

Preparation of Prussian Blue Analogue $\text{Ce}[\text{Co}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ Nanoparticles

Fan Li*

Chang'an University, Xi'an, China

*Corresponding author: Fan Li, 1205848410@qq.com

Abstract: Prussian blue analogue $\text{Ce}[\text{Co}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ nanoparticles were prepared by water bath coprecipitation for the first time. The effects of reaction parameters on the morphology and particle size of the synthesized products were revealed by controlling the variable method. The synthetic product has the characteristics of simple preparation method, low cost, small particle size and MOF (Metal organic framework). The cerium and cobalt elements contained in it are common catalytic active elements, which provides ideas and reference for the design and preparation of high-efficiency and low-cost catalysts.

Keywords: Electrocatalytic; Oxygen evolution reaction; Prussian blue analogue; Composite oxide

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1. Introduction

Prussian Blue was found to be used as a dye for more than three hundred years, which is the oldest metal organic frame compound. In the 18th century, "diesbach," a German dyestuff worker, mixed and heated plant ash with cow blood to obtain the yellow crystal $\text{K}_4\text{Fe}(\text{CN})_6$. The yellow crystal was added to the ferric chloride solution to produce a blue precipitation, which is Prussian blue, such as ferrocyanide, with the chemical molecular formula of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ^[1]. Prussian blue has been used as a dye since it was found. It was not until the concept of metal organic framework compounds was put forward in the 1970s that Prussian blue gradually attracted people's attention. As shown in **Figure 1**^[2], Prussian blue is a face centered cubic structure. Carbon and nitrogen are covalently combined to form an octahedron. Iron ions and ferrous ions are located in the octahedron to form a coordination bond with cyanogen.

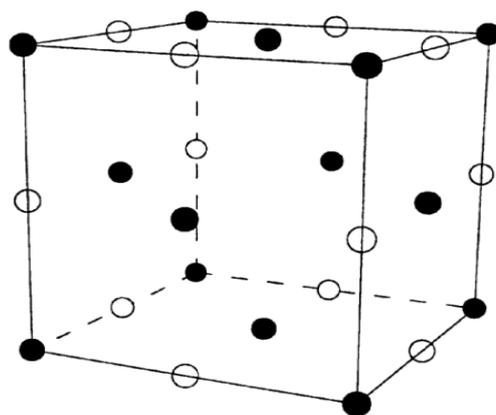


Figure 1. Prussian blue crystal structure ● Fe^{3+} ○ Fe^{2+} ^[2]

Prussian blue has the characteristics of easy regulation of metal ions. Therefore, researchers have prepared a large number of transition metal cyanide with similar structure by replacing iron ions and ferrous ions in Prussian blue with transition metal ions. These compounds are called Prussian Blue Analogues (PBAs). The common PBAs chemical formula is $A_x[B(CN)_6]_y \cdot nH_2O$ (A is Co, Fe, Ni, Mn, Cu, etc; B is Co, Fe, etc.). Due to the diversity of metal ions in PBAs, different metal ions may show different structural and chemical properties. Therefore, PBAs has greatly broadened its application in various fields [3].

Due to the advantages of high specific surface area, tunability of metal ions in the structure and adjustable proportion of bimetals, Prussian blue analogues can be used as templates or precursors to prepare or convert metal compounds with special morphology, especially some catalysts, which show good electrocatalytic performance and stability. Chen et al [4] synthesized the Prussian blue analog precursor of $Zn_3[Co(CN)_6]_2$ by liquid-phase coprecipitation method. Co_3ZnC/CO nano junctions encapsulated in nitrogen doped graphene layer were prepared by annealing pbas, which showed excellent catalytic activity for electrolytic water. Mascaros et al [5] used electrochemical deposition method to deposit cobalt ferric cyanide Prussian blue on fluorine doped tin oxide electrode to prepare Prussian blue coordination polymer CoHCF, which has stronger catalytic activity and excellent corrosion resistance compared with the most advanced metal oxides.

In this paper, Ce/Co Prussian blue nanoparticles were prepared by Co-precipitation method by adjusting the synthesis parameters. The influence of reaction parameters on the morphology and particle size of the synthesized products was revealed by controlling the variable method, which has important reference significance for the development of low-cost and high-efficiency catalysts.

2. Experimental section

2.1. Preparation of dodecahedral cerium cobalt Prussian blue nanoparticles

0.148 g of cerium chloride and 0.222 g of PVP are added to 25 ml of deionized water, stirred to fully dissolve them to prepare solution A; 0.133 g of potassium cobalt cyanide is added to 25 ml of deionized water, stirred it to fully dissolve it to prepare solution B. Solution A is heated to 80°C with a constant temperature magnetic stirrer. In the case of stirring, the solution B is slowly added to the solution A, and the reaction time is 12 hours. After the reaction is retained for 24 hours, the upper clarification liquid is poured out, collects the bottom white powder, and adds the amount of absolute ethanol to sufficiently dispersed the powder in the ultrasonic instrument. Then, the powder is collected using a centrifuge, and the process is repeated several times. After the centrifugation is completed, the powder is dried in a drying tank at 60°C for 3 hours to obtain a cobalt cyanide Push Blue.

3. Results and discussion

Figure 2 shows the XRD pattern of the precursor cerium cobalt cyanide. Since this is the first time to synthesize this kind of substance, and there is no corresponding card in XRD database and literature, $CeKFe(CN)_6 \cdot 4H_2O$ card (pdf#83-2292) with similar peak value to the measured XRD spectrum is selected as the comparative data and analyzed. It can be seen from the figure that the synthesized $CeCo(CN)_6 \cdot nH_2O$ shows the characteristic diffraction peaks of $CeKFe(CN)_6 \cdot 4H_2O$ (pdf#83-2292), and the peaks at 15.25°, 18.89°, 23.83°, 24.04°, 33.98° and 35.53° are in good agreement with the $CeKFe(CN)_6 \cdot 4H_2O$ card, corresponding to (101), (102), (103), (110), (203) and (114) planes respectively.

Figure 3 is a thermogravimetric analysis of $CeCo(CN)_6 \cdot nH_2O$ precursor particles. It can be seen from the figure that the precursor heating in air atmosphere contains three stages of decomposition steps. In the first step, decomposition occurs between 100°C and 200°C, and the weight loss is 17.3%, because the adsorbed water molecules in the precursor are evaporated into gas; In the second step, the decomposition occurred at the temperature of 400°C ~ 450°C, and the weight loss is 5.4%, indicating that the crystal water

between $\text{CeCo}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ molecules in the precursor is evaporated; In the third step, decomposition occurs at a temperature of about $580^\circ\text{C} \sim 650^\circ\text{C}$, and the weight loss is 9.5%, indicating that the decomposition reaction of precursor occurred at $580^\circ\text{C} \sim 650^\circ\text{C}$, but it was not complete. Formula 1 is the reaction equation for heating $\text{CeCo}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ in air.

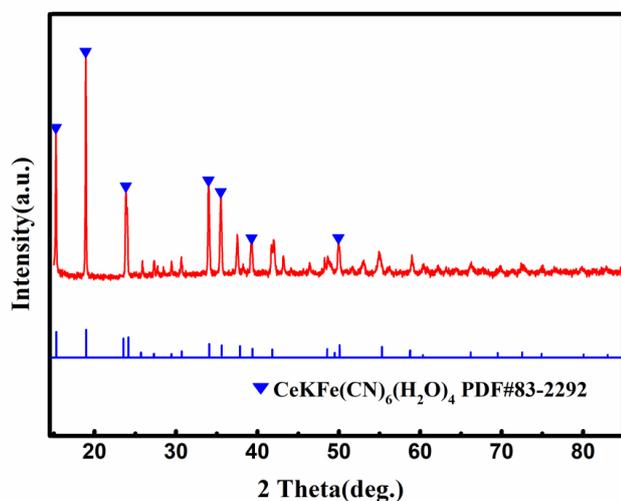
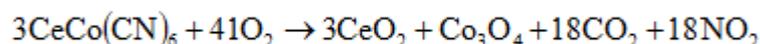


Figure 2. XRD spectrum of precursor cerium cobalt cyanide

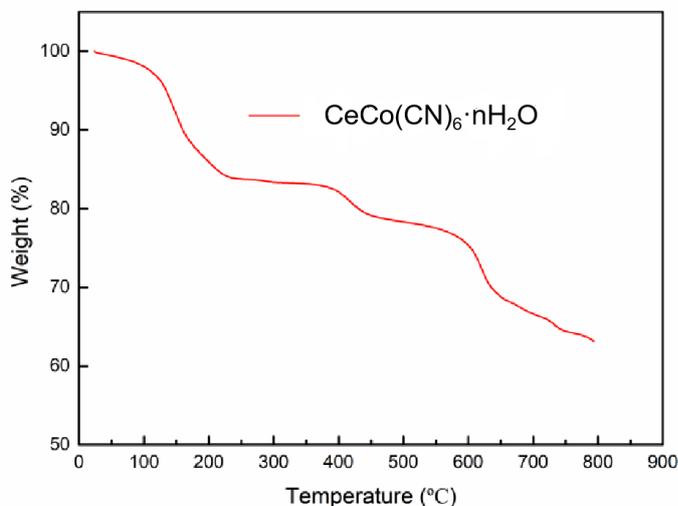
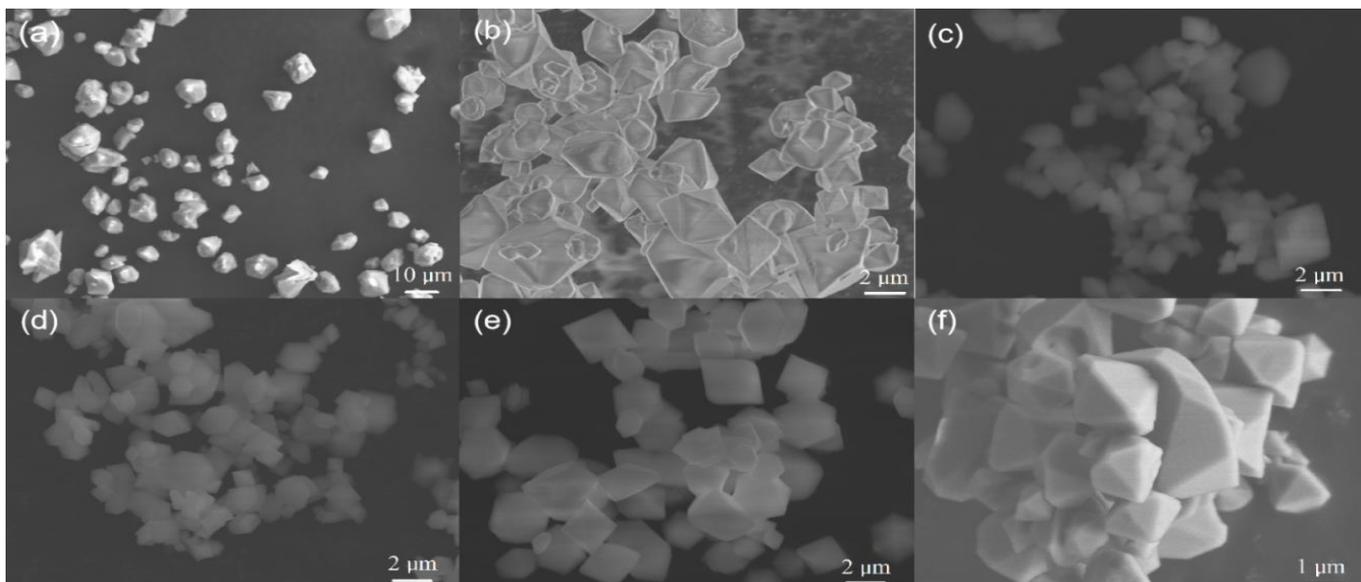


Figure 3. thermogravimetric analysis curve of precursor $\text{CeCo}(\text{CN})_6$

Figure 4 shows SEM images of synthetic products with different reactant concentrations. It can be seen from the figure that when the reactant concentration is 0.16 mol / L. The synthesized particle size is large and there is no fixed morphology. With the decrease of reactant concentration, the particle size of the synthesized particles decreased gradually. **Figure 5** shows the statistics of particle size using ImageJ software. It can be seen that the particle size of the product gradually decreases with the decrease of concentration. When the concentration is 0.016 mol/L, the minimum particle size is reached, and the average particle size is 1.41 μm . Then, with the further decrease of concentration, the particle size increases gradually. Although the slower nucleation rate is conducive to the formation of more regular morphology, at the same time, the product yield is significantly reduced due to too low reactant concentration ^[6], which has no practical application value. Therefore, the concentration of 0.016 mol /L was selected to synthesize the nanoparticles.

Figure 6 shows the SEM images of synthetic products with different surfactants, and **Figure 7** shows the statistics of average particle size of synthetic products with different surfactants. It can be seen from the figure that when the surfactant is PVP, the product is regular polyhedron and the average particle size is 1.4 μm . When the surfactant surface is SDBS, the product becomes an irregular polyhedron, and the average particle size is only 202 nm. When the Surfactant CTAB was added, the morphology of the product changed into aggregated micron lines with a diameter of 3.3 μm . The reason is that the crystal nuclei and crystal planes adsorbed by different surfactants are different. Compared with PVP, CTAB, the complex formed by SDBS and Co ions is more firmly bound, which makes the growth restriction more significant, resulting in a significant reduction of grains ^[7]. To sum up, SDBS is finally selected as the surfactant in this paper.



NOTE: (a) 0.16 mol/L; (b) 0.035 mol/L; (c) 0.016 mol/L; (d) 0.011 mol/L; (e) 0.008 mol/L; (f) 0.0064 mol/L

Figure 4. SEM images of synthetic products with different reactant concentrations

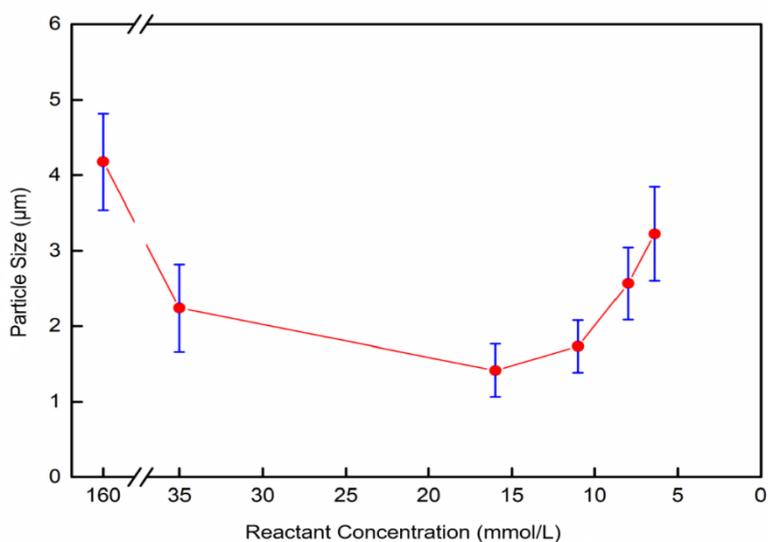
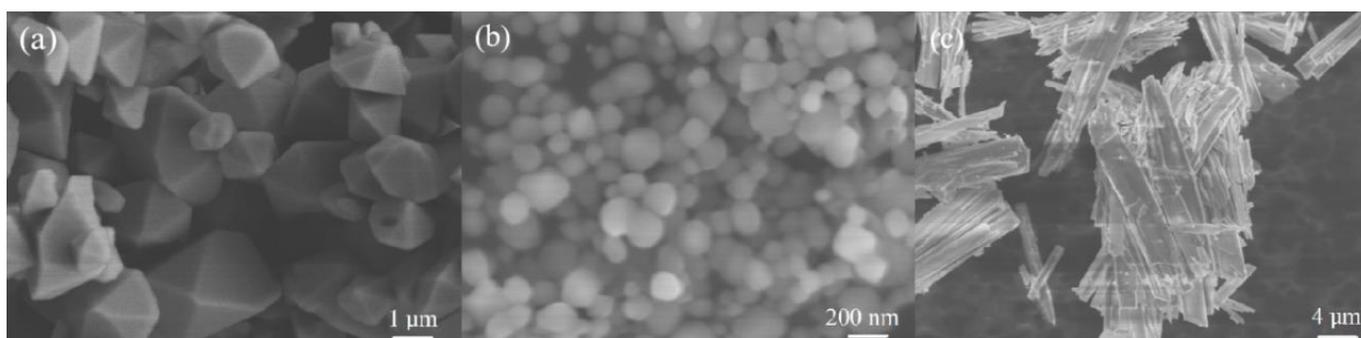


Figure 5. Particle size statistics of synthetic products with different reactant concentrations



NOTE: (a) PVP; (b) SDBS; (c) CTAB

Figure 6. SEM images of synthetic products of different types of surfactants

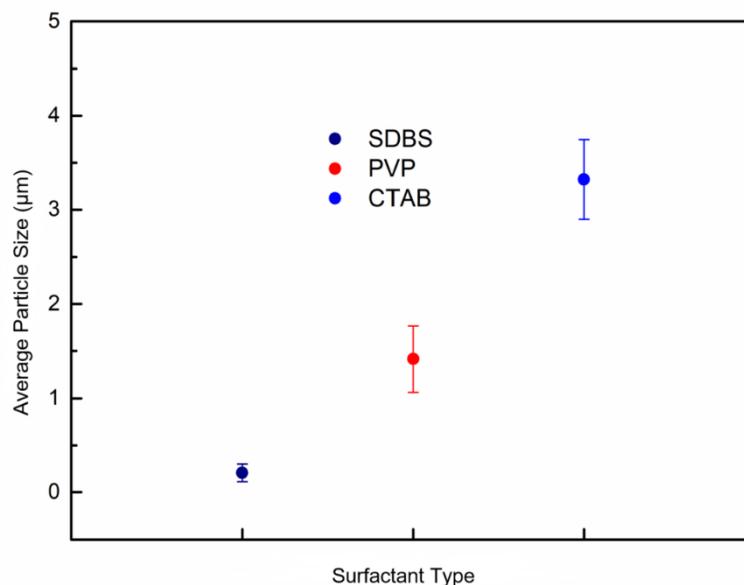


Figure 7. Particle size statistics of synthetic products of different types of surfactants

4. Conclusions

In conclusion, the reactant concentration has little effect on the morphology of the product, mainly on the particle size. The specific performance is that with the reactant concentration from large to small, the synthesized particle size first increases and then decreases in a V-shaped trend. Among them, the particle size of the product is the smallest when the concentration of potassium cobalt cyanide and cerium chloride is 0.016 mol / L; The type of surfactant has a great influence on the morphology and particle size. When the surfactant is PVP, the particle size of the product is large and the morphology is regular dodecahedron. When SDBS is added, the particle size of the product decreases greatly and the morphology is similar to spherical. When CTAB is added, the morphology of the product becomes rod and the diameter is large.

In this paper, the process and variation law of the synthesis of cerium cobalt Prussian blue analogues by liquid-phase coprecipitation were systematically studied, so as to provide experience for the preparation and development of low-cost and high-efficiency catalysts.

Disclosure statement

The author declares no conflict of interest.

References

- [1] Goda ES, Lee S, Sohail M, et al., 2020, Prussian Blue and Its Analogues as Advanced Supercapacitor Electrodes. *Journal of Energy Chemistry*, (11).
- [2] Karyakin, Arkady A, 2015, Prussian Blue and Its Analogues: Electrochemistry and Analytical Applications. *Electroanalysis*, 13(10): 813-819.
- [3] Azhar A, Y Li, Cai Z, et al., 2019, Nanoarchitectonics: A New Materials Horizon for Prussian Blue and Its Analogues. *Bulletin of the Chemical Society of Japan*, 92(4): 875-904.
- [4] Su J, Xia G, Li R, et al., 2016, Co₃ZnC/Co Nano-Heterojunctions Encapsulated in Nitrogen-Doped Graphene Layers Derived from PBAs as Highly Efficient Bi-Functional Electrocatalysts for both OER and ORR. *Journal of Materials Chemistry A*, 4(23): 9204-9212.
- [5] Pintado S, Goberna-Ferron S, Escudero-Adan E C, et al., 2013, Fast and Persistent Electrocatalytic

Water Oxidation by Co-Fe Prussian Blue Coordination Polymers. *Journal of the American Chemical Society*, 135(36): 13270-13273.

- [6] Wen J, Chu W, Jiang C, et al., 2010, Growth of Carbon Nanotubes on the Novel FeCo-Al₂O₃ Catalyst Prepared by Ultrasonic Coprecipitation. *Journal of Natural Gas Chemistry*, 2: 66-70.
- [7] Hao G, Wang W, Gao G, et al., 2015, Preparation of Nanostructured Mesoporous NiCo₂O₄ and Its Electrocatalytic Activities for Water Oxidation. *Journal of Natural Gas Chemistry*, 024(003): 271-277.