

Revealing the effect of indium on the ordering of PdCu in PdCu/PdIn heterostructure

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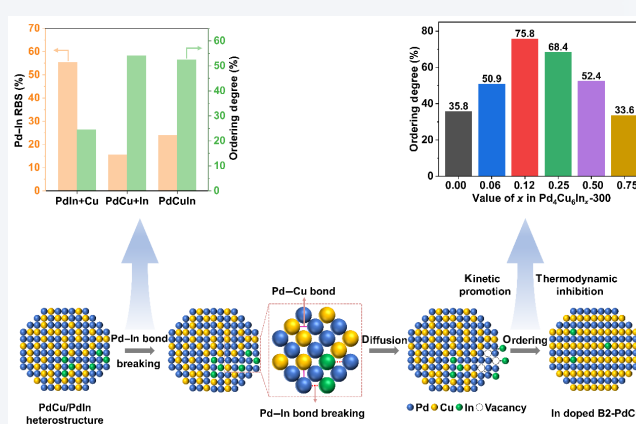
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ABSTRACT: The promotion of intermetallic compound (IMC) formation by a third element has emerged as a promising yet largely underexplored research topic; however, the specific regulation mechanism of the third element on IMC ordering and the influence of its doping content remain unclear. Herein, we comprehensively elucidate the intricate mechanism of indium (In)-induced PdCu ordering in PdCu/PdIn heterostructures. A unique “volcano-type” relationship between the ordering degree of $\text{Pd}_4\text{Cu}_6\text{In}_{x-300}$ (the annealed product of the $\text{Pd}_4\text{Cu}_6\text{In}_x$) and In doping content is reported, which originates from the competition between the kinetic promotion and thermodynamic inhibition effects induced by In doping during high-temperature annealing. The annealing process involves distinct sequential stages: Pd–In bond cleavage generates diffusible In atoms, and the high diffusivity of In atoms subsequently induce vacancy formation to accelerate the ordered rearrangement of Pd/Cu atoms. Notably, a critical and previously overlooked insight is that only diffusible In species can effectively modulate PdCu ordering, with a clear negative correlation between relative bonding strength of Pd–In and annealing-induced ordering degree. This study provides novel insights into the regulation of Pd-based IMCs formation by third-element doping, and provides vital guidance for the rational design of high-performance IMC materials and the optimization of their ordered microstructures.

KEYWORDS: PdCu intermetallics, PdCu/PdIn heterostructure, In-promoted phase transition, bonding strength of Pd–In, ordering degree



1 Introduction

Amid the global energy crisis and environmental pollution, electrochemical energy conversion devices, typified by fuel cells and electrolyzers, have become pivotal in addressing these challenges due to their high efficiency and environmental benignity [1, 2]. However, electrocatalyst performance still represents a critical bottleneck for their commercialization. Compared with traditional single-metal catalysts, alloy catalysts enable electronic structure modulation through multi-metal synergistic effects, thus exhibiting broad application prospects [3–6]. Among these, intermetallic compounds (IMCs) with ordered atomic arrangements are

regarded as promising catalyst candidates [7–10]. The stronger interactions resulting from their negative formation enthalpy can effectively suppress active metal diffusion, enhance the resistance to alloy dissolution, and reduce active component leaching, thereby achieving both high catalytic activity and stability simultaneously. Nevertheless, the synthesis of intermetallic compounds generally requires high-temperature and time-consuming annealing to overcome high atomic diffusion barriers, which presents considerable challenges for controlling the size and structure of intermetallic compounds.

Recently, inducing the formation of IMCs by introducing a third metal has emerged as an emerging yet largely underexplored research topic [11–21]. Current studies have only attributed such promotional effects to enhanced vacancy formation and reduced atomic diffusion barriers, lacking systematic mechanistic insights. In addition, the influence of third-metal doping content on the ordering degree of IMCs remains insufficiently understood

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[22–25]. The annealing process of IMCs generally requires high temperatures ($> 500\text{ }^{\circ}\text{C}$) [26–28], and the coexistence of multiple ordering stages further complicates mechanistic analysis. In contrast, PdCu IMCs can be prepared via low-temperature annealing ($300\text{ }^{\circ}\text{C}$) [29], providing a well-defined model for exploring the influence mechanism of the third metal. Generally, the formation of highly ordered IMCs usually relies on high-temperature annealing, a comprehensive understanding of structural evolution during annealing is crucial for guiding the rational design and synthesis of IMCs.

Traditionally, annealing precursors are mostly disordered alloys synthesized by liquid-phase methods [4, 30]. Limited by detection accuracy of X-ray diffraction (XRD) and the two-dimensional projection nature of scanning transmission electron microscopy with energy-dispersive spectroscopy (STEM-EDS), heterogeneities or heterostructures within particles are easily overlooked [31, 32]. In contrast, using heterostructures with distinct and resolvable XRD signals as annealing precursors can more clearly reveal structural changes during the annealing. For instance, the core-shell PdCu@PtNiCo system was chosen to investigate possible intermediates and the formation mechanism of high-entropy alloys (HEAs) upon heating, owing to the distinguishable XRD reflections from the body-centered cubic (BCC)-PdCu core and the face-centered cubic (FCC)-PtNiCo shell [32]. Therefore, employing heterostructures as annealing precursors is essential for an in-depth understanding of structural evolution mechanisms during annealing.

In this work, Pd₄Cu₆In_x alloys with PdCu/PdIn heterostructure were synthesized via a seed-mediated approach using Pd nanosheets (NSs) as seeds. A distinct “volcano-type” relationship exists between the ordering degree of the Pd₄Cu₆In_x-300 and the In doping content, originating from the synergistic interplay of kinetic promotion and thermodynamic inhibition induced by In incorporation. Systematic time and temperature-dependent XRD and high-resolution transmission electron microscopy (HRTEM) characterizations elucidate the multi-step annealing mechanism: First, the cleavage of Pd–In bonds generates diffusible In atoms; subsequently, the high mobility of In atoms induces abundant lattice vacancies, which in turn accelerate the ordered rearrangement of Pd and Cu atoms to form ordered PdCu intermetallic structures. Notably, the diffusivity of In atoms is a previously neglected yet essential factor for ordering promotion. Quantitative analysis reveals a clear negative correlation between relative bonding strength of Pd–In of unannealed samples and the ordering degree of annealed samples, where stronger Pd–In bonds impede bond cleavage, suppress In diffusion, and ultimately hinder the ordering process of the PdCu. This study provides novel insights into the mechanism by which third-element doping regulates the formation of Pd-based IMCs, offering important guidance for the rational design of high-performance IMCs and the optimization of their ordered microstructures.

2 Experimental

2.1 Materials and reagents

Palladium(II) acetylacetonate (Pd(acac)₃, 99%) was purchased from Sigma Aldrich, copper(II) acetylacetonate (Cu(acac)₃, 99%) was purchased from Adamas Reagent, and indium acetylacetonate (In(acac)₃, 99%) was purchased from Aladdin. Poly(vinylpyrrolidone) (PVP, $M_w = 30,000$) was purchased from Yuanye Co., Ltd. PVP ($M_w = 58,000$) was purchased from Aladdin.

Citric acid (CA) was purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium bromide (NaBr, 99%) was purchased from Aladdin. N-N dimethylformide (DMF, HCON(CH₃)₂, AR) and ethanol (CH₃CH₂OH, AR) were purchased from Tianjin Yuanli Chemical Co., Ltd. Benzyl alcohol (BA, C₇H₈O, AR) was purchased from Shanghai Macklin Biochemical Co., Ltd. Acetone (C₃H₆O, AR) was purchased from Tianjin Damao Chemical Co., Ltd. Milli-Q water (DI water, $18.2\text{ M}\Omega\cdot\text{cm}^{-1}$) was used in all experiments. Argon (Ar, ultra-purity) was purchased from Tianjin Liufang Gases Co., Ltd and carbon monoxide (CO, ultra-purity) was purchased from Air Liquid-TPCC Gases Co., Ltd. All the reagents used in this work were used directly without any further purification.

2.2 Synthesis of Pd nanosheets

First, hexagonal Pd NSs were synthesized according to the previously reported method [33, 34]. 32.0 mg of Pd(acac)₃, 60.0 mg of PVP ($M_w = 30,000$), 35.0 mg of NaBr, and 40.0 mg of CA were added into a 50 mL of custom-made pressure-resistant reaction flask. 20.0 mL of DMF and 4.0 mL of deionized water were added into the bottle. After ultrasonication for 1 min, the mixture was charged with CO for 15 min at $30\text{ }^{\circ}\text{C}$. The capped mixture was pressurized with CO for 0.1 MPa and heated from 30 to $60\text{ }^{\circ}\text{C}$ in 1 h, and maintained at $60\text{ }^{\circ}\text{C}$ for another 2 h. After the mixture cooled down, 32.0 mg of Pd(acac)₃ was added into the mixture, ultrasonicated 1 min, and again charged CO for 15 min and finally kept at 0.1 MPa. After capped, the mixture was heated for 3 h at $60\text{ }^{\circ}\text{C}$. The product was collected by centrifugation by adding sufficient acetone at 10,800 rpm for 2 min and re-dispersed in 10.0 mL of BA and restored in a refrigerator at $4\text{ }^{\circ}\text{C}$.

2.3 Synthesis of Pd₄Cu₆In_x heterostructure

For a typical procedure of Pd₄Cu₆In_{0.50}, 41.0 mg of Cu(acac)₃, 5.4 mg of In(acac)₃, and 300.0 mg of PVP ($M_w = 58,000$) were dispersed in 10.0 mL of BA, subsequently shaken during ultrasonication for 30 min. After 5.0 mL of the above Pd/BA solution was mixed with the Cu(acac)₃-In(acac)₃/BA solution, subsequently shaken during ultrasonication for 30 min again. Then, the mixture was pumped with Ar for 30 min. Finally, the mixture was transferred into a 50 mL Teflon-autoclave and heated at $200\text{ }^{\circ}\text{C}$ for 12 h. The product was collected by centrifugation with acetone and ethanol for three times, and re-dispersed in 5.0 mL ethanol. The synthesis procedure of the other Pd₄Cu₆In_x was identical to the Pd₄Cu₆In_{0.50} alloy except the amount of In(acac)₃, the specific amount of precursor added is shown in Table S1 in the Electronic Supplementary Material (ESM).

2.4 Synthesis of carbon (Vulcan XC-72R) loaded Pd₄Cu₆In_x nanoparticles

84.0 mg of Vulcan XC-72R was dispersed into 10.0 mL of ethanol and ultrasonicated for 2 h. Then, the above Pd₄Cu₆In_x/ethanol solution was added into the carbon/ethanol solution and ultrasonicated for 1 h. Finally, the product was obtained after removal of ethanol solvent by rotary evaporation at $60\text{ }^{\circ}\text{C}$.

2.5 Thermal annealing approach for the Pd₄Cu₆In_x heterostructure alloy

Using carbon-loaded Pd₄Cu₆In_x as precursor, we annealed it in a tube furnace under the flow of 5 vol.% H₂/Ar ($100\text{ mL}\cdot\text{min}^{-1}$) atmosphere at $300\text{ }^{\circ}\text{C}$ for 3 h with a temperature increase rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The annealed product was named as Pd₄Cu₆In_x-300.

2.6 Characterization

Transmission electron microscopy (TEM) was performed on a JEOL-1230 at 100 kV and JEOL-2100Plus at 200 kV. HRTEM, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and EDS elemental mapping analysis were performed on a JEOL-F200 at 200 kV and Talos-F200X at 200 kV. Aberration-corrected HAADF-STEM (AC HAADF-STEM) was performed on JEOL JEM-ARM200F. Powder XRD patterns were collected on a Smartlab diffractometer (Rigaku) using Cu K α radiation ($\lambda = 0.15418$ nm) with a current of 60 mA and a voltage of 60 kV and a D8-Focus diffractometer (Bruker AXS) using Cu K α radiation ($\lambda = 0.15418$ nm) with a current of 40 mA and a voltage of 40 kV. The elemental content of the as-prepared nanocrystals was determined by the inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Agilent instrument.

2.7 Calculation of ordering degree

It is known that the XRD pattern of B2-PdCu IMCs exhibits six diffraction peaks at 30.03°, 42.99°, 53.33°, 62.42°, 70.81°, and 78.79°, corresponding to the (100), (110), (111), (200), (210), and (211) crystal planes. The diffraction peaks located at 30.03°, 62.42°, and 78.79° belong to the superlattice peaks of B2-PdCu IMCs. Considering that the diffraction peak position of C is close to the (100) diffraction peak position of B2-PdCu IMCs, and the (311) diffraction peak of FCC-PdIn solid solution is close to the (211) diffraction peak position of B2-PdCu IMCs, the selected superlattice peak is the (200) diffraction peak. The main peak is the superposition peaks (40°–45°) of the (110) diffraction peak of B2-PdCu and the (111) diffraction peak of FCC-PdCu solid solution. To decouple their individual contributions, rigorous peak deconvolution was performed for all XRD patterns, separating the integrated peak areas of FCC-PdCu(111) and B2-PdCu(110) prior to quantitative calculation.

The ordering degree is calculated according to the following Eq. (1)

$$\text{Ordering degree (\%)} = \frac{A_{B2-200} / (A_{FCC-111} + A_{B2-110})}{I_{B2-200} / I_{B2-110}} \quad (1)$$

where A_{B2-200} is the peak area of superlattice peak (200) in the annealed Pd₄Cu₆In_x samples. The overlapping diffraction signal in the 40°–45° range was resolved by rigorous peak deconvolution to separate the contributions from the FCC-PdCu(111) and B2-PdCu(110) reflections; $A_{FCC-111}$ and A_{B2-110} denote the deconvoluted integrated areas of these two individual sub-peaks, respectively. I_{B2-200} and I_{B2-110} are the peak intensity obtained from the standard JCPDF card.

2.8 Calculation of relative bonding strength of Pd-In (Pd-In RBS)

Firstly, deconvolution fitting was performed on the carbon peak and main peak of PdIn sample and Pd-Cu-In systems, including PdIn + Cu, PdCuIn, and PdCu + In. The bonding strength (BS) of Pd-In was calculated according to the following Eq. (2)

$$\text{BS (system)} = \frac{A_{\text{PdIn-111}}}{A_{\text{carbon}}} \quad (2)$$

where $A_{\text{PdIn-111}}$ is the peak area of PdIn(111) in the Pd-Cu-In samples and PdIn samples, A_{carbon} is the peak area of carbon.

To compare the BS values of each Pd-Cu-In systems, using PdIn

as the standard, the relative bonding strength of Pd-In (Pd-In RBS) was calculated according to the following Eq. (3)

$$\text{RBS (\%)} = \frac{\text{BS}_{\text{system}}}{\text{BS}_{\text{PdIn}}} \quad (3)$$

3 Results and discussion

3.1 Synthesis of Pd₄Cu₆In_x heterostructure alloy

Pd₄Cu₆In_x heterostructure alloys were synthesized via a seed-mediated two-step strategy. Uniform ultrathin Pd NSs with an average size of 18.8 ± 1.5 nm (Fig. S1 in the ESM) were first prepared according to a previously reported protocol [34, 35]. Subsequently, the Pd₄Cu₆In_x heterostructures were fabricated by employing the as-prepared Pd NSs as seeds, and Cu(acac)₂ and In(acac)₃ as precursors [33, 35–37]. The co-introduction of Cu and In did not alter the product morphology compared with the Cu-only sample (Fig. S2 in the ESM) [35]. Taking Pd₄Cu₆In_{0.50} as a representative sample, its structure was characterized by XRD, HRTEM, selected area electron diffraction (SAED), and EDS mapping. The low-magnification TEM image (Fig. 1(a)) shows uniform flat nanoparticles with a size of 8.1 ± 0.9 nm. The XRD results (Fig. 1(b)) reveal the coexistence of FCC-PdCu and FCC-PdIn solid solutions. The HRTEM image (Fig. 1(c)) exhibits lattice fringes of 0.218 and 0.198 nm, corresponding to the (111) plane of FCC-PdCu and the (200) plane of FCC-PdIn, respectively, which is consistent with the SAED pattern (Fig. 1(d)) and the additional HRTEM observations (Fig. S3 in the ESM). EDS mapping results (Fig. 1(e)) demonstrate the homogeneous distribution of Pd, together with the elemental segregation of Cu and In, confirming the formation of heterostructures between the PdCu and PdIn domains. EDS analysis yields a Pd:Cu:In molar ratio of 41.45:53.70:4.86 (Fig. S4 in the ESM). For the Pd₄Cu₆In_x series, the FCC-PdIn peaks intensify with increasing In contents (Fig. S5 in the ESM), demonstrating the controllable synthesis of PdCu/PdIn heterostructures with tunable phase composition. ICP-OES results (Table S2 in the ESM) show that the atomic ratios are close to the feeding ratios, indicating the complete reduction of the precursors.

To reveal the formation mechanism of Pd₄Cu₆In_{0.50} heterostructure, control experiments were performed. First, irregular Cu (PDF # 04-0836) particles were formed in the absence of Pd NSs and In(acac)₃, and In₂O₃ (PDF # 06-0416) [38] nanocubes with non-uniform sizes were formed without Pd NSs and Cu(acac)₂; regular Cu particles and In₂O₃ nanocubes were obtained by excluding Pd NSs only (Fig. S6 in the ESM). These results indicate that Cu²⁺ can be reduced by benzyl alcohol, whereas In³⁺ remains unreduced under the hydrothermal conditions (200 °C 12 h) [39]. Consistent with previous report [35], the PdCu alloy (Pd/Cu = 4:6, molar ratio) exhibited monodispersed nanoparticles (Fig. S2(a) in the ESM) with FCC solid solution phase (Fig. 1(b)). Second, Pd-In alloys maintained monodispersed nanosheets (Fig. S7 in the ESM) over a wide Pd:In molar ratio range (32:1 to 2:3), attributed to the high diffusivity of In [40], indicating that Cu incorporation caused the morphology change from Pd NSs to Pd₄Cu₆In_{0.50} nanoparticles [35]. The XRD results (Fig. S8(a) in the ESM) show that the Pd-In NSs retain FCC solid solution phase when the Pd:In molar ratio is greater than or equal to 2. With the increase of In content, all diffraction peaks shift to lower angles, indicating lattice expansion due to the incorporation of In (atomic

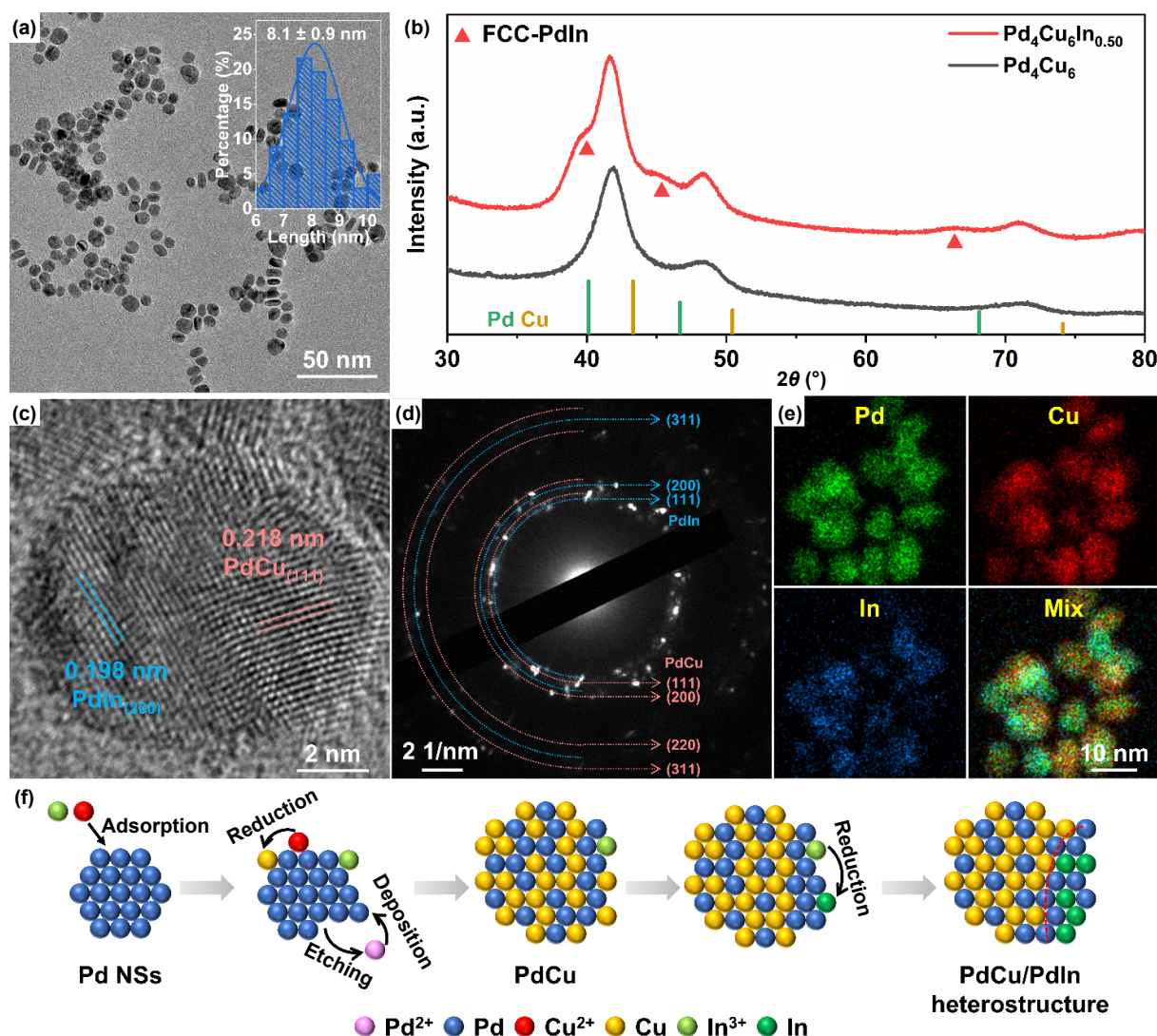


Figure 1 Structural characterization of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ heterostructure. (a) TEM image of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$, the inset shows the diagonal length distribution. (b) XRD patterns of Pd_4Cu_6 and $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$. (c) HRTEM image, (d) SAED pattern, and (e) EDS mapping of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$. (f) Schematic illustration showing the formation mechanism of PdCu/PdIn heterostructures of $\text{Pd}_4\text{Cu}_6\text{In}_x$ at the atomic level.

radius: 0.142 nm) into the Pd (atomic radius: 0.139 nm) lattice [41]. According to Vegard's law, the calculated Pd:In atomic ratio is close to the feeding ratio (Table S3 and Fig. S8(b) in the ESM), verifying complete reduction and alloying. When the Pd:In molar ratio was 1, the PdIn alloy exhibited ordered B2-PdIn IMCs (JCPDS # 73-8988) [41–43]. The HRTEM image (Fig. S9 in the ESM) shows a lattice fringe spacing of 0.228 nm corresponding to the (110) plane of B2-PdIn IMCs, and the SAED result (Fig. S9(c) in the ESM) confirms the ordered phase of PdIn NSs; the inevitable In_2O_3 formation is attributed to the oxidation of the ultrathin nanosheets, which is consistent with the XRD result (Fig. S8(a) in the ESM). EDS mapping (Fig. S9(d) in the ESM) shows uniform distribution of Pd and In, with a Pd:In molar ratio of 52.14:47.86 that is close to the feed ratio. When the Pd:In molar ratio was 2:3, B2-PdIn IMCs coexisted with In_2O_3 derived from the unreduced In precursor. These results suggest an autocatalytic surface reduction process for In precursor reduction, where *in situ* produced CO adsorbed on Pd NSs acts as a strong reducing agent for In^{3+} [35, 37], with a limited amount of reducible In. The exclusive formation of B2-PdIn IMCs (instead of Pd_3In , Pd_2In , or Pd_2In_3 IMCs) is governed by

thermodynamics and kinetics factors, as B2-PdIn IMCs have the lowest formation energy and the closest crystal structure to Pd [42].

To further elucidate the formation mechanism of the $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ heterostructure, time-dependent morphological and structural evolutions were tracked by TEM and XRD. Pd NSs gradually transformed into nanoparticles with increasing reaction time (Fig. S10 in the ESM). From 5 min to 2 h, the Pd diffraction peak shifted to higher angles, indicating the formation of PdCu alloy, consistent with the gradual disappearance of the nanosheet morphology. From 2 to 12 h, PdIn diffraction peaks appeared, indicating the reduction of In^{3+} to In^0 and subsequent alloying with Pd in PdCu alloy (Fig. S11(a) in the ESM). The complete disappearance of Pd peaks and appearance of PdIn peaks at high angles (Fig. S11(b) in the ESM) verified the sequential formation of PdCu and PdCu/PdIn heterostructure. The TEM and XRD analyses revealed the asynchronous reduction of Cu^{2+} and In^{3+} . Cu^{2+} is reduced first due to the much higher standard redox potential of Cu^{2+}/Cu (0.34 V vs. RHE) than that of In^{3+}/In (−0.34 V vs. RHE) [41]. Meanwhile, the Pd-In interaction exhibits a more negative formation energy (−0.521 eV·atom^{−1}) than Pd-Cu (−0.127 eV·atom^{−1}) and Cu-In

(-0.018 eV/atom $^{-1}$) [44], indicating a stronger Pd–In bonding tendency, which results in the coexistence of FCC–PdCu and FCC–PdIn and ultimately the formation of the ternary alloy heterostructure.

Based on the above analysis, a plausible formation mechanism of the PdCu/PdIn heterostructure was proposed, as schematically illustrated in Fig. 1(f). Pd NSs catalyze the oxidation of benzyl alcohol to benzaldehyde, which subsequently decarboxylates to benzene and CO adsorbed on Pd NSs [33, 35, 37]. Cu^{2+} and In^{3+} are co-adsorbed on Pd NSs. Owing to the higher standard redox potential of Cu^{2+}/Cu (0.34 V vs. RHE) than that of In^{3+}/In (-0.34 V vs. RHE) [41], Cu^{2+} is first reduced to Cu atoms, forming PdCu alloy through etching, deposition, and interatomic diffusion. Subsequently, adsorbed In^{3+} is reduced to In atoms via CO and Pd NSs-mediated autocatalytic surface reduction, forming PdIn alloy under prolonged high-temperature reaction conditions [37, 45]. The asynchronous reduction of Cu^{2+} and In^{3+} , together with the difference in binary formation energies between the respective elements, causes the formation of PdCu/PdIn heterostructures.

3.2 Effect of In content on the ordering degree

To explore the effect of In doping content on the ordering degree of

annealed $\text{Pd}_4\text{Cu}_6\text{In}_x$ ($\text{Pd}_4\text{Cu}_6\text{In}_x\text{-300}$), the as-synthesized $\text{Pd}_4\text{Cu}_6\text{In}_x$ nanocrystals were supported on Vulcan XC-72R carbon and annealed at 300 °C for 3 h in 5 vol.% H_2/Ar . The annealed products are uniformly dispersed on the carbon support without obvious aggregation (Fig. S12 in the ESM). The influence of In content on PdCu ordering can be preliminarily analyzed from the XRD patterns (Fig. 2(a)). The XRD patterns (Fig. 2(a)) reveal that when the In content is ≤ 7.0 at.% ($\text{Pd}_4\text{Cu}_6\text{In}_{0.75}\text{-300}$), all annealed products contain B2–PdCu IMCs (ICDD 01-078-4406) [46–48] but with distinct ordering degrees. Owing to the larger atomic radius of In (0.142 nm) compared with Pd (0.139 nm) and Cu (0.132 nm) [35, 41], the diffraction peaks shift to lower angles with increasing In contents, indicating lattice expansion induced by In diffusion into the B2–PdCu lattice (Fig. 2(b)). Further increasing In to 9.1 at.% ($\text{Pd}_4\text{Cu}_6\text{In}_{1.00}\text{-300}$) leads to the disappearance of the ordered phase, leaving only FCC–PdCu and FCC–PdIn solid solutions. In content has a significant impact on the ordering degree of $\text{Pd}_4\text{Cu}_6\text{In}_x\text{-300}$ samples. To fully illustrate the effect of In on PdCu ordering, the ordering degrees (Fig. S13 in the ESM) of $\text{Pd}_4\text{Cu}_6\text{In}_x\text{-300}$ were quantified by the area ratio of the superlattice diffraction peak (200) to the summed deconvoluted areas of the overlapping FCC–PdCu(111) and B2–PdCu(110) main peaks (Tables S4–S9 in

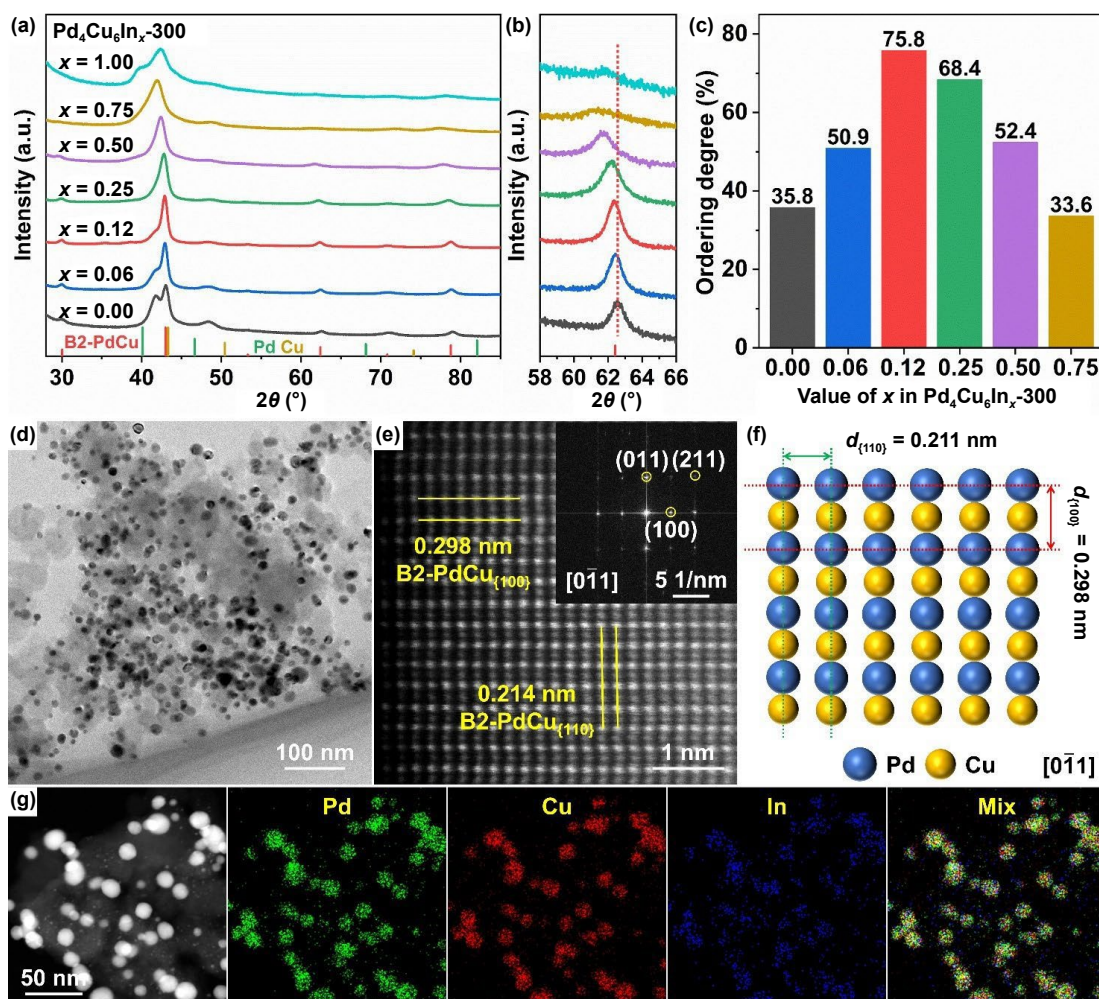


Figure 2 Structural characterization of $\text{Pd}_4\text{Cu}_6\text{In}_x\text{-300}$. (a) XRD patterns of $\text{Pd}_4\text{Cu}_6\text{In}_x\text{-300}$ samples with different In contents. (b) The enlarge patterns of (a) in 58° – 66° . (c) The “volcano-type” relationship between In content and the ordering degree of $\text{Pd}_4\text{Cu}_6\text{In}_x\text{-300}$. (d) TEM image and (e) aberration-corrected HAADF-STEM image of $\text{Pd}_4\text{Cu}_6\text{In}_{0.12}\text{-300}$ with the highest ordering degree, the inset is the FFT image. (f) The projection of B2–PdCu IMCs along the $[0\bar{1}1]$ direction [49]. (g) EDS mapping of $\text{Pd}_4\text{Cu}_6\text{In}_{0.12}\text{-300}$.

the ESM), and its dependence on In content was plotted in Fig. 2(c), showing a maximum at 1.2 at.% In ($\text{Pd}_4\text{Cu}_6\text{In}_{0.12}$ -300). Kinetically, In features a markedly lower melting point (157 °C) than Pd (1554 °C) and Cu (1085 °C) [50, 51]. As demonstrated in previous theoretical and experimental investigations, the introduction of low-melting-point metals including In, Ga and Sn can weaken metallic bonding and reduce vacancy formation energy, thereby lowering atomic diffusion barriers and accelerating the disorder-to-order phase transition of intermetallics [19, 52]. In line with these mechanisms, doped In atoms facilitate atomic diffusion and lower the diffusion barrier, thus promoting B2-PdCu IMCs formation. Thermodynamically, B2-PdIn IMCs (formation energy: $-0.521 \text{ eV}\cdot\text{atom}^{-1}$) are more stable than B2-PdCu IMCs (formation energy: $-0.127 \text{ eV}\cdot\text{atom}^{-1}$) [44], which suppresses PdCu ordering, as confirmed by the dominant B2-PdIn IMCs and Cu phases (PDF # 04-0836) in the In-rich $\text{Pd}_4\text{Cu}_6\text{In}_{4.00}$ -300 sample (Fig. S14 in the ESM). Consequently, the competing kinetic promotion and thermodynamic inhibition result in a typical “volcano-type” relationship between In content and the ordering degree of $\text{Pd}_4\text{Cu}_6\text{In}_x$ -300, with the optimal promotion effect at 1.2 at.% In.

Taking $\text{Pd}_4\text{Cu}_6\text{In}_{0.12}$ -300 (the sample with the highest ordering degree) as an example, its detailed structure was characterized by HAADF-STEM. The HRTEM image (Fig. S15(a) in the ESM) shows a lattice fringe of 0.307 nm was observed, which matches the (100) plane of B2-PdCu IMCs. The SAED pattern (Fig. S15(b) in the ESM) shows diffraction rings corresponding to B2-PdCu IMCs, which is in good agreement with the results of XRD and HRTEM. To further confirm the ordered structure, aberration-corrected HAADF-STEM image (Fig. 2(e)) reveals periodic intensity oscillations resulting from Z-contrast differences between Pd (a heavy element) and Cu (a light element) in the ordered lattice. The measured interplanar distances of 0.298 nm (100 plane) and 0.214 nm (110 plane) are consistent with the $[0\bar{1}1]$ projection of B2-PdCu IMCs (Fig. 2(f)). Superlattice reflections in the fast Fourier

transfer (FFT) image (inset of Fig. 2(e)) further confirm the ordered structure [53]. EDS mapping (Fig. 2(g)) shows a homogeneous distribution of Pd, Cu, and In without segregation. Due to its low melting point (157 °C) [50, 51] and high diffusivity, In is partially dispersed on the carbon support. The atomic ratio of Pd:Cu:In is 42.08:56.69:1.23 (Fig. S16 in the ESM), which is consistent with the feeding ratio. Importantly, the elemental composition remains unchanged before and after annealing, indicating that annealing only regulates the ordering degree without altering the overall elemental content.

3.3 Time and temperature dependence of structural evolution in annealed $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ and annealed Pd_4Cu_6

To thoroughly investigate the structural evolution and the effect of In on the ordering of $\text{Pd}_4\text{Cu}_6\text{In}_x$ ternary heterostructures during annealing, $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ (with identifiable phase separation signals) was used as the experimental example and Pd_4Cu_6 as the control, XRD and HRTEM analyses were conducted on the products annealed at 300 °C for different durations. After annealing, the sample exhibits a slight increase in size with no obvious agglomeration observed (Figs. S17 and S18 in the ESM). For Pd_4Cu_6 annealed at 300 °C (Fig. S19 in the ESM), the main peak (41.8°) splits into two peaks corresponding to FCC-PdCu and B2-PdCu IMCs. With increasing annealing time, the intensity of the FCC-PdCu peak weakens, while the intensity of the B2-PdCu IMCs peak intensifies, indicating a progressive increase in the proportion of B2-PdCu IMCs. The ordering degree reaches a value of 49.5% at 5 h; further extending the annealing time to 7 h only slightly raises the ordering degree to 51.0%, with negligible variation observed on the curve (Fig. 3(b) and Fig. S20 in the ESM). For $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ (Fig. 3(a)), with increasing annealing time, the intensity of the PdIn peak weakens, and the PdCu main peak shifts to higher angle, consistent with the calculated ordering degree (Fig. 3(b) and Fig. S21 in the ESM). At 5 h, the PdIn peaks disappear and the B2-

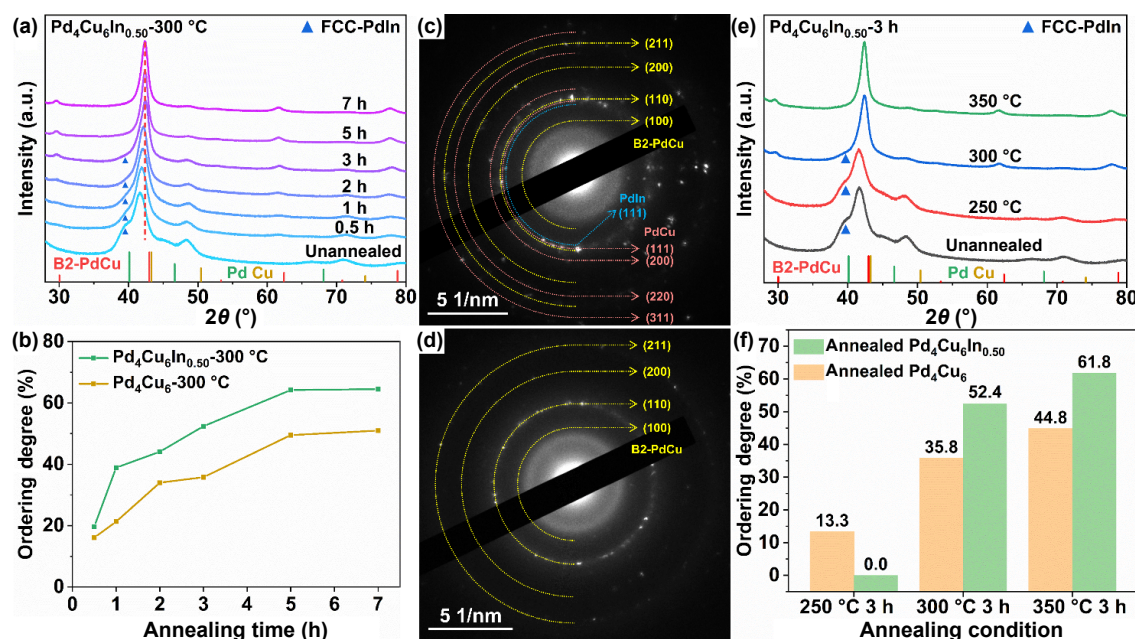


Figure 3 Evolution of phase and ordering degree of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ and Pd_4Cu_6 under different annealing conditions. (a) XRD patterns of the $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ annealed at 300 °C for various times. (b) Ordering degrees of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ and Pd_4Cu_6 annealed at 300 °C for different times. (c) and (d) SAED patterns of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ annealed at 300 °C for 3 and 5 h, respectively. (e) XRD patterns of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ annealed at different temperatures for 3 h. (f) Ordering degrees of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ and Pd_4Cu_6 annealed at different temperatures for 3 h.

PdCu IMCs(110) peak exhibits a symmetrical profile. No obvious changes are observed at 7 h, with the maximum ordering degree reaching 64.2% [54]. A comparison of the ordering degrees of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ and Pd_4Cu_6 annealed at 300 °C (Fig. 3(b)) confirms that the addition of In facilitates PdCu ordering. HRTEM was further employed to characterize the lattice structure. Lattice fringes of 0.214 nm (Fig. S22(b) in the ESM) matching the (110) plane of B2-PdCu IMCs are observed, together with 0.217 nm fringes corresponding to the (111) plane of the FCC-PdCu solid solution (Fig. S22(c) in the ESM) from incomplete ordering, consistent with the XRD and SAED results (Fig. 3(c)), indicating the coexistence of B2-PdCu IMCs, FCC-PdCu, and FCC-PdIn phases in $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ annealed at 300 °C for 3 h. After annealing for 5 h, the HRTEM image (Fig. S23(b) in the ESM) shows a lattice fringe of 0.212 nm assigned to the (110) planes of B2-PdCu IMCs. The SAED pattern (Fig. 3(d)) exhibits only B2-PdCu IMC-related diffraction rings, verifying a fully maximized ordering degree. EDS mapping (Fig. S23(c) in the ESM) reveals that In is partially distributed on the carbon support, which is ascribed to the solidification of diffused In during cooling. Overall, In diffusion and PdCu ordering occur simultaneously at 300 °C. A comparison of ordering degrees (Fig. 3(b)) clearly demonstrates that In doping promotes the ordering of PdCu.

To further investigate the mechanism of In diffusion and PdCu ordering during annealing of the $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$, XRD and HRTEM analyses were performed at various temperatures with a fixed annealing time of 3 h, using Pd_4Cu_6 as a control. After annealing, the sample exhibits a slight increase in size with no obvious agglomeration observed (Fig. S24 in the ESM). As shown in Fig. 3(e), the sample annealed at 250 °C ($\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ -250 °C-3 h) yields an XRD pattern identical to that of the unannealed $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$, with no superlattice peak of B2-PdCu IMCs, consistent with the coexistence of FCC-PdIn and FCC-PdCu phases (Figs. S25(a)-S25(c) in the ESM). In contrast to the ordered phase in Pd_4Cu_6 -250 °C-3 h (Fig. S26 in the ESM), this indicates a low annealing temperature (250 °C) is insufficient to cleave Pd-In bonds, inhibiting atomic diffusion and the formation of B2-PdCu IMCs. This further indicates that the cleavage of Pd-In bond is essential to render In diffusible and promote PdCu ordering. Increasing the annealing temperature to 300 °C leads to obvious B2-PdCu peaks and weak FCC-PdIn peaks. Further heating to 350 °C eliminates PdIn peaks, with a symmetric B2-PdCu IMCs(110) peak, indicating a maximum ordering degree of 61.8%, which is comparable to that of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ annealed at 300 °C for 5 h. For Pd_4Cu_6 , the main peak splits into FCC-PdCu and B2-PdCu IMCs signals, with the ordering degree increasing with temperature (Fig. S26 in the ESM). Figure 3(f) illustrates the relationship between the ordering degree of the annealed samples and the annealing temperature. At low temperatures (250 °C), unbroken Pd-In bonds inhibit atomic diffusion and the formation of B2-PdCu IMCs; at elevated temperatures (≥ 300 °C), In's low melting point (157 °C) enhances atomic diffusion and vacancy generation, thereby promoting PdCu ordering [19, 51, 52]. These results reveal that the ordering process of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ involves three steps: Pd-In bond cleavage, In diffusion, and PdCu ordering. The cleavage of Pd-In bonds and the formation of diffusible In species are essential for In to promote PdCu ordering.

3.4 Effect of relative bonding strength of Pd-In on the ordering degree

To better understand the effect of Pd-In bond cleavage on PdCu

ordering, the Pd-In RBS of unannealed samples is used as an indicator to evaluate the tendency of Pd-In bond cleavage. Taking $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$ as an experimental example, three Pd-Cu-In samples with identical Pd:Cu:In ratio but different Pd-In RBS were synthesized by adjusting the precursor feeding sequence, namely: PdCuIn (simultaneous addition of In and Cu precursors), PdIn + Cu (PdIn formed first, then Cu added), and PdCu + In (PdCu formed first, then In added). Different feeding sequences result in different crystal structures, which is consistent with a previous report on Ag-promoted PdCu ordering [55]. The correlation between Pd-In RBS of unannealed samples and the ordering degree of annealed samples was then analyzed.

PdIn (Pd:In = 8:1, molar ratio) forms monodispersed nanoplates (Fig. S28(a) in the ESM) with an FCC solid solution phase (Fig. 4(a)), while PdCu (Pd:Cu = 4:6, molar ratio) exhibits monodispersed nanoparticles (Fig. S28(b) in the ESM) with an FCC structure (Fig. 4(a)) [35]. The PdIn + Cu product (Fig. S28(c) in the ESM) has increased thickness [35] and non-uniform size compared with PdIn (Fig. S28(a) in the ESM), and the XRD pattern (Fig. 4(a)) reveals well-crystallized FCC-PdIn (39.6°) and poorly crystallized FCC-PdCu (42.5°). In contrast, the PdCu + In product (Fig. S28(d) in the ESM) retains a PdCu-like morphology (Fig. S28(b) in the ESM), with poorly crystallized FCC-PdIn (39.6°) and FCC-PdCu (42.1°) (Fig. 4(a)). The lower crystallinity of PdCu + In relative to PdCu arises from In alloying with Pd, which promotes Pd atom migration and induces partial amorphization. To further quantify the bonding strength of Pd-In in Pd-Cu-In systems, the relative bonding strength of Pd-In (Pd-In RBS) is employed as a descriptor. Based on deconvolution fitting results (Fig. 4(b)) of the carbon peak and the main peak (35°-55°) for the PdIn reference and Pd-Cu-In samples, the Pd-In RBS was quantified using the area ratio of PdIn₁₁₁ peak to the carbon peak, normalized to the PdIn reference. The Pd-In RBS of the samples follows the order: PdIn + Cu > PdCuIn > PdCu + In (Fig. 4(d)).

Subsequently, the Pd-Cu-In nanocrystals were loaded onto Vulcan XC-72R carbon and annealed at 300 °C for 3 h in 5 vol.% H_2/Ar . The annealed nanocrystals are uniformly dispersed on the carbon substrate without obvious aggregation (Fig. S29 in the ESM). The XRD patterns (Fig. 4(c)) confirm the presence of B2-PdCu IMCs in all annealed products, with varying superlattice peak intensities. A distinct PdIn signal remains in annealed PdIn + Cu, indicating incomplete cleavage of Pd-In bonds at high temperature. The ordering degrees of the annealed samples were calculated from XRD patterns (Fig. S30 in the ESM). As shown in Fig. 4(d), the ordering degrees of the annealed samples exhibit a negative correlation with the Pd-In RBS of the unannealed sample: the PdIn + Cu sample, which has the strongest Pd-In bonds, displays the lowest ordering degree after annealing. These results demonstrate that the Pd-In RBS strongly regulates the cleavage of Pd-In bond, In diffusion, and PdCu ordering during annealing.

Based on the above findings, Fig. 5 illustrates the In-mediated PdCu ordering process in the PdCu/PdIn heterostructure: First, the cleavage of Pd-In bonds at elevated temperatures renders In atoms diffusible. Second, the higher diffusivity of In compared with Pd and Cu induces abundant lattice vacancies, which accelerate the atomic rearrangement of Pd and Cu to form highly ordered structures. Thus, it can be inferred that the addition of In readily generates vacancies, which lowers the energy barrier for the ordering transition. Meanwhile, the competing interaction between kinetic promotion (due to In's lower melting point) and

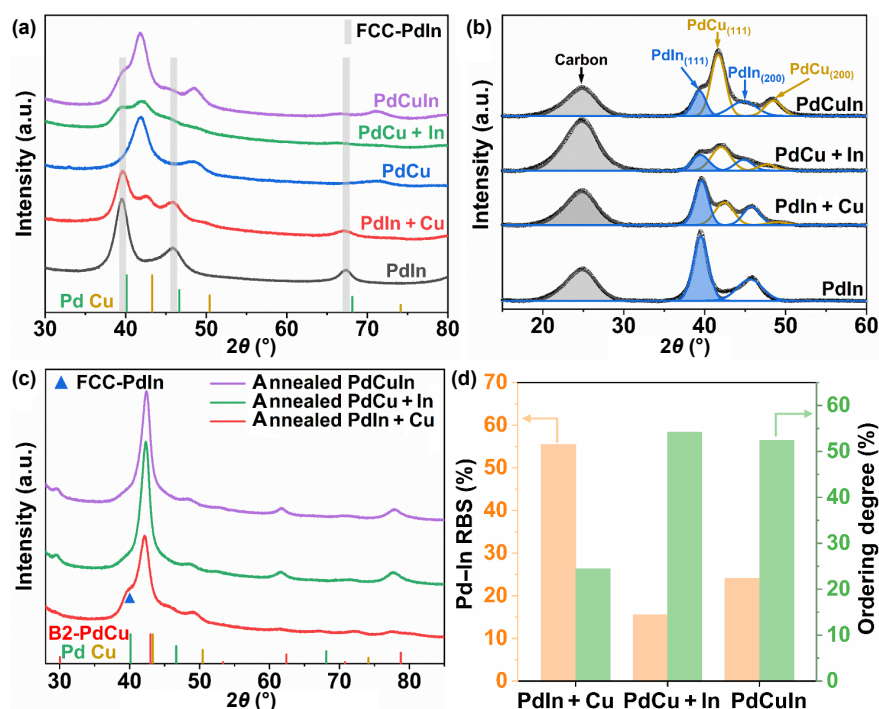


Figure 4 Phase structure and structure-ordering correlation of Pd-Cu-In nanocrystals with identical Pd:Cu:In ratio. (a) XRD patterns of the synthesized PdIn, PdIn + Cu, PdCu, PdCu + In, and PdCuIn. (b) Deconvoluted XRD patterns of the carbon peak and main peak of the PdIn, PdIn + Cu, PdCu + In, and PdCuIn samples. (c) XRD patterns of the Pd-Cu-In samples annealed at 300 °C for 3 h. (d) The correlation between relative bonding strength of Pd-In (Pd-In RBS) of unannealed samples and ordering degree of annealed samples.

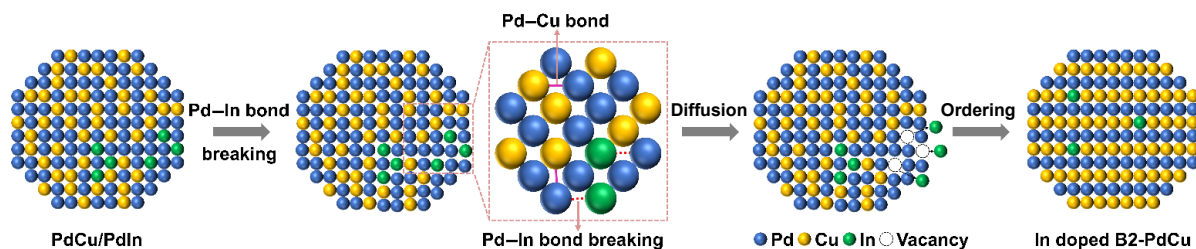


Figure 5 Schematic illustration of PdCu disorder-order transition promoted by In doping in PdCu/PdIn heterostructure of $\text{Pd}_4\text{Cu}_6\text{In}_x$ at the atomic level.

thermodynamic inhibition (due to the higher stability of B2-PdIn than B2-PdCu) induced by In doping, results in a distinct “volcano-type” relationship between In doping content and the ordering degree of $\text{Pd}_4\text{Cu}_6\text{In}_x$ -300 samples.

4 Conclusion

In conclusion, this work comprehensively elucidates the intricate mechanism of In-induced PdCu ordering in PdCu/PdIn heterostructures. $\text{Pd}_4\text{Cu}_6\text{In}_x$ heterostructures with varying In contents were synthesized via a seed-mediated method. Annealing experiments reveal a typical “volcano-type” relationship between In content and the ordering degree of $\text{Pd}_4\text{Cu}_6\text{In}_x$ -300, with the strongest ordering promotion at 1.2 at.% In, which reflects the competitive interplay between kinetic promotion and thermodynamic inhibition effect. Annealing results confirm that In promotes PdCu ordering through two key steps: cleavage of Pd-In bonds to release diffusible In atoms, and the high diffusivity of In inducing lattice vacancies that accelerate the ordered rearrangement of Pd and Cu atoms. Notably, diffusible In is essential for modulating PdCu ordering, and a clear negative correlation exists between Pd-In RBS and the ordering degree of the annealed

samples. This study provides a new theoretical basis for understanding Pd-Cu-In atomic interactions and offers practical guidance for the rational design of highly ordered Pd-based intermetallics.

Electronic Supplementary Material: Supplementary material (TEM and size distribution of Pd NSs, TEM and XRD of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$, HRTEM, EDS and time-dependent evolution of $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$, TEM and XRD of control experiments (without Pd NSs or Cu precursor), TEM and XRD deconvolution of $\text{Pd}_4\text{Cu}_6\text{In}_x$ -300, pre-/post-annealing TEM and XRD of $\text{Pd}_4\text{Cu}_6\text{In}_{4.00}$, HRTEM, SAED and EDS of $\text{Pd}_4\text{Cu}_6\text{In}_{0.12}$ -300, time- and temperature-dependent morphology-structure evolution and XRD deconvolution of Pd_4Cu_6 & $\text{Pd}_4\text{Cu}_6\text{In}_{0.50}$, pre-/post-annealing TEM and XRD deconvolution of Pd-Cu-In with different precursor feeding sequences) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908962>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary

Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Q. Q. R.: Conceptualization, investigation, data curation, formal analysis, visualization, and writing – original draft. L. X. S.: Conceptualization, data curation, writing – review & editing. W. B. Z.: Data curation, writing – review & editing. S. Y. W.: Visualization. A. A.: Visualization. S. H.: Resources, supervision, project administration, funding acquisition, writing – review & editing.

Use of AI statement

None.

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