Metallopolymer precursors to $L1_0$-CoPt nanoparticles: synthesis, characterization, nanopatterning and potential application

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Abstract

Ferromagnetic ($L1_0$ phase) CoPt alloy nanoparticles (NPs) with extremely high magnetocrystalline anisotropy are promising candidates for the next generation of ultrahigh-density data storage systems. It is a challenge to generate $L1_0$ CoPt NPs with high coercivity, controllable size, and a narrow size distribution. We report here the fabrication of $L1_0$ CoPt NPs by employing a heterobimetallic CoPt-containing polymer as a single-source precursor. The average size of the resulting $L1_0$ CoPt NPs is 3.4 nm with a reasonably narrow size standard deviation of 0.58 nm. The coercivity of $L1_0$ CoPt NPs is 0.54 T which is suitable for practical application. We also fabricated the $L1_0$ CoPt NP-based nanoline and nanodot arrays through nanoimprinting the polymer blend of CoPt-containing metallopolymer and polystyrene followed by pyrolysis. The successful transfer of the pre-defined patterns of the stamps onto the surface of the polymer blend implies that this material holds great application potential as a data storage medium.

Introduction

Magnetic metal alloy nanoparticles (NPs) have been explored widely in recent years for advanced applications such as permanent magnets,[1,2] ultrahigh density magnetic data recording system,[3–5] magnetic resonance imaging (MRI),[6,7] drug delivery,[8,9] biosensors,[10] recyclable catalysts,[11,12] *etc*. Among the various magnetic metal alloy NPs, ferromagnetic chemically ordered face-centered tetragonal (fct or $L1_0$ phase) CoPt alloy NPs have attracted particular interest of researchers in the last decade, because of their potential application as the next generation ultrahigh-density magnetic data storage media. This is due to the extraordinarily large uniaxial magnetocrystalline anisotropy $K_u \approx 4.9 \times 10^6$ J m^{-3} of $L1_0$ CoPt NPs in the bulk phase and high chemical stability.[13] Usually, $L1_0$ CoPt NPs are synthesized through high-temperature transformation of chemically disordered face-centered cubic (fcc) CoPt NPs, which are commonly generated by refluxing a Co-source and a Pt-source together in a high boiling organic solvent with the presence of surfactant molecules.[14–18] However, problems such as sintering, coalescence, broad size distribution, *etc*., are concomitant with this method. This might be attributed to the fact that the elements Co and Pt reside in separate compounds which have different onset decomposition temperatures.[19,20] Du *et al*. recently reported the one-step synthesis of $L1_0$ CoPt NPs with separate precursors through a solid-phase reaction method.[21] Lukehart *et al*. also reported the direct synthesis of $L1_0$ CoPt NPs by using a single-source molecular precursor.[22] However, as far as the magnetic data recording application is concerned, it is still very desirable to develop a suitable precursor with excellent film-forming properties and solution processability which can be used for the direct nanopatterning of $L1_0$ CoPt NPs.

Bit patterned media (BPM) is a perpendicular magnetic recording system, where each bit is exchanged decoupled and can store data independently. BPM made with ferromagnetic alloy

NPs such as $L1_0$ FePt or CoPt offers a potential path to achieve next-generation ultrahigh-density data storage with capacities beyond 5 Tbits per in^2.[23]

Metallopolymers have attracted intense research interest over the last two decades owing to their practical applications in, *e.g.* photovoltaic cells, nanocomposites, biosensors, polymer light-emitting diodes, *etc*.[24–29] In recent years, researchers have attempted to synthesize metal and metal alloy NPs by utilizing metallopolymers as templates which, upon pyrolysis or photolysis, generate NPs with narrow size distribution and precisely controllable composition as well as density per unit area.[30–32] Previously, we reported a one-pot method to directly synthesize $L1_0$ FePt alloy NPs through the pyrolysis of a metallopolymer containing both Fe and Pt atoms.[33,34] In this work, we report a novel organometallic polymer containing both Co and Pt atoms and investigate its use as a single source precursor to generate the $L1_0$ CoPt NPs by the one-step decomposition. We also performed a nanopatterning study of $L1_0$ CoPt NPs by nanoimprint lithography using a CoPt-containing polymer as the precursor, which has attractive prospects for application in the magnetic data storage systems.

Results and discussion

Synthesis and characterization of the target metallopolymer

Scheme 1 shows the detailed synthetic route of the target CoPt-containing metallopolymer. Here we took advantage of the templating effect of the porphyrin compounds to introduce the Co atom. To begin with, an aromatic aldehyde derivative was prepared from 4-bromobenzaldehyde according to the pathway shown in Scheme 1. 4-(2-(Trimethylsilyl)ethynyl)benzaldehyde was easily prepared through the Sonogashira coupling reaction from 4-bromobenzaldehyde in triethylamine using $Pd(PPh_3)_4$ and CuI as catalysts. The *meso*-phenyldipyrromethane was

prepared through the acid-catalyzed condensation of pyrrole and benzaldehyde using an excessive amount of pyrrole as the solvent. Then the key *trans*-substituted porphyrin (TPP-DTMS) was synthesized by the acid-catalyzed condensation of *meso*-phenyldipyrromethane with the aromatic aldehyde derivatives, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature. Finally, the trimethylsilyl (TMS) group was easily removed in the presence of potassium carbonate in methanol and dichloromethane at room temperature to give the free base porphyrin ligands with diethynyl terminal groups (TPP-DE). Then the TPP-DE was allowed to react with anhydrous $Co(OAc)_2$ in ethanol at reflux overnight to give rise to the diethynyl Co(II) porphyrin (TPP-Co), as depicted in Scheme 1. Afterwards, the diethynyl Co(II) porphyrin derivative (TPP-Co) was allowed to couple with the coordinated platinum(II) dichloride complex through the copper(I)-catalyzed dehydrohalogenation reaction to give the corresponding CoPt-containing porphyrin-based metallopolymer (**P_{CoPt}**) with high yield.

Pyrolysis of CoPt-containing metallopolymer

The metallopolymer **P_{CoPt}** was placed in a ceramic boat, which was then put into a tube furnace for pyrolytic treatment in a nitrogen atmosphere with the heating rate of 20 °C min^{-1} at 800 °C. Finally, the tube furnace was allowed to cool down to ambient temperature to obtain a black powder of $L1_0$ CoPt NPs.

Characterization of the CoPt alloy NPs

Powder X-ray diffraction (PXRD) measurement was performed in order to identify the composition and phase of the resulting NPs as-generated from pyrolysis of **P_{CoPt}**. Fig. 1a shows the PXRD pattern of as-synthesized CoPt NPs, in which each peak was identified (see Tables S1

and S2†). On comparing with the PXRD pattern in the database (JCPDS no. 43-1358), the resulting CoPt NPs are confirmed to be fct-structured NPs. (001) and (110) peaks (which are the characteristic peaks for $L1_0$ phase CoPt alloy NPs) are clearly observed at ~24° and ~33°, respectively.[21,22] The apparent splitting of the (200)/(002) peak signifies a tetragonality of the NPs. Besides, no Co_xN_y and Pt_xN_y phases are observed in the PXRD pattern. Thus, the result of PXRD measurement suggests that the structure and composition of the resulting NPs correspond to the pure chemically ordered $L1_0$ phase CoPt NPs. Energy-dispersive X-ray (EDX) elemental analysis of bulk CoPt NPs further verifies that the ratio of Co and Pt is approximately 48 : 52 as expected for $L1_0$ CoPt NPs (see Fig. S1 and Table S3†). This is in close agreement with the composition as inferred from the (111) peak in the PXRD pattern, and is also consistent with the stoichiometry of the metallopolymer with the atomic ratio of Co to Pt close to 1.

Morphologies of the resulting CoPt alloy NPs were investigated by transmission electron microscopy (TEM), as shown in Fig. 1b. It can be seen clearly that the resulting CoPt alloy NPs exhibit spherical morphology. Fig. 1c displays the histogram of the size distribution of the resulting CoPt NPs through the analysis of the TEM image (Fig. 1b), indicating that the as-synthesized $L1_0$ CoPt NPs have an effective average size of 3.4 nm with a reasonably narrow standard deviation of 0.58 nm. According to the equation $D = 0.9\lambda/(\beta \cos 2\theta)$, Scherrer's analysis of the experimental $L1_0$ CoPt NPs PXRD (111) diffraction peak width gives a volume-weighted average crystallite size of 3.8 nm, which is consistent with the number-average particle size of 3.4 nm determined from the TEM image (see Tables S1 and S2†). Fig. 1d is a high-resolution TEM image of a single CoPt NP, which appeared as uncapped nanocrystals with rounded facets. The continuous fringe-pattern with interplanar distances of around 0.181 nm, corresponding to

(200) *d*-spacing as expected for $L1_0$ CoPt NPs, can be observed.[22] The observation of fringe patterns in the TEM of the NP indicates that the NP is highly crystalline.

Magnetic properties of the as-synthesized $L1_0$ CoPt alloy NPs

Fig. 2 shows the M–H loops of the resulting $L1_0$ CoPt NPs as a powder at 300 K and 5 K. We can learn from Fig. 2 that the coercivity (H_c, an indicator of magnetocrystalline anisotropy) of $L1_0$ CoPt NPs at 300 K is 0.54 T, which is satisfactory for practical magnetic data storage application at room temperature because the data can be manipulated easily by an external magnetic field with a magnetic field strength achievable in typical magnetic data storage systems. As mentioned above, the average size of the CoPt NPs is around 3.4 nm and hence, the NPs at room temperature display both ferromagnetic and superparamagnetic behaviours due to the thermal disturbance. However, with the disappearance of thermal disturbance at low temperature, both the remnant magnetization and coercivity of the $L1_0$ CoPt NPs increased dramatically, which can reach as high as 4.22 emu g^{-1} and 2.75 T, respectively.

Nanopatterning of the CoPt-containing metallopolymer

We performed a nanopatterning experiment with this metallopolymer to explore its application in the perpendicular magnetic data recording system. We blend here the CoPt-containing metallopolymer together with polystyrene (PS) to lower the cost and increase the film-forming quality of the polymers. We first used a hard anodized aluminium oxide (AAO) nanodot mold with the periodicity and feature size of 550 nm and 460 nm to nanoimprint the blend of CoPt-containing metallopolymer and PS. Fig. 3a shows the SEM image of a nanoimprinted dot array pattern of the polymer blend. We can see that the negative pattern of the stamp was transferred

onto the surface of the polymer blend with high fidelity and conformity after nanoimprinting. We then used an AAO nanodot mold with the periodicity and feature size of 100 nm and 70 nm to perform the nanoimprinting. As we can see in Fig. 3b, the resulting nanodot array of the polymer blend is physically well separated and the areal density can reach up to 60 Gbits per in^2. The zoom out images of the nanodot and nanoline array pattern of the polymer blend nanoimprinted by AAO template can be found in Fig. S2,† showing the applicability of the technique in preparing NP arrays over extended regions. While AAO nanopores are generally aligned over only limited regions (less than 100 microns), it is possible to extend the alignments over macroscopic distances (up to cm) by either two-step anodization[36] or prepatterning of aluminium before anodization,[37] allowing truly production-scale fabrication of BPM. We also attempted to use the soft PDMS nanoline mold with the periodicity and feature size of 550 nm and 300 nm to nanoimprint the polymer blend. Fig. 3c shows the nanoline array pattern of the blend, which was then allowed to undergo pyrolysis at 800 °C for 10 min under an argon atmosphere. The nanoline array structural pattern after pyrolysis can be well-preserved with the same pre-defined periodicity on the sample as indicated in Fig. 3d.

Conclusions

We have presented the synthesis of a CoPt-containing metallopolymer with an approximately equal atomic ratio of Co and Pt. By taking this metallopolymer as a precursor, nearly equiatomic $L1_0$ CoPt alloy NPs were synthesized in a single step without the need for any post annealing treatment. The resulting NPs have a narrow size distribution with an effective average size of 3.4 nm. The TEM images indicated that the resulting CoPt NPs were spherical NPs within a carbonaceous matrix which could immobilize and protect the CoPt NPs. The magnetic properties

of the resulting CoPt NPs were investigated by VSM, which shows that NPs are ferromagnetic and possess a reasonably high coercivity of 2.75 T and 0.54 T at 5 K and 300 K, respectively. By taking the blend of CoPt-containing metallopolymer and PS as the precursor, the nanoimprinted dot array and line array patterns were generated successfully by using the hard AAO nanodot mold and soft PDMS nanoline mold. Moreover, after pyrolysis, the pattern can be preserved well with high shape fidelity and conformity. Thus, this novel material as the precursor of $L1_0$ CoPt NPs holds a great potential to be used in the perpendicular magnetic data recording and quantum computation system. Besides, in view of the template effect of the porphyrin ligand, various metal or metal alloy NPs can be synthesized directly with the introduction of different metal atoms in the porphyrin ring according to the method reported in this work.

Experimental

General information

All reactions were carried out under nitrogen unless otherwise stated. Commercially available reagents were used as received without further purification. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated glass plates. Compounds were visualized with UV light irradiation at 254 and 365 nm. Separation or purification of the products was achieved by column chromatography or preparative TLC using silica gel from Merck (230–400 mesh). NMR spectra were recorded in $CDCl_3$ on a Bruker AV 400 NMR instrument with chemical shifts being referenced against tetramethylsilane as the internal standard for ^{1}H and ^{13}C NMR data. IR spectra were recorded on a Nicolet Magna 550 Series II FTIR spectrometer using KBr pellets for solid state spectroscopy. Thermal analyses were performed with a Perkin-Elmer TGA 6 thermal analyzer. The molecular weight of the polymer was determined by GPC using a

HP 1050 series HPLC with visible wavelength and fluorescent detectors against polystyrene standards.

Preparation of 4-(2-(trimethylsilyl)ethynyl)benzaldehyde

To an ice-cooled solution of 4-bromobenzaldehyde (1.513 g, 8.22 mmol) in freshly distilled triethylamine (30 mL) were added CuI (78 mg) and $Pd(PPh_3)_4$ (280 mg). After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (2.3 mL, 16.32 mmol) was then added and the mixture was stirred for 30 min in an ice-bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was heated to 50 °C for 12 h. The solution was then allowed to cool to room temperature and the solvent mixture was evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1 : 1, v/v) as an eluent to provide the target product as a pale-yellow solid (1.81 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, *δ*/ppm): 10.00 (s, 1H, CHO), 7.83 (m, 2H, Ar–*H*), 7.61 (d, *J* = 8.0 Hz, 2H, Ar–*H*), 0.27 (s, 9H, TMS); ^{13}C NMR ($CDCl_3$, 125 MHz, *δ*/ppm): 191.71 (CHO), 135.74, 132.68, 129.66, 129.54, 104.01 (Ar), 99.24, 77.45 (C≡C), 0.28 (TMS).

Preparation of *meso*-phenyldipyrromethane

A solution of benzaldehyde (0.1 mL, 1 mmol) and pyrrole (2.8 mL, 40 mmol) was degassed by bubbling with argon for 10 min, and then trifluoroacetic acid (8 μL, 0.1 mmol) was added. The solution was stirred for 15 min at room temperature, at which point no starting aldehyde was shown by TLC analysis. The mixture was diluted with CH_2Cl_2 (50 mL), then washed with 0.1 N aq NaOH and water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and then the unreacted pyrrole was removed by vacuum distillation at room

temperature. The resulting yellow amorphous solid was dissolved in a minimal quantity of the eluent and was purified by column chromatography on silica gel eluting with hexane/ethyl acetate/triethylamine (80 : 20 : 1, v/v/v) to give the *meso*-phenyldipyrromethane as a pale-brown solid (92 mg, 39%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.93 (m, 2H, Ar–*H*), 7.31 (d, J = 4.8 Hz, 2H, Ar–*H*), 7.23 (m, 2H, Ar–*H*), 6.70 (d, J = 1.2 Hz, 2H, Ar–*H*), 6.16 (d, J = 3.0 Hz, 2H, Ar–*H*), 5.92 (d, J = 0.4 Hz, 2H, Fc–*H*), 5.48 (d, 1H, Fc–*H*); ^{13}C NMR ($CDCl_3$, 125 MHz, δ/ppm): 142.09, 132.55, 128.68, 128.44, 127.02, 117.30, 108.43, 107.27 (Ar), 43.96 (CH).

Preparation of TPP-DTMS

A solution of 4-(2-trimethylsilylethynyl)benzaldehyde (421 mg, 1.48 mmol) and *meso*-phenyldipyrromethane (350 mg, 1.48 mmol) in CH_2Cl_2 (100 mL) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (118 mg, 1.04 mmol) was added. The mixture was stirred for 3 h at room temperature, and then DDQ (680 mg, 2.96 mmol) was added. After the mixture was stirred at room temperature for an additional 30 min, the reaction was quenched by adding triethylamine (2 mL). The solvent was removed, and the residue was purified by flash column chromatography on silica gel using CH_2Cl_2/hexane (1 : 1, v/v) as the eluent. Recrystallization from CH_2Cl_2/methanol gave TPP-DTMS as a purple solid (233 mg, 39%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.81 (d, 8H, J = 8.0 Hz, Ar–*H*), 8.18 (m, 8H, Ar–*H*), 7.86 (d, J = 8.0 Hz, 4H, C=C*H*), 7.73 (d, J = 8.0 Hz, 6H, Ar–*H*), 0.38 (s, 18H, TMS), −2.80 (t, J = 8.0 Hz, 2H, N–*H*); ^{13}C NMR ($CDCl_3$, 125 MHz, δ/ppm): 142.34, 142.31, 142.24, 141.98, 141.90, 134.42, 134.32, 130.26, 127.70, 127.65, 126.63, 122.55, 122.50, 122.48, 120.41, 120.31, 120.18, 119.39, 119.25, 104.90, 104.87, 95.54, 95.49 (Ar).

Preparation of TPP-DE

A mixture of TPP-DTMS (100 mg, 0.13 mmol) and K_2CO_3 (38 mg, 0.27 mmol) in a methanol (20 mL) and CH_2Cl_2 (30 mL) solution mixture was stirred overnight under a nitrogen atmosphere at room temperature. The completion of the reaction was verified by spot TLC. The solvent was removed by rotary evaporation. The resulting mixture was redissolved in CH_2Cl_2 (50 mL) and washed with three portions of 20 mL water. The light yellow organic phase was dried over anhydrous sodium sulfate and evaporated to dryness. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (1 : 2, v/v) to provide TPP-DE as a pale-yellow solid (80 mg, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, *δ*/ppm): 8.82 (m, 8H, Ar–*H*), 8.19 (m, 8H, Ar–*H*), 7.90–7.75 (m, 10H, Ar–*H*), 3.31 (s, 2H, C≡C–*H*), −2.81 (s, 2H, N–*H*); ^{13}C NMR ($CDCl_3$, 125 MHz, *δ*/ppm): 142.76, 142.07, 141.97, 134.54, 130.52, 127.81, 127.75, 126.73, 121.64, 120.57, 120.45, 120.29, 119.20, 119.08 (Ar), 83.64, 76.69 (C≡C).

Preparation of TPP-Co

In a 250 mL distillation flask, TPP-DE (36 mg, 0.055 mmol) and NaOAc (20.5 mg, 0.25 mmol) were stirred in 75 mL of chlorobenzene and 50 mL of DMF. After the addition of two equivalents of $Co(OAc)_2$ (15.5 mg, 0.11 mmol), a Soxhlet extractor with a cellulose filter thimble filled with 3 g of K_2CO_3 was attached to the distillation flask. The assembly was completed with a condenser on the top of the extractor; and then the mixture was heated to reflux at 150 °C overnight. The reaction was monitored by TLC or UV–Vis until all of the TPP-DE was consumed. After the reaction was complete, the solvent was removed under vacuum. The remaining solid was dissolved in 150 mL of chloroform, and washed with water. The organic layer was further washed with a saturated sodium bicarbonate solution, and then dried over

anhydrous K_2SO_4. After the evaporation of the solvent, the solid was recrystallized from chloroform/heptane. A pink-purple crystalline solid was collected. Yield: 12 mg, 30%. IR (KBr): 3288 ($\nu_C{\equiv}C{-}H$) cm^{-1}; 2105 ($\nu_C{\equiv}C$) cm^{-1}.

Preparation of metallopolymer P_{CoPt}

A Pt(II) dichloride complex [$PtCl_2$(^{n}Non$_2$bipy)] was synthesized according to the same procedure we reported previously.[33,35] To a solution of TPP-Co (40 mg, 0.055 mmol) in 30 mL of dichloromethane/triethylamine (1 : 1, v/v) were added [$PtCl_2$(^{n}Non$_2$bipy)] (37 mg, 0.055 mmol) and copper iodide (5 mg). The mixture was allowed to stir at room temperature overnight under a nitrogen atmosphere. Afterwards, the solvent was removed and the mixture was redissolved in a small amount of CH_2Cl_2 and reprecipitated with the addition of methanol. Centrifugation was performed to give a residual solid. The porphyrin-based metallopolymer **P_{CoPt}** was isolated as a red solid (56 mg, 73%). IR (KBr): 2116 ($\nu_C{\equiv}C$) cm^{-1}. GPC (THF): M_w = 10 383, M_n = 7290, M_w/M_n = 1.42; Anal. Calc. for $C_{77}H_{72}N_6CoPt$: C, 69.25; H, 5.43; N, 6.29. Found: C, 69.42; H, 5.55; N, 6.08%; T_{decomp} = 300 °C.

Pyrolysis experiment

The as-synthesized metallopolymer was placed in a ceramic boat, which was then placed inside a quartz reaction tube equipped with temperature and gas-flow controls. Then, the whole set-up was heated up to the desired temperature at a rate of 10 °C min^{-1} and the polymer was allowed to pyrolyze at 800 °C for 1 h under a nitrogen atmosphere.

Nanoparticle characterization

Structural characterization of as-synthesized CoPt NPs was performed by PXRD on a Bruker AXS D8 Advance X-Ray Diffractometer, with Cu $K_{\alpha 1}$ (λ = 540 nm, 40 kV, and 40 mA) for analyzing the composition and phase purity of the resulting NPs. TEM was performed using a Tecnai G2 20 S-TWIN for probing the morphology, particle size and size distribution of NPs. EDX spectra were recorded using a LEO 1530 scanning electron microscope for studying the ratio of Co and Pt in the resulting metal alloy NPs. The magnetic properties of the as-prepared CoPt NPs were investigated at room temperature and 5 K by a Quantum Design system with a vibrating sample magnetometer (VSM), at an applied field of up to 7 T.

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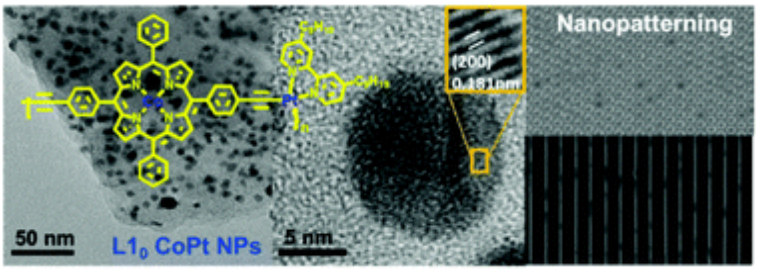
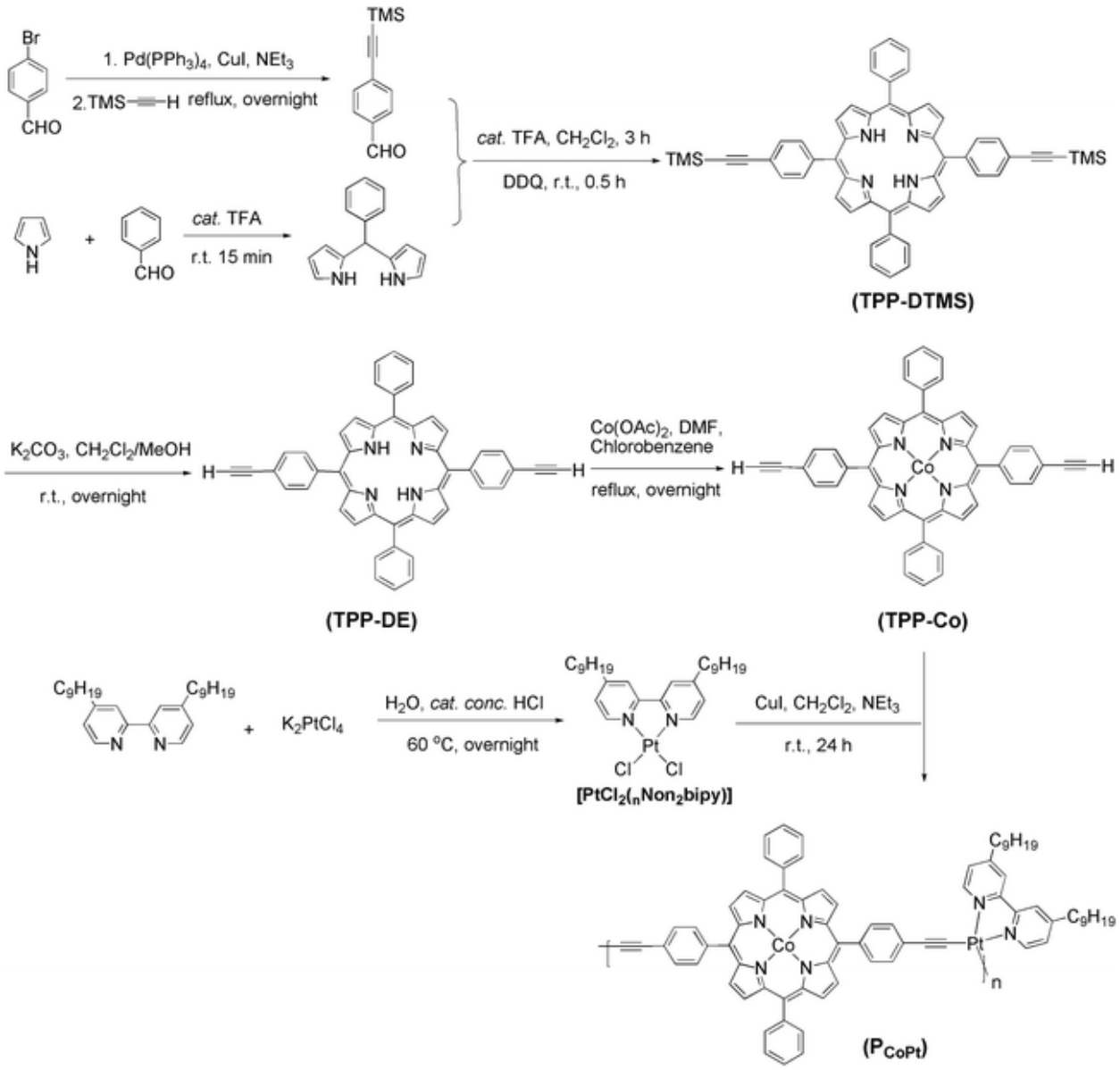
Graphical abstract





Scheme 1 General synthetic route of metallopolymer $\mathbf{P_{CoPt}}$.

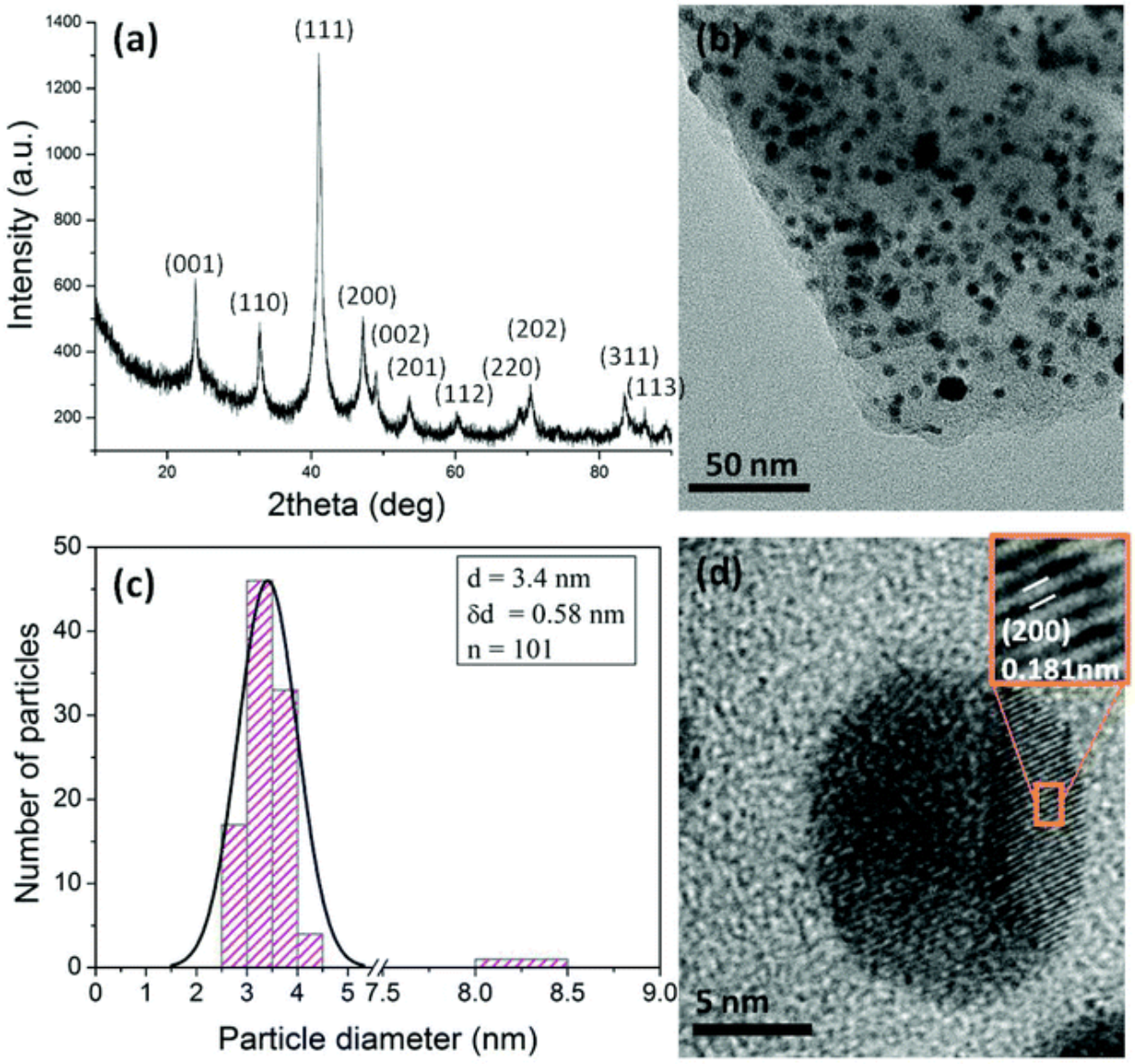


Fig. 1 (a) XRD spectrum of $L1_0$ CoPt NPs. (b) TEM image of as-prepared $L1_0$ CoPt NPs from pyrolysis of metallopolymer $\mathbf{P_{CoPt}}$ at 800 °C. (c) Size distribution of as-prepared $L1_0$ CoPt NPs. (d) High-resolution TEM image of a CoPt NP.

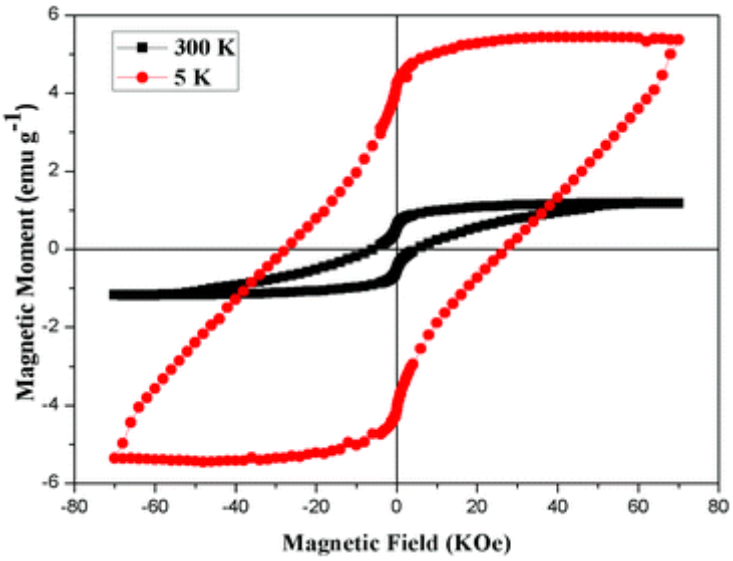


Fig. 2 M–H loops of the as-prepared $L1_0$ CoPt NPs measured at 300 K and 5 K, respectively.

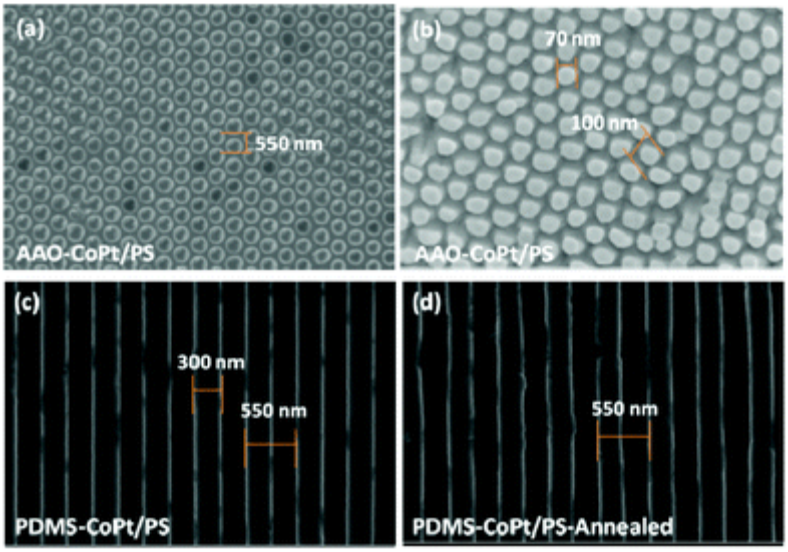


Fig. 3 SEM images of nanopatterned metallopolymers through nanoimprint lithography: nanodot patterns with periodicity of (a) 550 nm and (b) 100 nm which were fabricated by nanoimprinting with the AAO template, (c) nanoline pattern with periodicity of 550 nm and (d) magnetic ceramic nanoline pattern by pyrolysis of the nanopatterned metallopolymer.

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