

Review

Recent advances in Prussian blue and Prussian blue analogues: synthesis and thermal treatments

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ABSTRACT

Coordination polymers (CPs) have gained a great deal of attention over the years because of their beneficial uses in catalysis, drug-delivery, and energy storage and separation. Recent research efforts have been devoted to architecting CPs that satisfy the needs of applications that have recently been developed. Herein, we announce a survey of the latest developments in the synthesis of Prussian blue (PB) and Prussian blue analogues (PBAs) cyano-bridged CPs. The recent synthetic concepts and the modest control over the shape and size of particles are demonstrated to the present. Various ways have been taken to construct nanostructured inorganic materials from PB and PBAs. We surveyed one such example: the thermal decomposition of these materials in different environments. The regulated thermal treatment of their nanostructures as precursors, in air or inert atmosphere, yields nanoporous metal oxides and carbides or alloys, respectively. The resulting metal frameworks participate as metal sources, and the organic components, which can be removed by a simple process of calcination, produce pores. The original morphologies are almost retained, even after the thermal treatments. This strategy has proved to be a promising solid-state chemistry for the fabrication of nanoporous metal oxides and carbides or alloys with the similar morphology.

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Abbreviations: CPs, coordination polymers; MOFs, metal–organic frameworks; PCPs, porous coordination polymers; PB, Prussian blue; PBAs, Prussian blue analogues; 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; PVP, polyvinylpyrrolidone; CTAB, cetyltrimethylammonium bromide; AOT, sodium bis(2-ethylhexyl) sulfosuccinate; ITO, indium tin oxide; PAH, polyallylamine hydrochloride; PDDA, polydiallyldimethylammonium chloride; LbL, layer-by-layer structure; ORR, oxygen reduction reaction; OER, oxygen evolution reaction; PAA, porous anodic alumina; ODPB, octadecylpyrazinium bromide; rGO, reduced graphene oxide; GO, graphene oxide; PEI, polyethyleneimine; FeCNFe, iron hexacyanoferrate(III) hydrate; CoCNCo, cobalt hexacyanocobaltate(III) hydrate; NiCNCo, nickel hexacyanocobaltate(III) hydrate; MnCNCo, manganese hexacyanocobaltate(III) hydrate; CoCNFe, cobalt hexacyanoferrate(III) hydrate; MnCNFe, manganese hexacyanoferrate(III) hydrate; MnCNMn, manganese hexacyanomanganate(III) hydrate; NiCNFe, nickel hexacyanoferrate(III) hydrate; MnCNRu, manganese hexacyanoruthenate(II) hydrate; NiCNNi, nickel tetracyanonickelate(II) hydrate; CuCNPt, copper tetracyanoplatinate(II) hydrate; NiCNCr, nickel hexacyanochromate(III) hydrate; ICP-OES, inductively coupled plasma optical emission spectrometry; TSCD, trisodium citrate dihydrate; AuNPs, gold nanoparticles; THF, tetrahydrofuran; Fe-BI, pentacyanoferrate(II) ionomer; MOC, metal–organic capsules; MEPP, miniemulsion periphery polymerization; SSPA, single-source precursor approach; Hpyr, 1H-pyrazole; TPBA, titanium Prussian blue analogue; F127, polyethylene oxide – block – polypropylene oxide – block – polyethylene oxide triblock copolymer; P123, polyethylene glycol – block – polypropylene glycol – block – polyethylene glycol triblock copolymer; PEG, polyethylene glycol; HF, hydrofluoric acid; SEM, scanning electron microscope; HRTEM, high resolution transmission electron microscope; MUS, mesoporous silica.

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1. Introduction

The growing needs of nanoporous inorganic structures and/or organic blocks with defined compositions, excellent morphologies, and monocrystalline frameworks are stimulating scientists to find easy and new synthetic methods. To this end, coordination polymer assemblies (CPs), including porous coordination polymers (PCPs) and metal–organic frameworks (MOFs), have undergone extensive study in recent times. Such studies, which have recently increased rapidly, attract the interest in the area of industrial chemistry and the fields of materials science and engineering. These materials have definite compositions of metal cations, which act as nodes that are linked by organic or inorganic ligands that act in turn as bridges or linkers. They have recently gained much attention because they are a novel class of nanoporous materials. The materials can be used as potentials in many applications, such as advanced catalysis [1], drug delivery systems over prolonged times [2], energy conversion and storage systems [3], fluorescence sensing [4], synthesis and separation [3,5], and so on. They satisfy the requirements of the fast development of the aforementioned applications because of their interdisciplinary nature, structural diversity, and excellent physical and chemical properties such as high specific surfaces areas [6], porosity [7], tunable fluorescence [8], electrochemical activity [9], magnetic susceptibility [10], adsorption [3,11], biocompatibility [12], and selectivity [13].

PCPs are particularly attractive in this sense. Many attempts have been made to design them with various compositions and morphologies so as to improve their physical and chemical properties. Because of their functionality and the regularity of their porous shapes and sizes, PCPs are useful in separation, condensation, storage, catalysis, polymer synthesis, and switching (Fig. 1) [14]. Various PCPs, with different morphologies, have been reported to

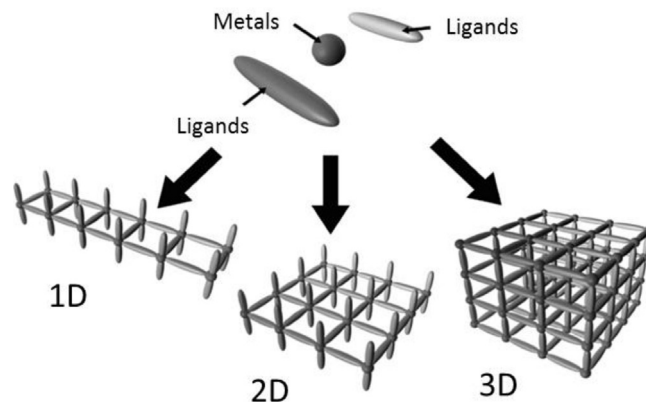


Fig. 2. Illustration of 1-, 2-, and 3-dimensionality of coordination polymers (CPs) [19a,b].

date [15]. Their sizes and shapes can be tuned using various precursors and/or controlling the synthetic conditions. The opportunity to realize a variety of metal frameworks makes it possible to prepare large numbers of PCPs with definite compositions and fine shapes. The final morphologies could be one- (1D) [5,10,16], two- (2D) [17], or three-dimensional (3D) structure [18,19]. 1D morphologies (e.g., nanotubes) extend in a straight line along one-axis, 2D morphologies (e.g., nanosheets and nanoflakes) extend in a plane along two-axes; and 3D morphologies (e.g., nanocubes) extend in all the three directions along the three-axes, as illustrated in Fig. 2 [16–18].

1.1. Morphology, composition, and properties of PB and PBAs

Two of the known PCPs, PB and PBAs comprise of compounds with unique properties that are useful for practical applications to date. The general chemical formula for PBAs is described as $A_nM_n[M_m(CN)_6]_x \cdot xH_2O$ (A corresponds to alkali metal ions (e.g., Na^+ and K^+), and M and M represent transition metal cations) [19b]. When $M=M=Fe$, the final composition will be $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$, which is generally known as PB or $FeCNFe$ [19c]. PB and PBAs heterostructures represent a well-known group of PCPs, where cyanide groups act as bridges between the transition metal ions ($M^{2+}-C \equiv N-M^{3+}$). There are two types of metal centers in the octahedral sites linked through cyanide chains in turn, as a general structural feature of PBAs. These materials are useful for many applications, including gas storage [20], batteries [21], catalysis [22], energy separation [23], charge transfer [24], drug delivery [25], sensors, and environmental cleanup [26]. One more promising application where they can be used is as precursors for nanostructured inorganic materials [27]. The obtained metal oxides or carbides preserve morphologies that are similar to the original PB and PBAs precursors. Recently, by developing

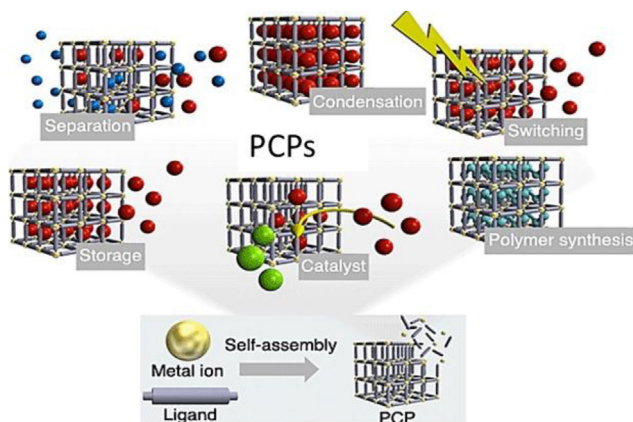


Fig. 1. Architecture of porous coordination polymers (PCPs) and their diverse functions in separation, storage, condensation, catalysis, switching, and polymer synthesis [14].

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