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Nanomaterials

Charged Metallopolymers as Universal Precursors for Versatile Cobalt Materials**

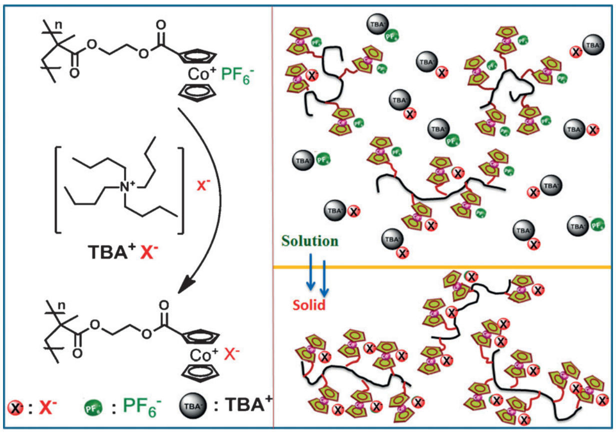
*Jiuyang Zhang, Yi Yan, Michael W. Chance, Jihua Chen, Jeffery Hayat, Shuguo Ma, and Chuanbing Tang**

Inorganic metal-based materials have been widely utilized in catalytic chemistry, life sciences, and engineering.[1] Cobalt-related materials, including metallic cobalt,[2] cobalt oxide,[3] cobalt alloy,[4] and cobalt phosphide,[5] have been used in magnetic materials, aerospace engineering, and energy storage. With the development of modern nanoelectronic technology and the increasing demand for nanostructured materials,[6] the preparation of nanostructured inorganic cobalt-containing materials has become a crucial technological challenge. Various methods have been developed to prepare nanoscale inorganic cobalt-containing materials, including electrodeposition,[7] polymeric precursor synthesis,[8] solvothermal/hydrothermal methods,[5b,9] and sol–gel precipitation.[10] Among them, the utilization of metal-containing polymer precursors to prepare nanostructured cobalt-based materials has been used in particular, for such reasons as controlled molecular weight and architectures offered by well-established controlled/living synthetic methods, various morphologies from polymer self-assembly,[11] and facile manipulation of polymers.[12] As a result, a myriad of metal-containing polymer precursors in the form of thin films, micelles, or fibers have been designed and utilized for preparation of functional inorganic materials.[8]

However, metal-containing polyelectrolytes or charged metallopolymers have been much less studied as precursors to prepare inorganic metal-based materials.[13] Compared with neutral metal-containing polymers, the existence of counterions in charged metallopolymers has several advantages as novel precursors, such as ion-dependent solubility[14] and ion-induced self-assembly.[15] Thus these polyelectrolytes could be universal precursors for access to multifunctional inorganic materials. Unfortunately, it is challenging to perform facile exchange of counterions for charged metallopolymers. Most studies have been limited to specific systems (usually small molecules[16] or super-macromolecules[17]), thus severely restricting the diversity of charged metallopolymers.

Phase transfer has been applied in various organic reactions[18] and utilized in applications such as ionic self-assembly,[19] heterogeneous catalysts,[18,20] and ionic liquids.[21] However, the utilization of phase transfer to tune metal-associated counterions for charged metallopolymers is much less explored.[15,19b] We have recently demonstrated ion exchange between hexafluorophosphate (PF_6^-) and tetraphenyl borate (BPh_4^-) ions in cationic cobaltocenium-containing monomers/polymers, which was clearly a phase transfer-driven reaction.[14b,22] But this specific reaction was only limited for BPh_4^- anions. It is still challenging to apply a powerful technique to access other types of counterions for cobaltocenium-containing polymers.

Herein, we report a facile phase-transfer ion-exchange method to prepare cationic cobaltocenium-containing polyelectrolytes with diverse counterions by the use of tetrabutylammonium salts (Scheme 1). These cobalt-containing polyelectrolytes were further utilized as a class of “universal” precursors to prepare versatile inorganic cobalt materials (Scheme 2). Cobalt monoxide, cobalt metal, cobalt phosphide, and cobalt ferrite were obtained from the same polymeric frameworks by simply changing the counterions. Furthermore, diverse cobalt nanomaterials (including nano-



Scheme 1. Phase-transfer ion-exchange to prepare cationic cobaltocenium-containing polyelectrolytes with different counterions by the use of tetrabutylammonium salts (TBAX, with X as anion).

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[*] J. Zhang, Dr. Y. Yan, M. W. Chance, J. Hayat, Prof. Dr. C. Tang
Department of Chemistry and Biochemistry
University of South Carolina, Columbia, SC 29208 (USA)
E-mail: tang4@mailbox.sc.edu

Dr. J. Chen
Center for Nanophase Materials Sciences
Oak Ridge National Laboratory, Oak Ridge, TN 37831 (USA)

Dr. S. Ma
Department of Chemical Engineering
University of South Carolina, Columbia, SC 29208 (USA)

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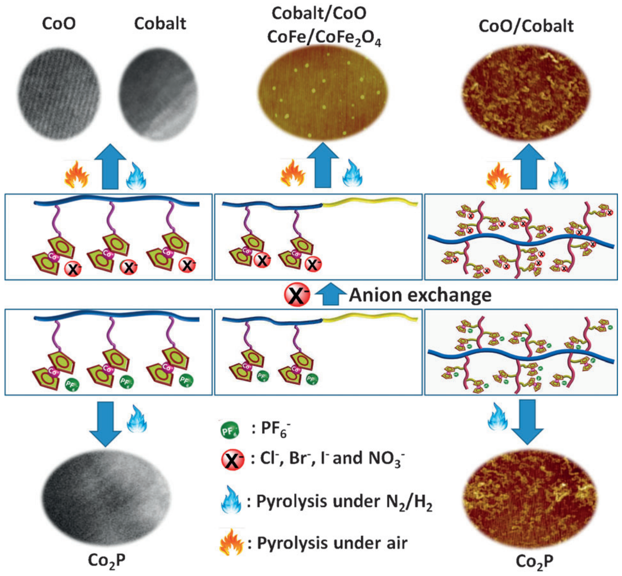


Scheme 2. Precursors to prepare versatile cobalt-based bulk materials, nanoparticles, and 1D nanowires from cationic cobaltocenium-containing homopolymers, block copolymers, and polymer brushes.

particles and 1D nanowires) were produced by integrating these polyelectrolytes into nanoscale precursors.

Hexafluorophosphate (PF$_6^-$)-paired cobaltocenium-containing methacrylate polymer, poly(2-(methacrylolyoxy)ethyl cobaltoceniumcarboxylate hexafluorophosphate) (PMAE-CoPF$_6$, $M_n = 22\,000$ g mol^{-1}, $M_w/M_n = 1.25$), was synthesized according to our previous method.[23] PF$_6^-$-paired cobaltocenium-containing polymers showed good solubility in acetonitrile that is also a good solvent for a variety of tetrabutylammonium salts (TBAX, X as anion). The anion exchange-process occurred immediately when PF$_6^-$-paired polymer solution was added into TBAX solution (Scheme 1). The X anions in TBAX salts firstly diffused into acetonitrile solution and then exchanged with PF$_6^-$ that is associated with the cobaltocenium moiety. Owing to the limited solubility of X anion-associated cobaltocenium polymers in acetonitrile, these polymers immediately precipitated out of the solution. The driving force for quantitative counterion exchange was irreversible phase separation between cobaltocenium-containing polyelectrolytes and the solvent. Because of the strong phase separation, complete ion exchange was achieved in only a few minutes. In comparison, anion exchange for PF$_6^-$-paired cobaltocenium-containing small molecules was limited, which is probably due to relatively good solubility of X anion-associated small molecules and therefore much-reduced phase separation.

^{19}F (Supporting Information, Figure S1) and ^{1}H NMR spectra (Figure S2) demonstrated that several different anions, including F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, and OAc$^-$ were able to perform quantitative anion exchange with PF$_6^-$-paired cobaltocenium-containing polyelectrolyte by TBAX salts. As shown in Figure S1a, PF$_6^-$-paired polymers had two symmetry peaks centered at −71.5 ppm.[14b] After exchanging with TBAF, the obtained F$^-$-paired polymers showed one broad peak at −125.0 ppm and one sharp peak at −129.3 ppm in deuterated water (Figure S1b), while in deuterated methanol, only one peak was observed at −152.3 ppm (Figure S3). The peak in D$_2$O at −125.0 ppm was from H-bonded fluoride with D$_2$O and the peak at −129.3 ppm was from free fluoride.[24] Furthermore, no fluorine signal was observed in ^{19}F NMR spectra after exchanging with Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, and OAc$^-$ anions, indicating the complete removal of PF$_6^-$ anions. The general properties of these new cobaltocenium-containing polymers were summarized in supporting information (Table S1, Figures S4–S6). ^{1}H NMR spectrum (Figure S2) demonstrated that the exchange processes of Cl$^-$, Br$^-$, I$^-$, and NO$_3^-$ for cobaltocenium-containing polyelectrolytes did not affect the polymer framework.

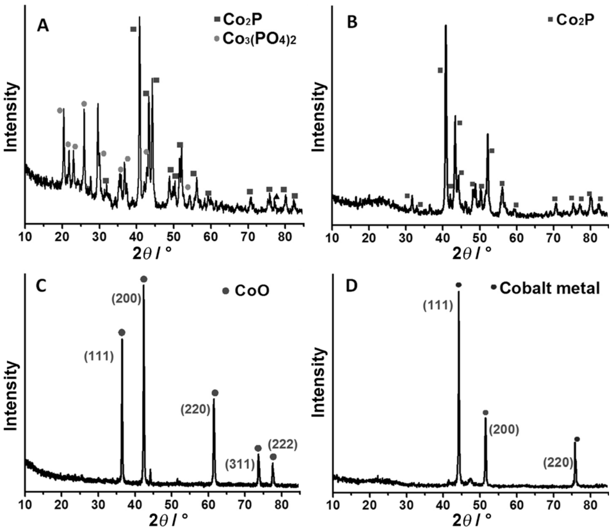


Figure 1. XRD patterns for inorganic cobalt-containing materials from cobaltocenium-containing polyelectrolytes with different counterions. A) UV/ozonolysis and pyrolysis of PF$_6^-$-paired polymers under air at 800 °C; B) pyrolysis of PF$_6^-$-paired polymers under H$_2$/N$_2$ atmosphere at 800 °C; C) UV/ozonolysis and pyrolysis of I$^-$-paired polymers under air at 800 °C; D) pyrolysis of I$^-$-paired polymers under H$_2$/N$_2$ atmosphere at 800 °C.

The utilization of cobaltocenium-containing polymers as precursors to prepare cobalt-based materials by UV/ozonolysis and further pyrolysis under air was reported recently.[8c] However, the resultant cobalt-containing materials prepared from PF$_6^-$-paired cobaltocenium-containing polymers could not avoid the binding with phosphorus and oxygen to produce a mixture of cobalt-containing materials (Figure 1 A). To obtain pure inorganic materials, the above PF$_6^-$-paired cobaltocenium-containing homopolymers were directly pyrolyzed at 800 °C under reductive H$_2$/N$_2$ atmosphere (5v/v % H$_2$; Scheme 2). As shown in Figure 1 B, the X-ray diffraction (XRD) pattern indicated the formation of high quality Co$_2$P, a class of transition-metal phosphides.[5,25] The material was also confirmed by high resolution transmission electron microscopy (HR-TEM; Figure S7A,B) and selected area electron diffraction (SAED) pattern (Figure S7C). Compared with traditional air-sensitive, highly reactive, and toxic phosphide precursors to prepare cobalt phosphide,[5a,25]

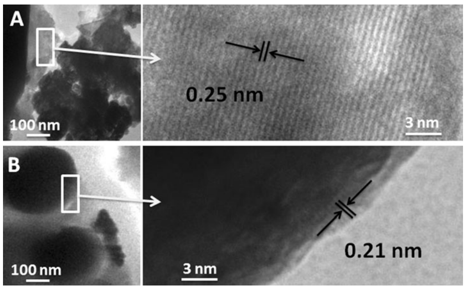
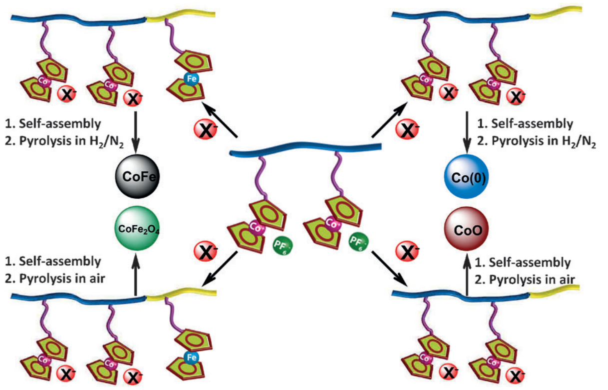


Figure 2. TEM images: A) cobalt monoxide (CoO) and B) cobalt metal prepared by pyrolysis of iodide-paired cobaltocenium-containing polyelectrolytes under air and a H_2/N_2 atmosphere, respectively, at 800 °C. On the right are HR-TEM images.

PF_6^--paired cobaltocenium-containing polymers with phosphorus and cobalt elements provide a new and convenient method for preparation of cobalt phosphide.

However, considering the difficulty to remove phosphorus from pyrolyzed products of PF_6^--paired cobaltocenium-containing polymers,[8c] synthesis of other cobalt-based materials was still restricted. The phase-transfer counterion exchange with TBAX salts offered an opportunity to greatly improving the synthesis of diverse cobalt-containing materials (Scheme 2). Cl^-, Br^-, I^-, and NO_3^- paired cobaltocenium-containing polymers were prepared as stable precursors by TBAX anion exchange. Through UV/ozonolysis and further pyrolysis in air at 800 °C, all of these precursors produced cobalt monoxide, which was confirmed by XRD pattern (Figure 1 C),[26] HR-TEM (Figure 2 A), and SAED pattern (Figure S8A). However, direct pyrolysis of these anion-paired polymers under reductive H_2/N_2 atmosphere (5v/v% H_2) at 800 °C led to the formation of cobalt metal, which was also respectively verified by XRD pattern,[27] HR-TEM, and SAED pattern (Figure 1 D, Figure 2 B; Supporting Information, Figure S8B). The composition and yield of inorganic cobalt materials from iodide-paired and PF_6^--paired cobaltocenium-containing homopolymers was further determined by thermogravimetric analysis (TGA; Figure S21 and Table S2). For pyrolysis of PF_6^--paired polymers under reductive atmosphere at 800 °C, the yield was about 48 %. For iodide-paired polymers, the yield was about 38 %. While for pyrolyzed materials obtained from iodide-paired polymers under air, the yield decreased to 22 %. However, the theoretical yield should be around 12–16 % if only pure inorganic cobalt compounds were obtained. The higher yield was mostly contributed by the coexisting carbonaceous materials, which was indicated by XRD spectra (Figure 1 B,D, the broad peak at ca. 24°) and a Raman spectrum (Figure S12; see below).[28] Inductively coupled plasma mass spectrometry (ICP-MS) was also used to characterize the cobalt content in final pyrolyzed materials. As shown in Table S2, the weight percentage of cobalt element was around 50 % (pyrolysis under air) and 30 % (pyrolysis under H_2/N_2). These data demonstrated that for final pyrolyzed materials, the inorganic cobalt materials coexisted or were embedded in a carbonaceous matrix. Our results were similar to previous reports on the pyrolysis of ferrocene-containing polymer precursors.[12b,29]



Scheme 3. Precursors to prepare versatile nanostructured cobalt-based materials via cationic cobaltocenium-containing block copolymer micelles: $X^- = Cl^-$, Br^-, I^-, and NO_3^-.

The simple and robust access to various bulk cobalt-based materials from cobaltocenium homopolymers with different counterions could be further extended to make similar inorganic materials in nanoscale by designing nanostructured precursors (Scheme 3). PF_6^--paired cobaltocenium-containing diblock copolymers with *tert*-butyl acrylate (tBA) as the second block were synthesized according to our previous work (PMAECoPF$_6$-*b*-PtBA, block ratio PMAECoPF$_6$:PtBA = 62:43, $M_n = 35\,800\ \mathrm{g\,mol^{-1}}$).[23] $TBANO_3$ was then used to replace PF_6^- anions by NO_3^- anions. ^1H and ^{19}F NMR spectra (Figure S9) demonstrated the successful synthesis and counterion exchange. After exchanging the anions, the PF_6^--paired hydrophobic cobaltocenium block was converted into hydrophilic NO_3^--paired block (PMAECoNO$_3$). With the presence of hydrophobic PtBA block, the new amphiphilic diblock copolymers self-assembled into nanoscale micelles in aqueous solution. As shown in AFM (Figure 3 A) and TEM image (Figure S10), cobaltocenium-containing diblock copolymers self-assembled into spherical micelles with an average diameter about 70 ± 10 nm. After pyrolysis in air at 800 °C, the removal of organic polymer framework and the decomposition of nitrate anions converted the micelles into inorganic cobalt monoxide nanoparticles with a diameter reduced to only about 15 ± 5 nm (Figure 3 B).

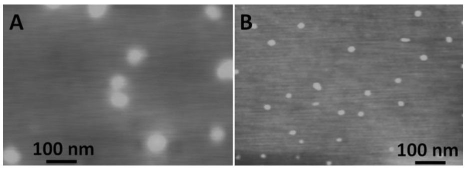


Figure 3. AFM height images: A) Micelles before pyrolysis and B) after pyrolysis under air at 800 °C from self-assembled micelles of cobaltocenium-containing diblock copolymers (PMAECoNO$_3$-b-PtBA) in water.

Similar to bulk cobalt-containing materials produced by cobaltocenium-containing homopolymers, PMAECoNO$_3$-*b*-PtBA block copolymer micelles were converted into cobalt monoxide (by UV/ozonolysis and pyrolysis under air at 800 °C) or elemental cobalt nanoparticles (by pyrolysis under

H_2/N_2 atmosphere at 800 °C), which were confirmed by XRD (Figure S11 A) and X-ray photoelectron spectroscopy (XPS; Figure S13, black curve). For nanoparticles obtained by pyrolysis in air, the XRD pattern indicated the formation of crystalline CoO nanoparticles.[26,30] However, when micelles were pyrolyzed under a H_2/N_2 atmosphere, cobalt metal nanoparticles were obtained, as demonstrated by XRD (Figure S11B) and XPS (Figure S13, red curve).[27] An additional peak at 26.13° in XRD indicated the co-existence of carbonaceous materials.[28] Raman spectrum (Figure S12) of pyrolyzed materials showed D, G and G' bands at about 1300, 1570, and 2660 cm^{-1}, characteristic for multi-walled carbon nanotubes.[31] Further discussion on these carbonaceous materials is beyond the current study.

A heterobimetallic diblock copolymer, PMAECoPF$_6$-*b*-PMAEFc (PMAEFc = poly(2-(methacrylolyoxy)ethyl ferrocenecarboxylate), block ratio = 45:30, $M_n = 32\,800\ g\,mol^{-1}$), was synthesized according to our previous work,[23] which could be used as precursors for preparation of nanostructured cobalt/iron hybrid materials. Counterion exchange with TBAI was used to replace PF_6^- anions. As shown in Figure S15, ^1H and ^{19}F NMR spectra demonstrated the successful synthesis and complete anion exchange for the heterobimetallic diblock copolymer. With iodide as the counterion, the cobaltocenium-containing block (PMAECoI) was turned hydrophilic with the presence of hydrophobic ferrocene-containing block, which formed micelles with ferrocene in the core and cobaltocenium in the shell in aqueous solution (Scheme S1).

As shown in Figure 4 A,C (AFM and TEM, respectively), spherical micelles of self-assembled diblock copolymers with a diameter of about 70 ± 15 nm were observed. Figure 4 B showed the nanoparticles (size: 40 ± 10 nm) after pyrolysis of micelles under air at 800 °C. XRD (Figure S16) showed the formation of cobalt ferrite ($CoFe_2O_4$),[32] which is a well-known hard magnetic material.[33] Peaks at 36.6°, 42.5°, 61.6°, and 73.7° indicated the existence of cobalt monoxide.[26] XPS spectrum (Figure S17) further demonstrated those materials. XRD pattern (Figure 4 D) showed that FeCo hybrid, a class of soft magnetic materials,[4,34] was obtained when pyrolyzed under a reductive atmosphere (H_2/N_2) at 800 °C. Considering excess cobalt element in block copolymers, insignificant cobalt metal was also identified.[27a] Additionally, carbonaceous materials were again observed for the materials in reductive atmosphere by XRD. These results indicated that the iodide anions in the hydrophilic cobaltocenium-containing block were removed and led to the formation of cobalt–iron hybrid materials or nanoscale cobalt ferrite.

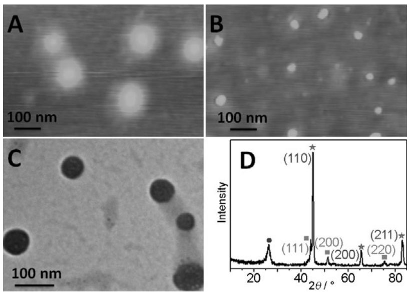


Figure 4. A) AFM height image and C) TEM image of I^- paired cobaltocenium-containing block copolymer micelles (PMAECoI-b-PMAEFc); B) AFM height image of pyrolyzed micelles under air at 800 °C; D) XRD pattern of pyrolyzed micelles under a reductive atmosphere (H_2/N_2) at 800 °C. ★ FeCo alloy, ■ cobalt metal, ● carbon materials.

Worm-like metal-containing polymer brushes have been utilized to prepare 1D inorganic nanowires for decades owing to their ability to form extended chain conformations and their unique solution and bulk properties.[13a,c] Considering the advantages of facile TBAX anion exchange, the cationic cobaltocenium-containing polymer brush may be a versatile precursor for preparation of inorganic cobalt-based nanowires (Scheme 2).

Cobaltocenium-containing polymer brush (poly(N-[4-cyano-4-(phenylcarbonothioylthio)-pentanoate]-cis-5-norbornene-*exo*-2,3-dicarboximide)-*g*-poly-(2 (methacrylolyoxy) ethyl cobaltoceniumcarboxylate hexafluorophosphate)) was synthesized according to our previous work ($M_n = 3\,083\,400\ g\,mol^{-1}$).[22] TBAI was utilized to perform anion exchange to replace PF_6^- anions with iodide ions (Scheme S2). Both PF_6^--paired and I^--paired cobaltocenium-containing polymer brushes showed a worm-like structure with a length at about 130–200 nm (Figure 5 A; Supporting Information, Figure S19A). Considering the high grafting density of cobaltocenium side chains in the polymer brush, such cylindrical metal-containing brush was then used as a precursor for the formation of 1D cobalt-based nanowire. After pyrolysis, cobalt-based 1D nanowires were observed from PF_6^--paired (Figure 5 B; Supporting Information, Figure S18B) and I^--paired cobaltocenium-containing polymer brushes (Figure S20B).

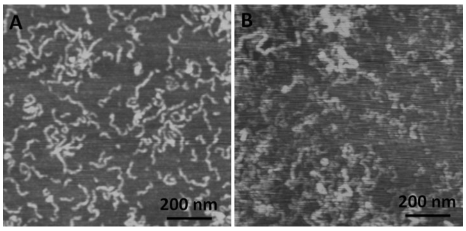


Figure 5. AFM height images for PF_6^--paired cobaltocenium-containing polymer brushes: A) before pyrolysis and B) after pyrolysis under H_2/N_2 at 800 °C.

By pyrolysis under H_2/N_2 atmosphere at 800 °C, PF_6^--paired cobaltocenium-containing polymer brushes were converted into 1D cobalt phosphide nanowires, which were identified by XRD (Figure S20A). For I^--paired brushes, nanowires of elemental cobalt metal (by pyrolysis under H_2/N_2 atmosphere at 800 °C) and nanowires of cobalt monoxide (by UV/ozonolysis and pyrolysis under air) were produced. These materials were confirmed by XRD (Figure S20B and S20C), which showed the same peaks as those in bulk and in nanoparticle, as discussed above. Along with the XRD data, TGA curves (Figure S21) of those polymer brushes indicated that carbonaceous materials coexisted with cobalt materials and facilitated the preservation of nanowire structures.

In conclusion, a facile phase-transfer ion-exchange strategy was applied to prepare charged cobalt-containing polyelectrolytes with various types of counterions, including F^-, Cl^-, Br^-, I^-, NO_3^-, and OAc^-. With this counterion exchange method, cobalt metal, cobalt monoxide, cobalt phosphide, cobalt-iron hybrid, and cobalt ferrite in bulk and in nanoscale were obtained from versatile cobaltocenium-containing polymeric precursors under different conditions. Through a similar procedure, inorganic cobalt-based 1D nanowires (including cobalt phosphide, cobalt monoxide, and cobalt metal) were prepared by using cobaltocenium-containing polymer brushes as precursors. Such cobalt-containing polymeric materials with a convenient and fast phase-transfer method could open a new avenue toward the preparation of advanced cobalt-containing materials.

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