Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

1. Quantitative Analysis of Atomic Structures

Quantitative analysis of atomic structures was carried out by Warren-Cowley chemical short-range order (CSRO) and structure factor (Fig. S1 - S3). CSRO has been widely used to quantify the degree of mixing tendency towards alloy system. Positive CSRO indicates a segregated or separated phase systems; the more separated structure the larger CSRO (core/shell > AgPd > CuPt). It becomes negative for homogeneous (CuPd) and alternatively ordered structure along (100) direction (PdPt). However, CSRO is not enough to distinguish all structures, for example in solid, it is zero for both random mixing and (111) ordering for 1:1 composition. Moreover, it depends on the particle size even for the same type of ordering.

Further classification was done with the structure factor, which can be measured by scattering or diffraction experiments. Structure factors for alternatively ordered structures (PdPt and CuPt) shows clear signals corresponding to (111) and/or (100) ordering. (100) ordering peak appears in structure factor of PdPt (the $L1_0$ structure), and (100) and (111) ordering peaks are observed for CuPt (the multi-shell structure). Core/shell structures are indistinguishable with the single element particles as two elements are completely separated. Structures having some degree of randomness show weakened oscillation amplitude in 2.9 – 4.2 Å, which corresponds to the range of the bond length to the lattice constant (i.e. between the first and second neighbors). It is interesting that, for CuPd, very broad peak appears between wave lengths corresponding to the lattice constant ((2) in Figure 5) and bond length ((3) in Figure 5); a signal of shorter wave length than the shortest alternative ordering length (i.e. (100) ordering) appears.

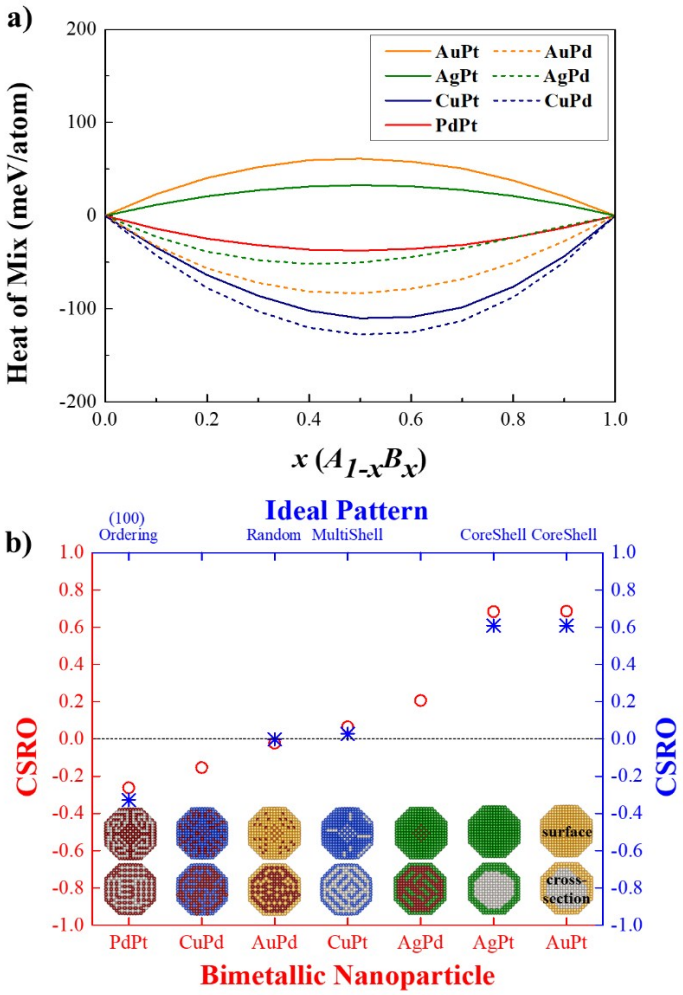

Fig. S1 a) Heat of mix for various FCC bulk alloys as a function of fraction of element *B* (= Pt, Pd). The results were calculated for a disordered solid solution by the EAM model. Au-Pt and Ag-Pt alloys showed positive heat of mix (endothermic) in all compositions, whereas other combinations exhibited negative values (exothermic). b) Warren-Cowley chemical short-range order (CSRO) parameter and predicted atomic structures of Pt and Pd based TOh nanoparticles with $A_{827}B_{827}$. CSRO value ranges from –1 to 1. CSRO parameters of four ideal mixing structures are also displayed as references (Top-right axis, asterisk). Pt atoms are in grey, Pd in red, Au in yellow, Ag in green and Cu in blue.

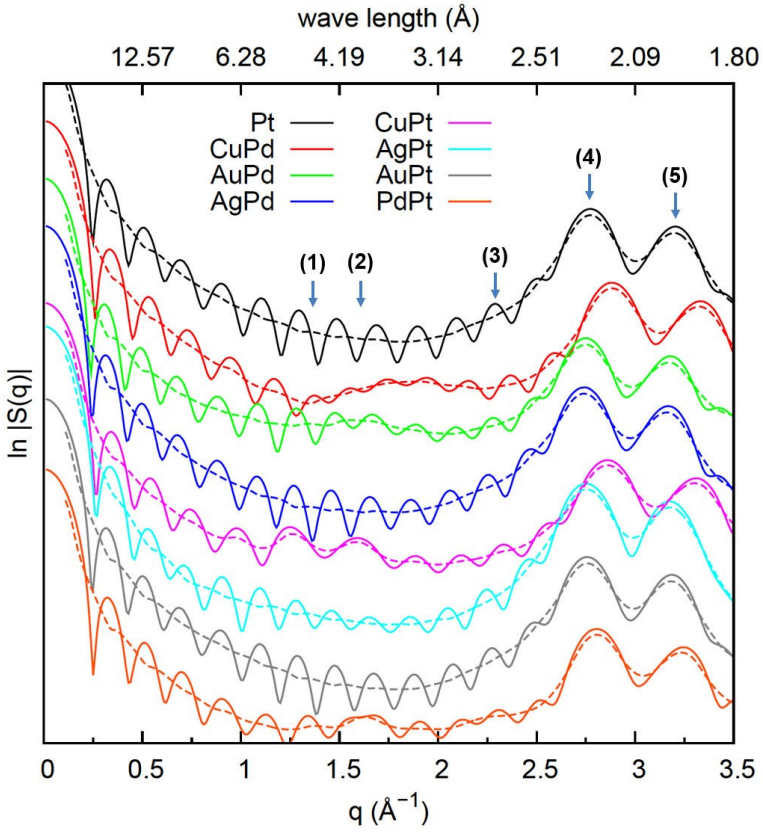

Fig. S2 Structure factors of bimetallic TOh 1654 particles with $A_{827}B_{827}$. The black one for Pt_{1654} is shown as a reference. Arrows point wave numbers corresponding to (1) 2×d(111), (2) 2×d(100), (3) d_{bond}, (4) d(111) and (5) d(100). Strong peak appears at (1) for (111)-order, and at (2) and (3) for (100)-order. Oscillation amplitude between (1) and (3) is reduced for random mixing (Supporting information). Oscillation period corresponds to the size of particles (~ 3.5 nm). Dashed lines are values averaged over oscillation period.

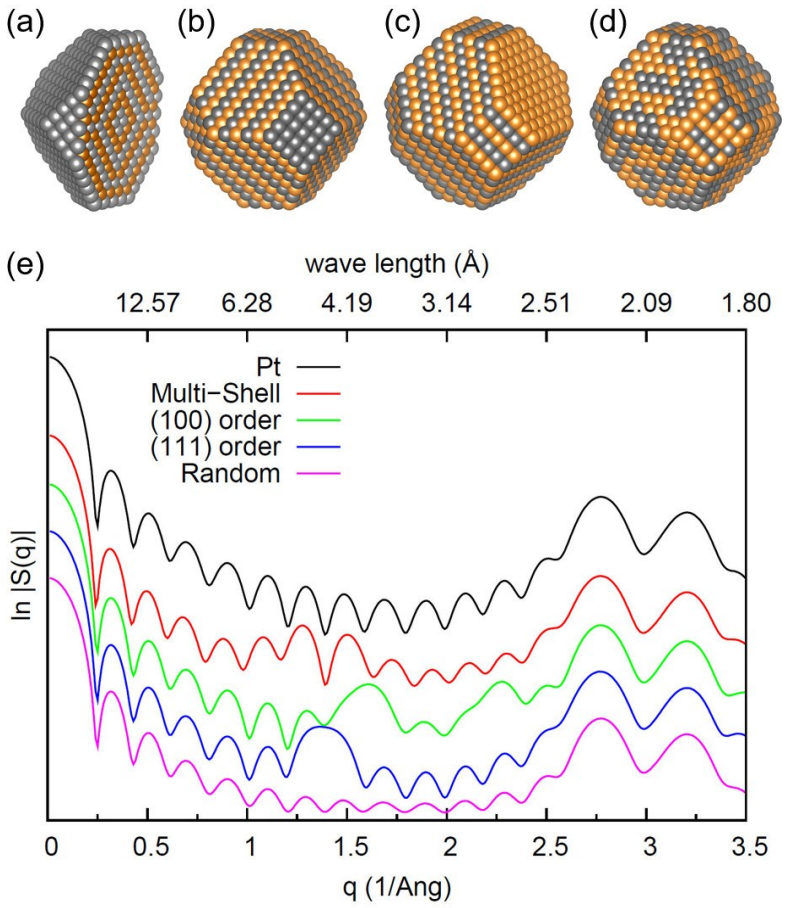

Fig. S3 Atomic structures and structure factor of unrelaxed ideal ordering structures. (a) multi-shell: (b) (100) ordering: (c) (111) ordering: (d) random

2. Detail of Bond Energy Model

For FCC bimetallic particles, the number of each bond type and atoms hold following relations;

$$6M_A = N_{AA} + \frac{1}{2}N_{AB} + N_A^{bb}$$

$$6M_B = N_{BB} + \frac{1}{2}N_{AB} + N_B^{bb}$$

$$N_{tot} = N_{AA} + N_{AB} + N_{BB} = 6M_A + 6M_B + N_A^{bb} + N_B^{bb}$$

M_α is the numbers of α (*A* or *B*) atoms; $N_{\alpha\beta}$ is the number of α-β bonds; N_α^{bb} is the number of broken-bonds of atom α. The total energy can be written in bond energy model as below.

$$\begin{aligned} E_{tot} &= N_{AA}\varepsilon_{AA} + N_{BB}\varepsilon_{BB} + N_{AB}\varepsilon_{AB} + N_A^{bb}\sigma_A + N_B^{bb}\sigma_B \\ &= 6M_A\varepsilon_{AA} + 6M_B\varepsilon_{BB} + N_{AB}\left(\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})\right) - N_A^{bb}(\varepsilon_{AA} - \sigma_A) - N_B^{bb}(\varepsilon_{BB} - \sigma_B) \\ &= -E_{coh}(A) - E_{coh}(B) + N_{AB}\varepsilon + N^{bb}\varepsilon_B^{bb} + N_A^{bb}\left(\varepsilon_A^{bb} - \varepsilon_B^{bb}\right) \end{aligned}$$

$E_{\mathrm{coh}}(A) = -6M_A\varepsilon_{AA}$ is the cohesive energy of element *A*, $\varepsilon_A^{bb} = -(\varepsilon_{AA} - \sigma_A)$ is the broken-bond energy of *A*, and $\varepsilon = \varepsilon_{AB} - 1/2(\varepsilon_{AA}+\varepsilon_{BB})$ is the energy of mix.

Table S1 Bond energies (ε_{AA}, eV), surface energies (γ, eV/atom) and broken bond energies (ε_A^{bb}, eV) calculated by the EAM model.

	Ag	Au	Cu	Pd	Pt
ε_{AA}	-0.475	-0.655	-0.590	-0.652	-0.962
γ_{100}	0.525	0.539	0.585	0.858	0.909
$(4\varepsilon_A^{bb})$	(0.529)	(0.529)	(0.591)	(0.866)	(0.893)
γ_{111}	0.400	0.389	0.447	0.656	0.658
$(3\varepsilon_A^{bb})$	(0.397)	(0.397)	(0.443)	(0.650)	(0.670)
$\sigma_A/\varepsilon_{AA}$	0.721	0.798	0.750	0.668	0.768

ε_A^{bb}	0.132	0.132	0.148	0.217	0.223

3. Atomic mixing patterns of bimetallic nanoparticles

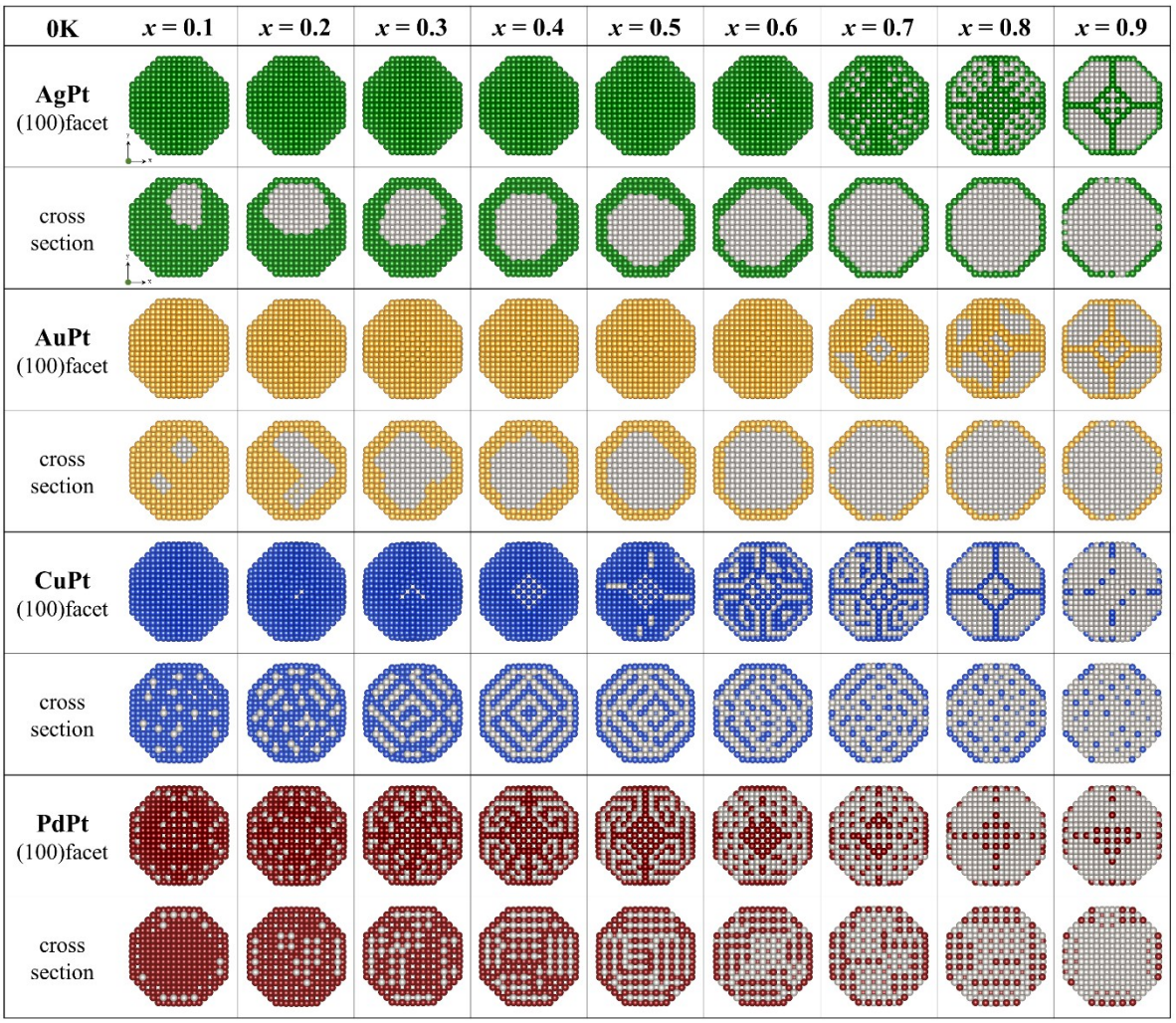

Fig. S4 Atomic mixing patterns of A_xPt_{1-x} binary systems at 0K.

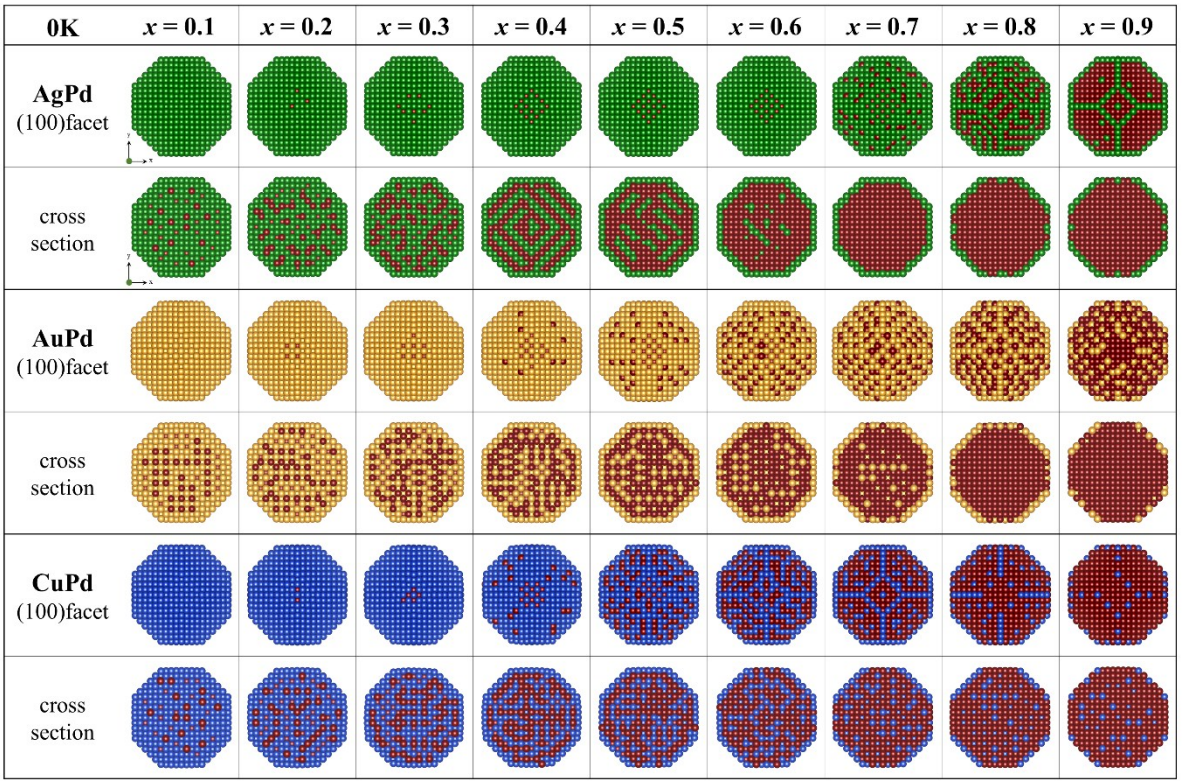

Fig. S5 Atomic mixing patterns A_xPd_{1-x} binary systems at 0K.

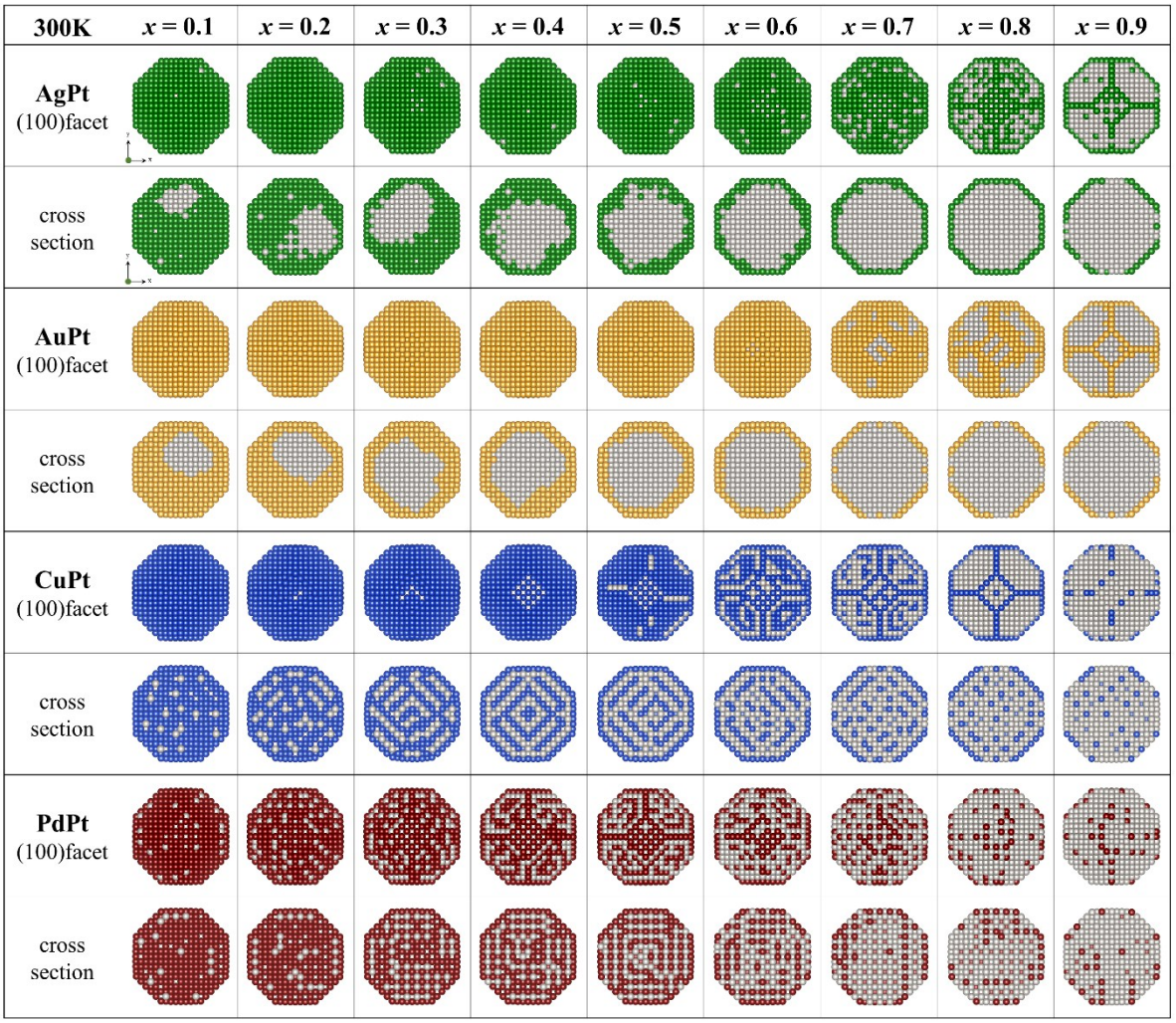

Fig. S6 Atomic mixing patterns A_xPt_{1-x} binary systems at 300K.

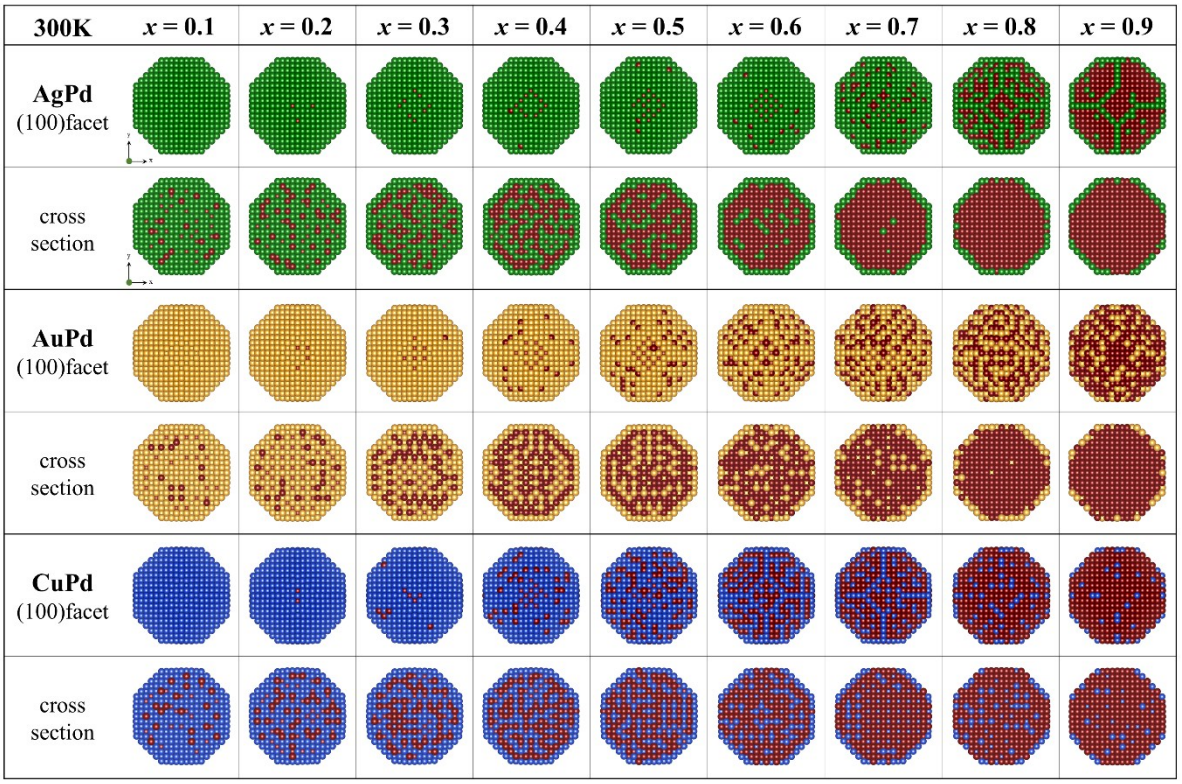

Fig. S7 Atomic mixing patterns A_xPd_{1-x} binary systems at 300K.

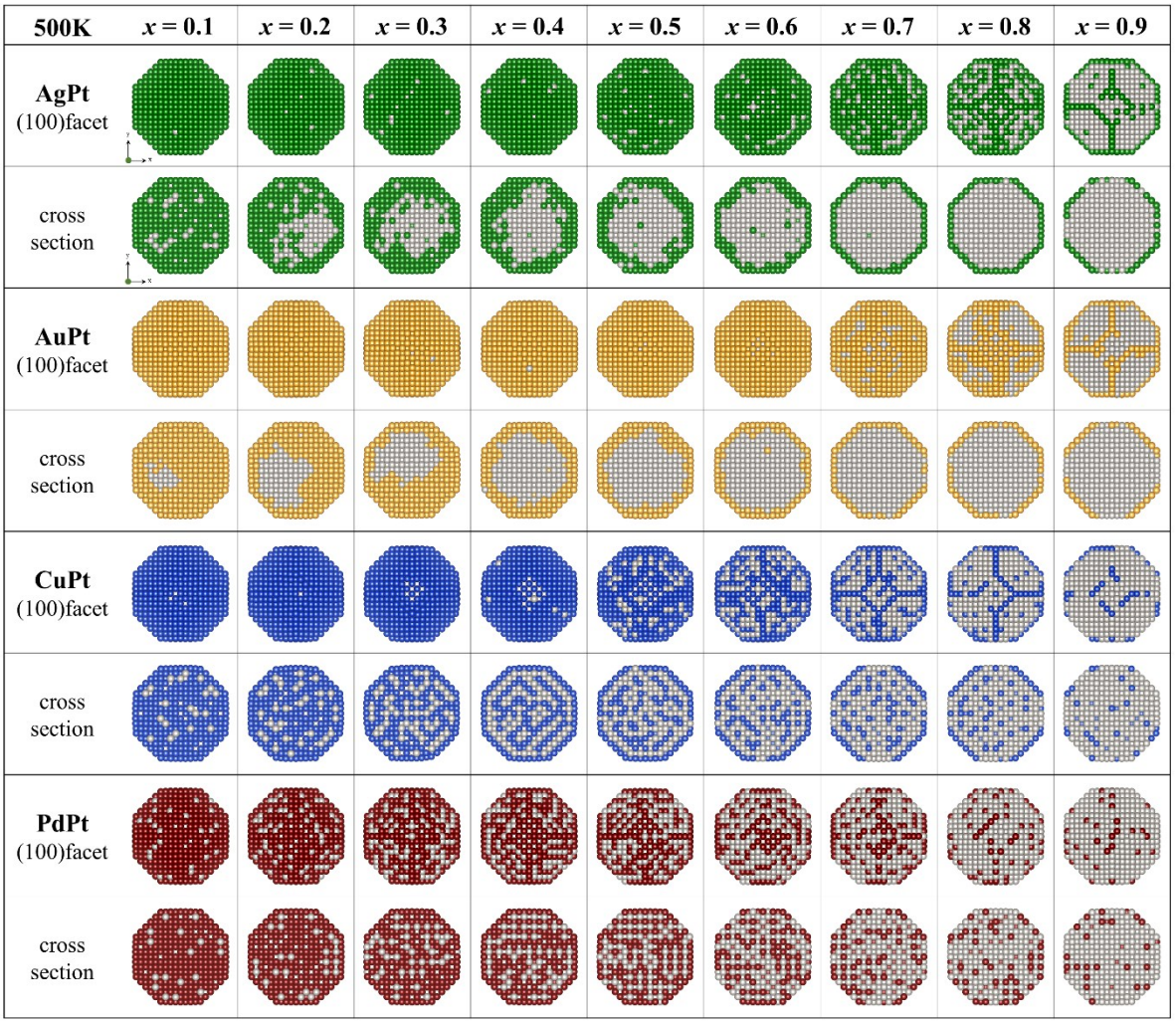

Fig. S8 Atomic mixing patterns A_xPt_{1-x} binary systems at 500K.

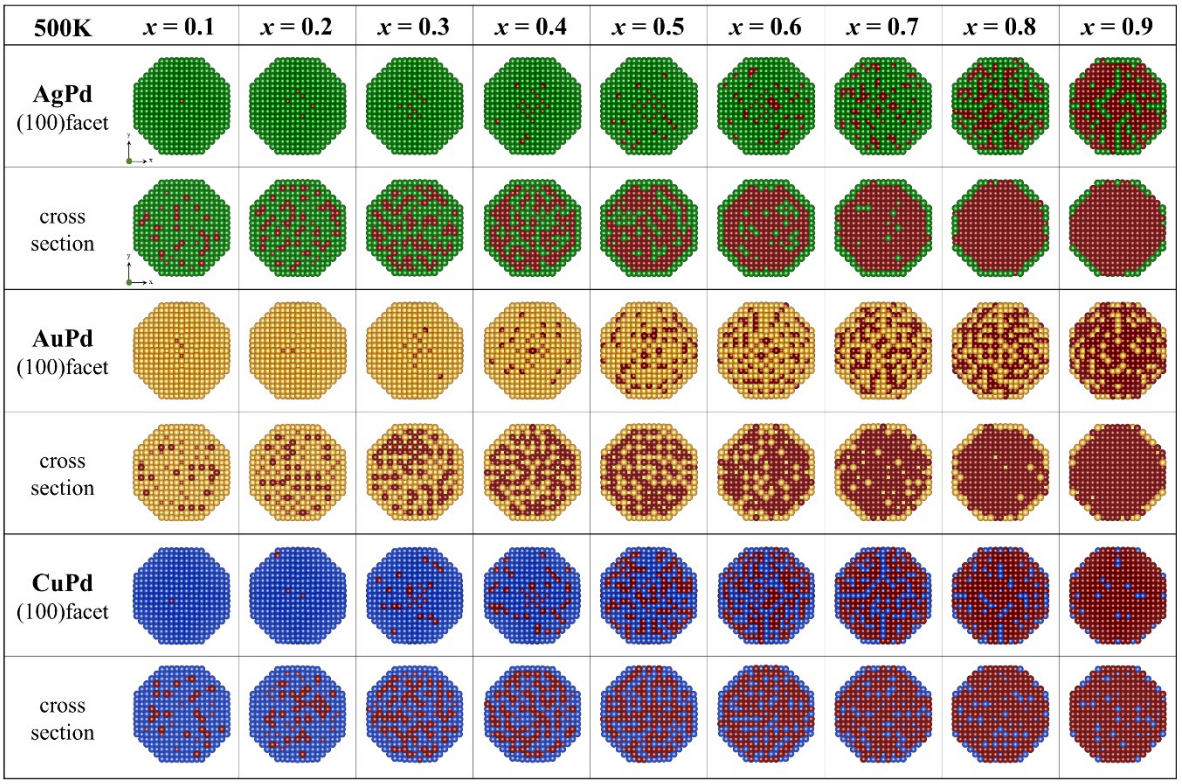

Fig. S9 Atomic mixing patterns A_xPd_{1-x} binary systems at 500K.