Monodisperse Pattern Nanoalloying for Synergistic Intermetallic Catalysis

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Supporting Information

ABSTRACT: Nanoscale alloys attract enormous research attentions in catalysis, magnetics, plasmonics and so on. Along with multicomponent synergy, quantum confinement and extreme large surface area of nanoalloys offer novel material properties, precisely and broadly tunable with chemical composition and nanoscale dimension. Despite substantial progress of nanoalloy synthesis, the randomized positional arrangement and dimensional/compositional inhomogeneity of nanoalloys remain significant technological challenges for advanced applications. Here we present a generalized route to synthesize single-crystalline intermetallic nanoalloy arrays with dimensional and compositional uniformity via self-assembly. Specific electrostatic association of multiple ionic metal complexes within self-assembled nanodomains of block copolymers generated patterned monodisperse bimetallic/trimetallic nanoalloy arrays consisting of various elements, including Au, Co, Fe, Pd, and Pt. The precise controllability of size, composition, and intermetallic crystalline structure of nanoalloys facilitated tailored synergistic properties, such as accelerated catalytic growth of vertical carbon nanotubes from Fe−Co nanoalloy arrays.

KEYWORDS: Alloy, block copolymer, nanopattern, catalysis

Alloys are ordered/disordered multimetallic solid solutions extensively utilized since Bronze Age. The old idea of alloying for synergistic material properties still holds great promise for current nanotechnology.1−6 Nanomaterials and nanostructures with extremely large surface areas generally suffer from subtle reactivity and sensitivity to surrounding environment. Synergistic material properties of nanoalloys offer promising opportunities to surpass the inherent weakness and strengthen the desired properties. Meanwhile, traditional alloying has relied on the metallurgical methods employing the simple melt mixing of bulk metals.7 Unfortunately, the traditional method does not ensure the size, shape, and compositional uniformity in nanoscale and is thus inapplicable for nanoalloying.8 Alternatively, several approaches, such as vacuum deposition of multiple metal precursors,9 liquid phase synthesis, and electrochemical methods10−12 have been introduced. Those methods frequently reveal hard controllability over subtle nucleation and growth kinetics of different metal precursors.1,13 More significantly, those methods produce randomly distributed inhomogeneous nanoparticles,14−16 whose structural/compositional distribution and spatial arrangement raise significant challenge for advanced applications, such as electronics,17,18 magnetic storage media,19−21 plasmonics/metamaterials,22,23 and patterned catalysis.24

We report a straightforward synthesis of patterned single-crystalline intermetallic nanoalloys with dimensional/compositional homogeneity exploiting block copolymer (BCP) self-assembly. The self-assembled nanodomains in BCP thin films25−36 confine the simultaneous deposition of multiple ionic metal precursors within nanoscale dimension and successfully generated nanopatterned bimetallic/trimetallic alloys. The size/thickness of self-assembled BCP nanodomains, charge states/molar ratio of metallic precursors, and precursor loading condition precisely control the size, composition, and single-crystalline intermetallic atomic structures of nanoalloys.

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The resultant synergistic properties, including catalytic properties of Fe–Co nanoalloys, are precisely tunable with alloy size and chemical composition.

Figure 1a schematically illustrates patterned monodisperse nanoalloying procedure. Thin films of asymmetric poly-(styrene-block-4-vinylpyridine) (PS-b-P4VP) were spin-cast onto a substrate and self-assembled into hexagonal vertical P4VP nanocylinder morphology by toluene/THF (tetrahydrofuran) mixture solvent annealing (Figure 1b). The nanodomains consisting of hydrophilic vertical P4VP nanocylinders enclosed by a hydrophobic PS matrix was then immersed in acidic aqueous solutions of multiple metal precursors. The protonated pyridinic nitrogen sites in P4VP nanocylinders attract the anionic metal complexes dissociated from metal precursors. After the specific precursor association in P4VP nanodomains, oxygen plasma treatment removes the nonmetallic elements and leaves hexagonally arranged multmetallic nanoclusters (Figure 1c). Subsequent thermal calcination under Ar/H₂ reductive atmosphere generated homogeneous single-crystalline nanoalloy arrays with intermetallic crystalline structures (Figure 1d). The nanoalloys typically exhibit the size significantly smaller than BCP nanodomains with a narrow distribution. The precise statistical analysis of TEM images revealed that nanoalloys with mean diameter of 4.4 nm could be generated from the cylindrical nanodomains with mean diameter of 11.5 nm. The standard deviation of nanoalloys was ∼0.3 nm, which corresponds to below 8% of mean diameter (Supporting Information Figure S1). The resultant nanoalloys shows highly ordered structure over a large surface area and can be perfectly aligned in a trench (Supporting Information Figure S2 and S3).

Our patterned nanoalloying is generally compatible with various available metal precursors to generate intermetallic alloys. Figure 1e,f shows the HRTEM images of bimetallic Co–Pt, Pd–Au binary alloys, and (g) Co–Pd–Pt ternary alloy.

Figure 1. Patterned intermetallic nanoalloying. (a) Schematic illustration of nanoalloying procedure. (b) SEM image of PS-b-P4VP thin film nanotemplate and the size distribution of P4VP nanocylinder cores. (c) TEM image of as-deposited Fe–Pt nanoclusters and their size distribution. (d) TEM image of thermal calcined intermetallic Fe–Pt nanoalloys and their size distribution. HRTEM images of single-crystalline, intermetallic (e) Co–Pt, (f) Pd–Au binary alloys, and (g) Co–Pd–Pt ternary alloy.
Pt and Pd–Au alloys synthesized from K$_3$Co(CN)$_6$, K$_2$PtCl$_4$, Na$_3$PdCl$_6$, and HAuCl$_4$ as the precursors for Co, Pt, Pd and Au elements, respectively (Supporting Information Figure S4). Precursor loading conditions for each alloy were 0.4 mM of K$_3$Co(CN)$_6$ and 0.6 mM of K$_2$PtCl$_4$ for Co–Pt and 0.35 mM of Na$_3$PdCl$_6$ and 0.65 mM of HAuCl$_4$ for Pd–Au in 3% HCl aqueous solution. The chemical compositions measured from energy dispersive X-ray spectroscopy (EDS) were 43/57 for Co–Pt and 45/55 for Pd–Au, respectively. The insets in Figure 1e,f illustrate the corresponding atomic crystal structures. The Co–Pt alloy at ~1:1 composition forms the intermetallic, L1$_0$ face-centered tetragonal (fct) structure. The Pd–Au alloy also forms L1$_0$ phase at 1:1 composition in nanoscale particle, while it is known to form disordered alloy in bulk. It is noteworthy that ternary or more component alloys could be readily prepared by simultaneous loading of three or more metal precursors. Figure 1g shows HRTEM image of a Co–Pd–Pt trimetallic alloy, whose atomic composition was measured to be 43/34.5/22.5 for Co/Pd/Pt. Precursor loading condition for this alloy was 0.4 mM of K$_3$Co(CN)$_6$, 0.3 mM of Na$_3$PdCl$_6$ and 0.3 mM of K$_2$PtCl$_4$. Pd and Pt have very small lattice mismatch (~0.7%) and belong to the same elemental family. The compositional ratio of Co/(Pd and Pt) was 43/57, which is close to 1:1. The created Co–Pd–Pt trimetallic nanoalloy shows the L1$_0$ phase with alternating Co and (Pd and Pt mixture) layers, as illustrated in the inset of Figure 1g. The lattice spacings indicated in TEM images match with the (111) $d$-spacing of the suggested structures.

Figure 2. Compositional tunability of Fe–Pt nanoalloys. EDS Elemental mapping of (a) Fe, (b) Pt, and (c) Fe–Pt superposition in STEM mode. (d) Atomic composition of nanoalloys vs metal precursor molar ratio in precursor solution. HRTEM images of single-crystalline intermetallic nanoalloys with the Fe/Pt compositional ratio of (e) 3/1, (f) 1/1, and (g) 1/3, respectively. Each inset shows the corresponding crystal structures.
(PtCl$_2^{2−}$) (Supporting Information Figure S5). This is attributed to the exchange of the chloro ligands with the aqua ligands.$^{40,41}$ Ligand exchange of chloroplatinate anion (PtCl$_2^{2−}$) may result in complex ions with different charge states, as follows

$$\text{PtCl}_4^{2−} + \text{H}_2\text{O} \leftrightarrow \text{PtCl}_3(\text{H}_2\text{O})^{+} + \text{Cl}^{−} \quad (1)$$

$$\text{PtCl}_4(\text{H}_2\text{O})^{−} + \text{H}_2\text{O} \leftrightarrow \text{PtCl}_2(\text{H}_2\text{O})_2 + \text{Cl}^{−} \quad (2)$$

The equilibrium constants for reactions 1 and 2 are 14.52 and 1.09, respectively.$^{42}$ The corresponding ligand exchanges of chloroplatinate anions (PtCl$_2^{2−}$) in 0.1, 0.3, and 3% HCl aqueous solutions are summarized in Table 1. The complex ions with low charge states of −1 or 0 are more populated at a low HCl concentration. The low charge anions with weak electrostatic attractions with P4VP nanodomains may cause a poor ordering of nanoalloy array. By contrast, negligible amount of ligand exchange occurs in the ferricyanide anion (Fe(CN)$_6^{3−}$) with a relatively large crystal field stabilization energy. For a highly ordered hexagonal distribution of nanoalloys, 3% HCl solution was principally used in this work.

Figure 2d shows the experimental and calculated plots presenting the nonlinear relationship between the Fe precursor molar ratio in the precursor solution and the resultant composition of Fe–Pt alloy. The atomic composition was measured from more than 50 nanoalloys using EDS analysis. The error bar simply means the maximum and minimum values of measured atomic compositions and the black dot means the representative value of all nanoalloys we measured. The calculation was based on following relationship

$$X_i = \frac{C_iF_i}{\sum F_i}$$

Where $X_i$ is the elemental atomic composition of $i$th component in an alloy, $C_i$ is the specific charge and $F_i$ is the molar fraction of the metal complex anion including $i$th element in a given precursor solution. The experimental results for 3% HCl aqueous solution (total precursor molar concentration is fixed at 1 mM) match well with the calculated line (green dash line). The specific loading rate ratio of Fe/Pt maintained ~1.5 over whole precursor concentrations ([specific loading rate] = [atomic composition in nanoalloy]/[precursor concentration], Supporting Information Figure S6). It is equivalent to an anionic charge ratio of 1.5 (~3 for Fe(CN)$_6^{3−}$ and ~2 for PtCl$_2^{2−}$). This confirms that electrostatic attraction plays a principal role in the ionic precursor loading. The charge state as well as compositional ratio of ionic metal precursors determines the precursor loading ratio.

Figure 2e–g shows the high-resolution TEM (HRTEM) images of single-crystalline intermetallic Fe–Pt nanoalloys, synthesized from different precursor molar ratios: 0.65 mM of K$_2$Fe(CN)$_6$ and 0.35 mM of Na$_2$PtCl$_4$ for Figure 2e), 0.35 mM of K$_2$Fe(CN)$_6$ and 0.65 mM of Na$_2$PtCl$_4$ for Figure 2f, and 0.2 mM of K$_2$Fe(CN)$_6$ and Na$_2$PtCl$_4$ for Figure 2g, respectively. After thermal calcination, the normalized atomic Fe/Pt ratios measured by EDS were 72/28 for Figure 2e, 47/53 for Figure 2f, and 27/73 for Figure 2g, respectively. The calcinated nanoalloys have projected shapes of hexagon along its [110] direction, and flat {100} and {111} facets with low surface energies were observed. The measured (111) d-spacing indicated in Figure 2e–g increases with Pt composition, whose atomic size is larger than Fe. Each inset illustrates the crystal structure of the Fe–Pt bimetallic phase. Fe$_x$Pt$_{1−x}$ phase (Figure 2e) and FePt$_3$ L1$_2$ phase (Figure 2g) show face-centered-cubic (fcc) crystal structures. The FePt L1$_0$ phase (Figure 2f) corresponds to fct crystal structure.$^{43}$ In the XRD analysis, the (111) peak at 2θ = 41.05°, the (001) and (110) peaks at 2θ = 23.97° and 32.84° confirmed the fct L1$_0$ phase (Supporting Information Figure S7).$^{44}$ The c-axis of fct is shorter than the other axes, as the atomic layers of Fe and Pt are alternate along the c-axis. This variation of bimetallic phase demonstrates that the chemical composition of nanoalloys is precisely controllable with the metal precursor molar ratio.

In addition to the fine controllability of chemical composition, our patterned nanoalloying also offers subnanometer-level tunability of alloy size. Several different processing parameters, including BCP molecular weight, BCP film thickness, precursor solution concentration, and precursor loading time could be manipulated for the wide range of size tunability in nanoscale (Supporting Information Figure S8). Figure 3 shows the average diameters of Fe–Pt nanoclusters and nanoalloys controlled by precursor loading time. Typically, the mean diameter of as-deposited nanoclusters employing 25 nm thick BCP film was controllable from 6 to 17 nm with loading time. The reason for larger diameter of nanoclusters than P4VP nanocylinder cores is a swelling of P4VP block during precursor loading in HCl aqueous solution. After

Table 1. Calculated Molar Composition of Various Metal Complex Anions As a Result of Aqua Ligand Exchange Reaction of Chloroplatinate

<table>
<thead>
<tr>
<th>HCl conc. (wt %)</th>
<th>PtCl$_2^{2−}$</th>
<th>PtCl$_3(\text{H}_2\text{O})^{+}$</th>
<th>PtCl$_4(\text{H}_2\text{O})_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td>~98.3%</td>
<td>~1.7%</td>
<td>~0%</td>
</tr>
<tr>
<td>0.3%</td>
<td>~84.8%</td>
<td>~15%</td>
<td>~0.2%</td>
</tr>
<tr>
<td>0.1%</td>
<td>~65%</td>
<td>~33.6%</td>
<td>~1.4%</td>
</tr>
</tbody>
</table>

Figure 3. Tunability of Fe–Pt nanoalloy size. Nanocluster and nanoalloy sizes vs precursor loading time in 0.4 mM Fe, 0.6 mM Pt, and 3% HCl aqueous solution.
thermal calcination, the corresponding diameter of single-crystalline intermetallic nanoalloy ranged from 3.5 to 8 nm. As an immediate application of monodisperse patterned nanoalloys, synergistic catalysis of bimetallic Fe−Co arrays was investigated for the vertical carbon nanotubes (CNTs) growth by plasma-enhanced chemical vapor deposition (PECVD). Fe−Co alloy arrays were prepared and thermally reduced under a slow stream of a H2/NH3 mixture. Afterward, acetylene (C2H2) feed gas was slowly streamed over nanoalloy arrays at 973 K to growth vertical CNTs under plasma environment. The uniform nanoalloy size minimizes the catalyst deactivation by Ostwald ripening. In addition, the fine controllability of nanoalloy size enables the tunability of CNT diameter and corresponding carbon wall number.25 More significantly, optimized nanoalloy composition demonstrated the synergistic enhancement of CNT growth yield. Figure 4a shows the relative growth rate plotted against alloy composition. Fe3Co alloy demonstrates the highest CNT growth rate, which is ∼25% enhancement from pure Fe catalyst. The growth rate gradually decreases with Co composition and eventually, pure Co particles generate barely grown CNTs (Supporting Information Figure S9).

The synergistic enhancement of CNT growth from Fe3Co1 nanoalloys was analyzed with density functional theory (DFT) calculations. CNT growth from Fe−Co nanoalloys under plasma activation consists of four distinct steps: (1) adsorption and (2) dissociation of the CH radical at Fe−Co alloy surface, and (3) solution and (4) diffusion of C atom in Fe−Co alloy volume, as schematically illustrated in Figure 4b.45−47 Owing to the highly reactive nanoalloy surface and plasma activation of carbon sources,55 the reaction steps of (1) and (2) are spontaneous without energy barrier. By contrast, either step (3) or (4) can be the principal rate-determining step for this reaction. Figure 4c,d and Supporting Information Table S1 summarizes the DFT dissolution energy and diffusion barrier for interstitial C atom in Fe−Co alloys. While C dissolution energy increases from 0.75 eV for pristine Fe to 1.28−1.87 eV for Fe−Co alloys, the diffusion barrier reduces from 0.86 eV for pristine Fe to 0.80−0.85 eV for Fe−Co alloys. In particular, the
diffusion barrier was minimum (0.80 eV) for Fe$_{0.96}$-Co$_{0.04}$ alloys. These DFT results indicate that the carbon diffusion in catalyst particle is noticeably enhanced when Co is alloyed with Fe (i.e., positive contribution to fast CNT growth), while the carbon solubility decreases with Co alloying (i.e., negative contribution to fast CNT growth). Consequently, growth rate is optimized when a small amount of Co is alloyed with Fe. This is consistent with our experimental result and the previously reported reduced activation energy for Fe$_{0.96}$Co$_{0.04}$ alloys. DFT electronic structure analyses (Supporting Information Figures S11 and S12) show that the alloying of Co into Fe increases Fermi energy and thus weakens C binding energy. Also, the impurity state at the Fermi energy is noticeably increased Fermi energy and thus weakens C binding energy. Consequently, growth rate is optimized when Co is alloyed with Fe (i.e., positive contribution to fast CNT growth), while the carbon particle is noticeably enhanced when Co is alloyed with Fe (i.e., negative contribution to fast CNT growth).

How to control the positional ordering and dimensional/compositional inhomogeneity has been a principal technological issue for the advanced applications of intermetallic nanooalloys in plasmonics, magnetics, catalysis, and so on. The highly specific, simultaneous deposition of multiple metal precursors within uniform self-assembled nanodomains in BCP thin films addresses these issues along with the facile and precise controllability of alloy size, composition, intermetallic crystalline structure and corresponding synergistic physical properties. We anticipate that this straightforward nanooallloying may offer a valuable route to novel intermetallic nanooalloys, as certain elements immiscible in bulk can be miscible in the nanoscale confinement with reduced atomic strain energy. Besides, this solution phase deposition in conjunction with BCP self-assembly is genuinely scalable to an arbitrary large area process, potentially required for device-oriented nanofabrication.

**ASSOCIATED CONTENT**

Supporting Information
Experimental, Methods, additional SEM and TEM images, and additional measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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