that the rate of etching at the \{111\} planes was much faster than at the \{100\} planes. The truncated cubes formed through etching at the corners of the cubes of soluble PB. Increasing the concentration of HNO\textsubscript{3} increased the

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**Notes**


Figure 2. SEM images of Prussian blue prepared with different concentrations of HNO\textsubscript{3}: (a) 8.0 × 10\textsuperscript{-3} M, (b) 1.6 × 10\textsuperscript{-1} M, (c) 2.0 × 10\textsuperscript{-1} M, (d) 2.4 × 10\textsuperscript{-1} M, (e) 3.4 × 10\textsuperscript{-1} M, (f) 3.9 × 10\textsuperscript{-1} M, (g) 4.8 × 10\textsuperscript{-1} M, and (h) 5.7 × 10\textsuperscript{-1} M.

Figure 3. Morphology evolution of the Prussian blue from cube to star-like hexapod with increasing concentrations of HNO\textsubscript{3}.
etched areas at the cubes' corners, leading them to being etched into cuboctahedrons and truncated octahedrons. Star-like hexapods were then obtained by etching almost all of the \{111\} planes and some of the \{100\} planes. Therefore, the morphology of crystal of the soluble PB, KFe[Fe(CN)_6]Cl, evolved from cubes to the star-like hexapods of insoluble PB, Fe_2[Fe(CN)_6]Cl_3·xH_2O, via the other shapes by increasing the reaction rate along the \{111\} planes with increased amounts of HNO_3.

The morphologies of PB particles formed under microwave irradiation by the reaction of KFe[Fe(CN)_6]Cl depended upon the concentration of HNO_3. Etching with HNO_3 was important in determining the morphology, as the etching reaction occurred preferentially along the \{111\} planes of the PB structures.

**Experimental Section**

KFe[Fe(CN)_6]Cl (Aldrich, 98.5%) and HNO_3 (Aldrich, 69%) were used as received. For the synthesis of soluble PB, 2.0 mmol KFe[Fe(CN)_6]Cl was dissolved in 100 mL distilled water and 0.6 mL HNO_3 (8.0 × 10^{-2} M) was added under stirring for 5 min. The mixture was carried to a domestic microwave oven (Amana M84T, 2.45 GHz, 25 W) for 3 min. The oven was operated in cycles of 30 s–on and 30 s–off to minimize solvent superheating. The morphology of the PB structures were analyzed by powder X-ray diffraction (XRD, PANanalytical, X'pert-proMPD) using Cu Kα radiation. Their morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4300) equipped with an energy-dispersive X-ray spectroscopy (EDS) operating at an accelerating voltage of 15 kV. The FT-IR spectra were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer in the attenuated total reflectance (ATR) mode over the range 650-4000 cm^{-1} at a resolution of 4 cm^{-1}.

**References**