Electronic Supplementary Information

Manipulating morphology and composition in colloidal heterometallic nanopods and nanodendrites

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A note on particles sizes

In this work, nanopods and nanodendrites have been assessed for mean size and size distribution. Nanopods are defined here as having more than 2 arms. In these particles, the size represents a measurement of the longest arm from particle centre to the arm-end (and in the size distribution the x-axis label is 'Arm length'). For pseudospheres and (near-)nanodendrite cases, a spherical shape was assumed and the diameter was measured (in the size distribution the x-axis label is 'Size'). In Fig. S16(c) and (d), a mixture containing both nanopods and nanodendrites is analyzed. The size distribution of the nanopods is given in (c) and that of the nanodendrites is given in (d). Throughout, $N = 100$ unless otherwise stated.

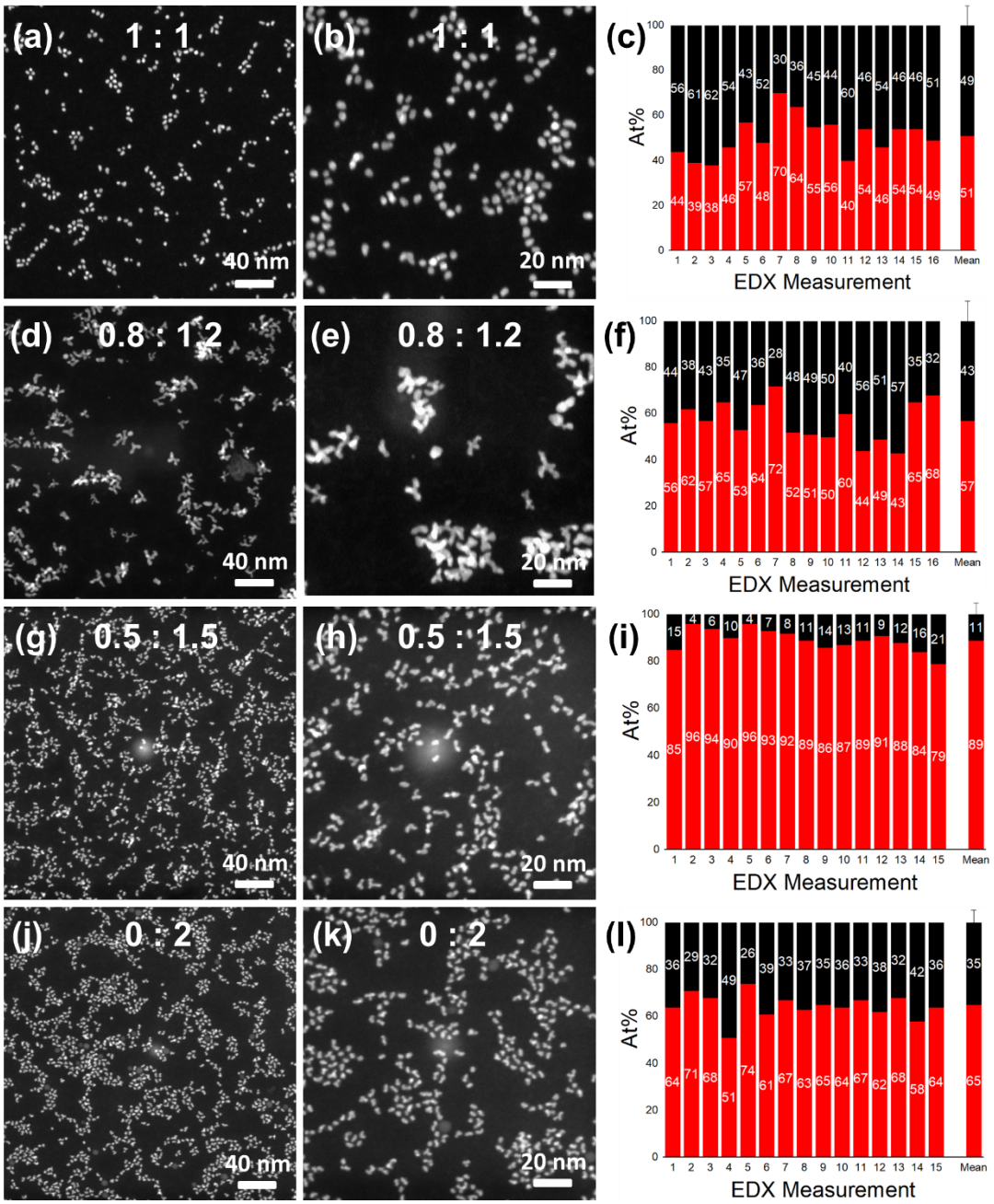

Fig. S1. Representative HAADF images of Pt/Fe NPs synthesized at 250 ˚C using OA:OAm volume ratios of (a)-(b) 1:1, (d)-(e) 0.8:1.2, (g)-(h) 0.5:1.5, (j)-(k) 0:2 (total volume in each case 2 mL); (c), (f), (i), (l) STEM EDX analysis of 15 randomly selected regions, alongside the corresponding mean composition (including the standard deviation in the 15 readings), in At% (Fe red, Pt black).

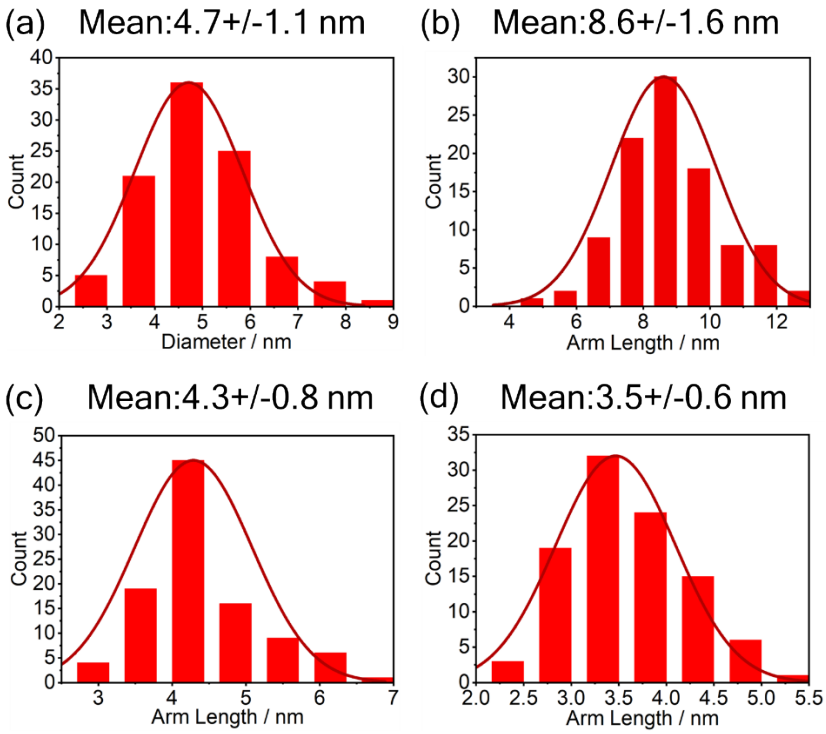

Fig. S2. Size distributions and mean sizes with standard deviations for Pt/Fe NPs shown in Fig. 1 of the main paper. Synthesis at 250 ˚C using OA:OAm volume ratios of (a) 1:1, (b) 0.8:1.2, (c) 0.5:1.5, (d) 0:2 (total volume in each case 2 mL). In (d), only heterobimetallic NPs are included, with monometallic Fe-based pseudospheres being excluded (see Fig. S6).

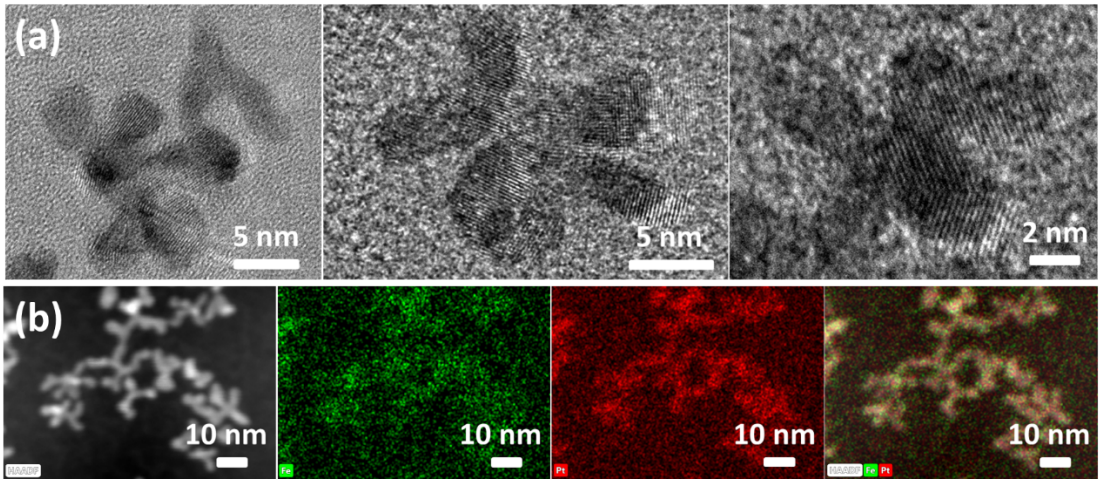

Fig. S3. (a) Representative HRTEM analyses of Pt/Fe NPs synthesized at 250 ˚C using OA:OAm volume ratios of 0.8:1.2; (b) Corresponding STEM HAADF and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps.

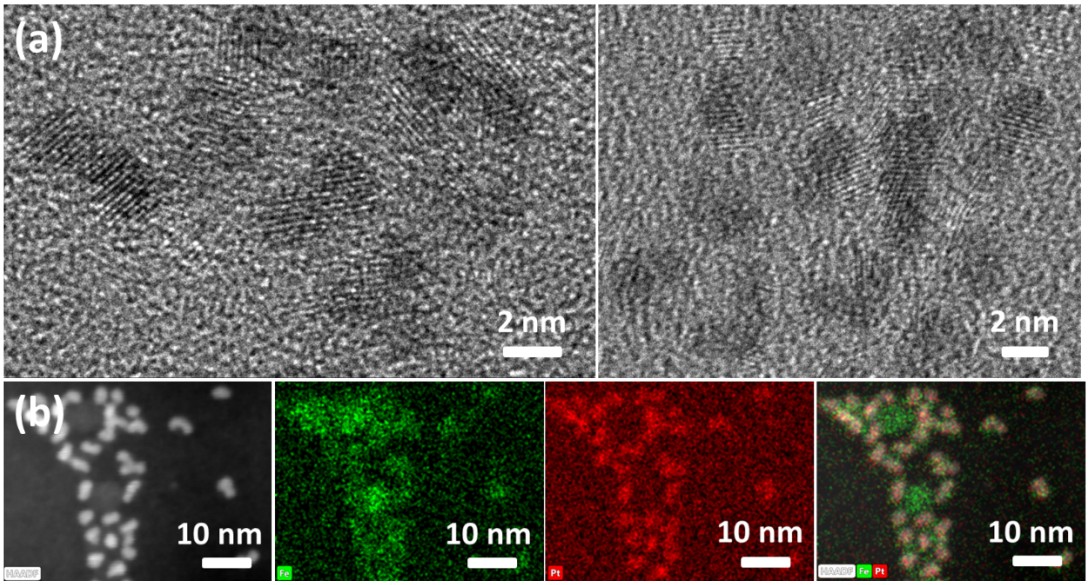

Fig. S4. (a) Representative HRTEM analyses of Pt/Fe NPs synthesized at 250 ˚C using an OA:OAm volume ratio of 0:2; (b) Corresponding STEM HAADF and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps, highlighting the monometallic nature of the pseudospheres formed in this system.

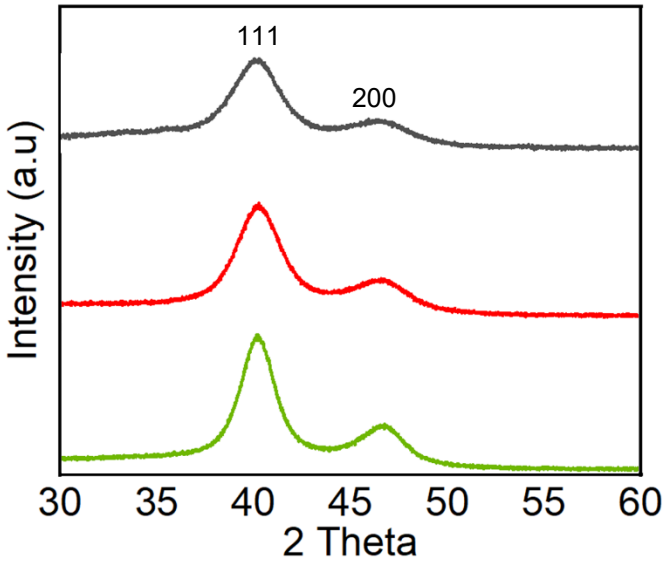

Fig. S5. Powder X-ray diffraction patterns of Pt/Fe NPs synthesized using 1:1 Pt:Fe and 0.8:1.2 mL OA:OAm at 250 ˚C for 30 mins (black); using 2:1 Pt:Fe and 0.5:1.5 mL OA:OAm at 250 ˚C for 30 mins (red); using 2:1 Pt:Fe and 0.5:2 mL OA:OAm at 300 ˚C for 30 mins (green).

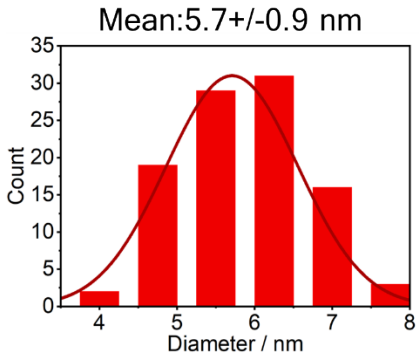

Fig. S6. Size distribution of exclusively the Fe-based pseudospheres made at 250 ˚C using an OA:OAm volume ratio of 0:2.

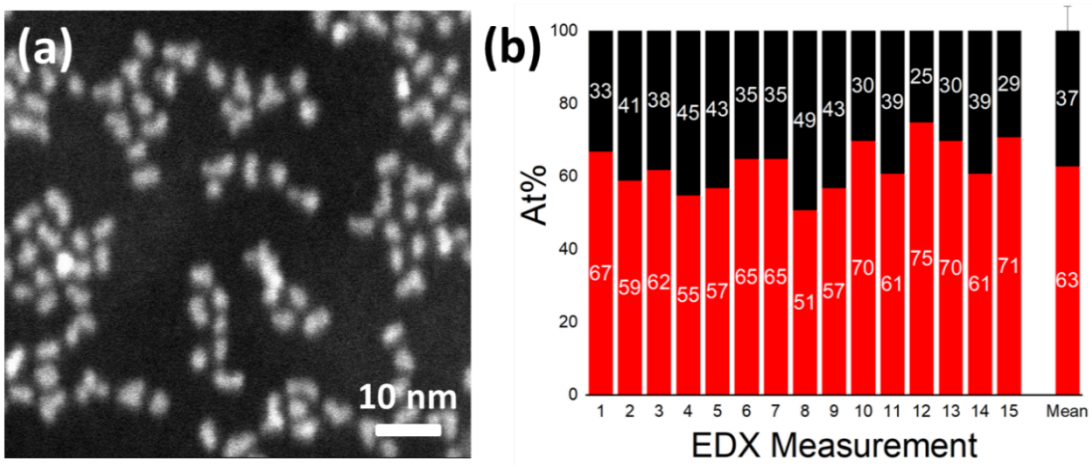

Fig. S7. (a) Representative HAADF image of Pt/Fe NPs synthesized at 250 ˚C using an OA:OAm volume ratio of 0:2; (b) STEM EDX analysis of 15 randomly selected regions that exclude Fe-based pseudospheres (see Fig. S1), alongside the corresponding mean composition (including the standard deviation in the 15 readings), in At% (Fe red, Pt black).

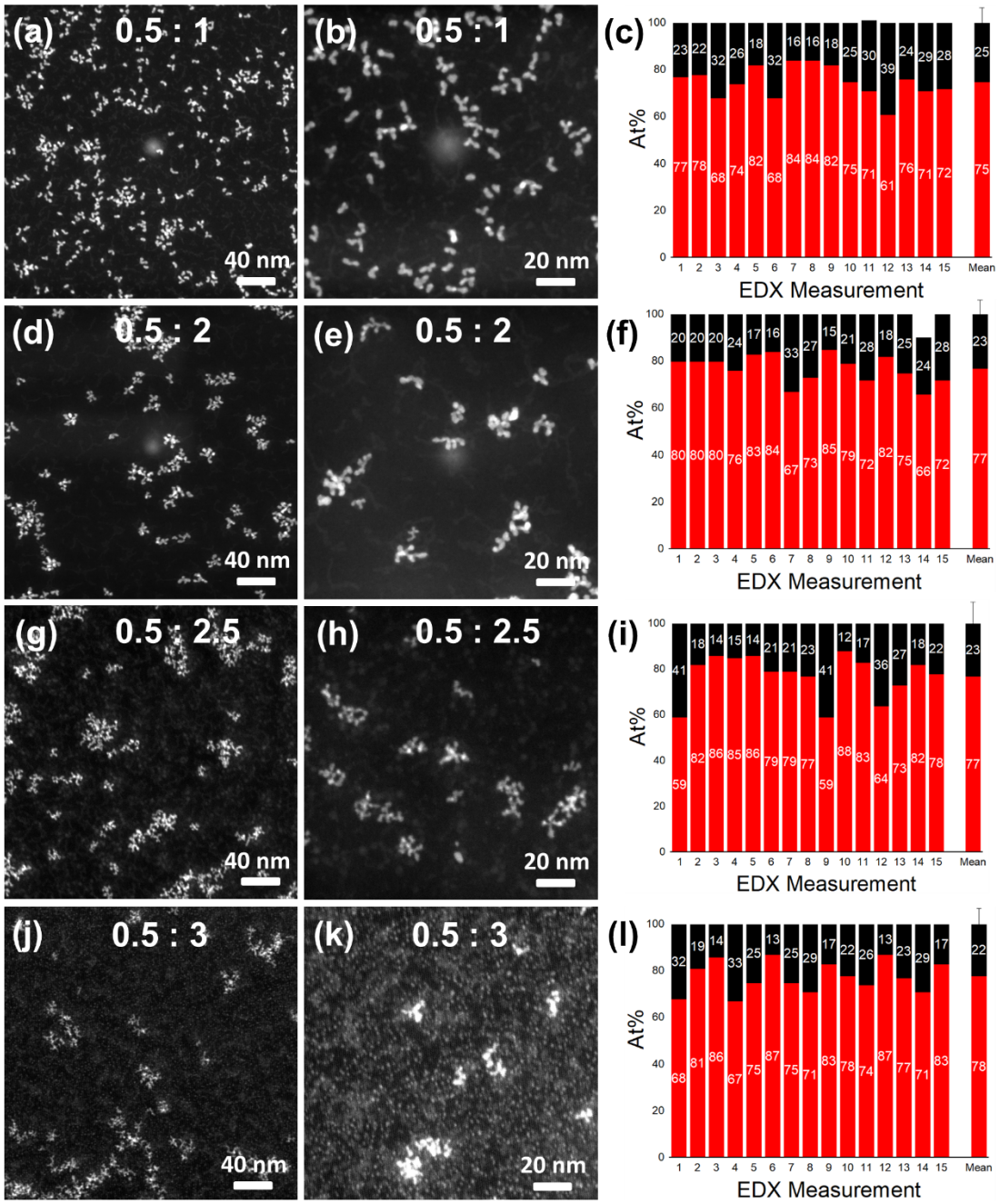

Fig. S8. Further representative HAADF images of Pt/Fe NPs synthesized at 250 ˚C using OA:OAm volume ratios of (a)-(b) 0.5:1, (d)-(e) 0.5:2, (g)-(h) 0.5:2.5, (j)-(k) 0.5:3; (c), (f), (i), (l) STEM EDX analysis of 15 randomly selected regions in each sample, alongside the corresponding mean composition (including the standard deviation in the 15 readings), in At% (Fe red, Pt black). For the corresponding HAADF images and STEM EDX analysis of Pt/Fe NPs synthesized at 250 ˚C with an OA:OAm volume ratio of 0.5:1.5 see Fig. S1(g)-(i).

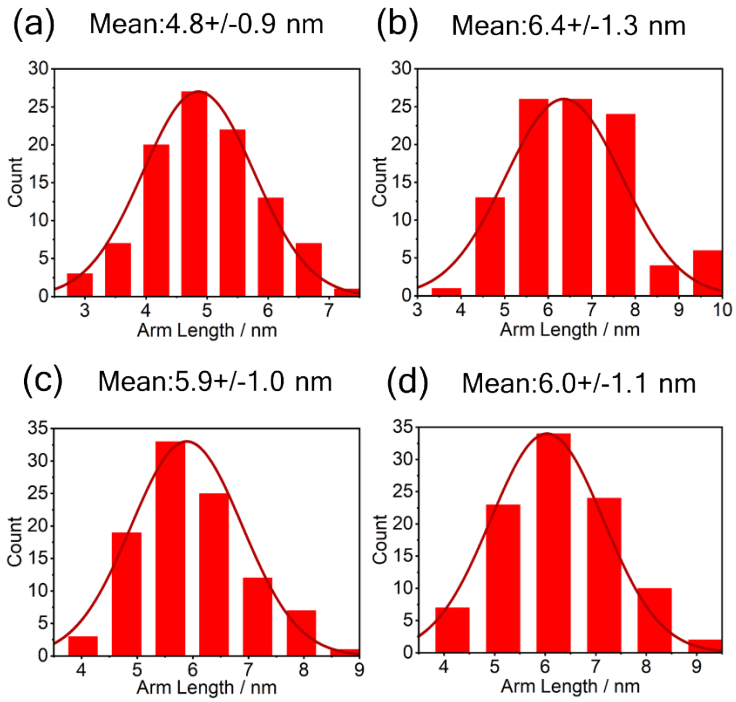

Fig. S9. Size distributions and mean sizes with standard deviations for Pt/Fe NPs synthesized at 250 ˚C using OA:OAm volume ratios of (a) 0.5:1, (b) 0.5:2, (c) 0.5:2.5, (d) 0.5:3. For the corresponding size analysis of Pt/Fe NPs synthesized at 250 ˚C with an OA:OAm volume ratio of 0.5:1.5 see Fig. S2(c). See Fig. S8 for representative microscopy and compositional analysis.

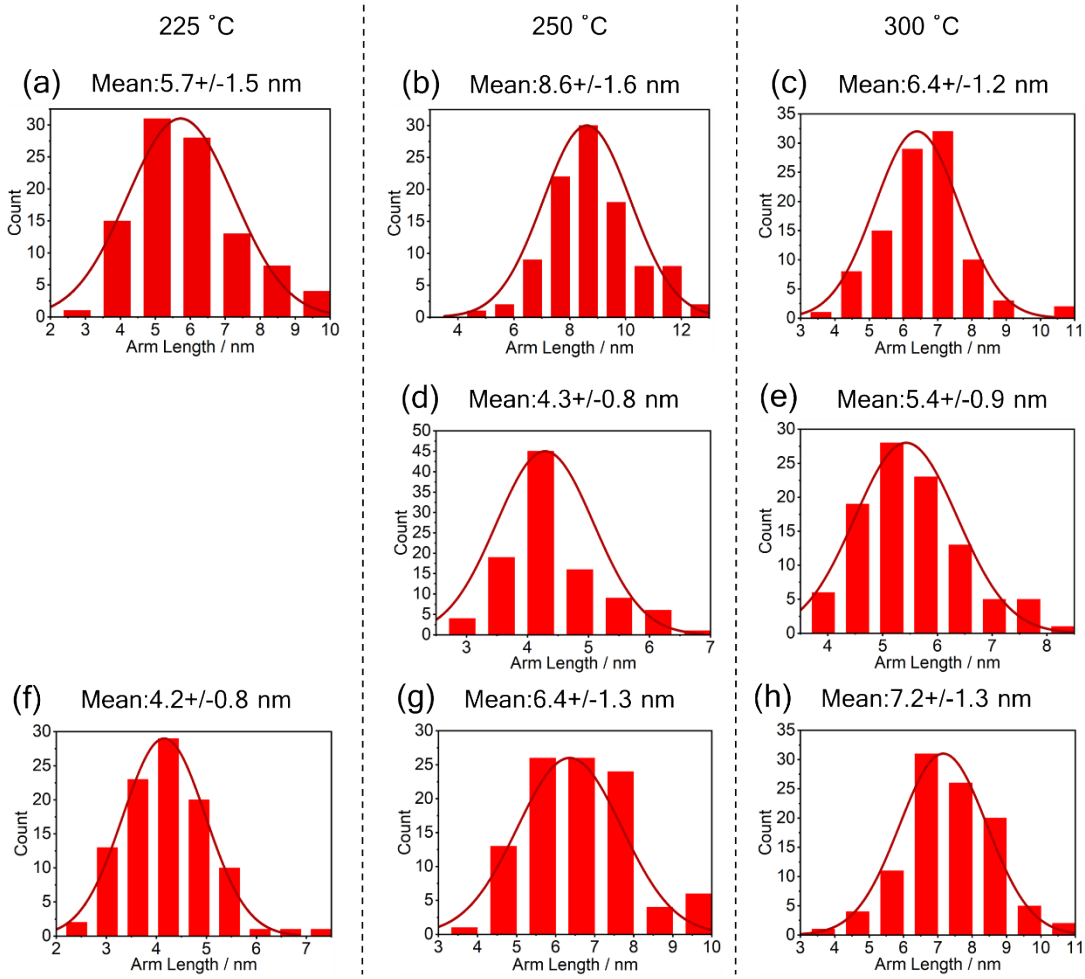

Fig. S10. Size distributions and mean sizes with standard deviations for Pt/Fe NPs synthesized at 225, 250 or 300 ˚C using OA:OAm volume ratios of 0.8:1.2 (a)-(c), 0.5:1.5 (d)-(e), 0.5:2 (f)-(h). See main manuscript Fig. 2 for representative microscopy and compositional analysis. Weak reduction in the OA:OAm 0.5:1.5 system at 225 ˚C prevented calculation of an accurate size distribution (Fig. 2(d)).

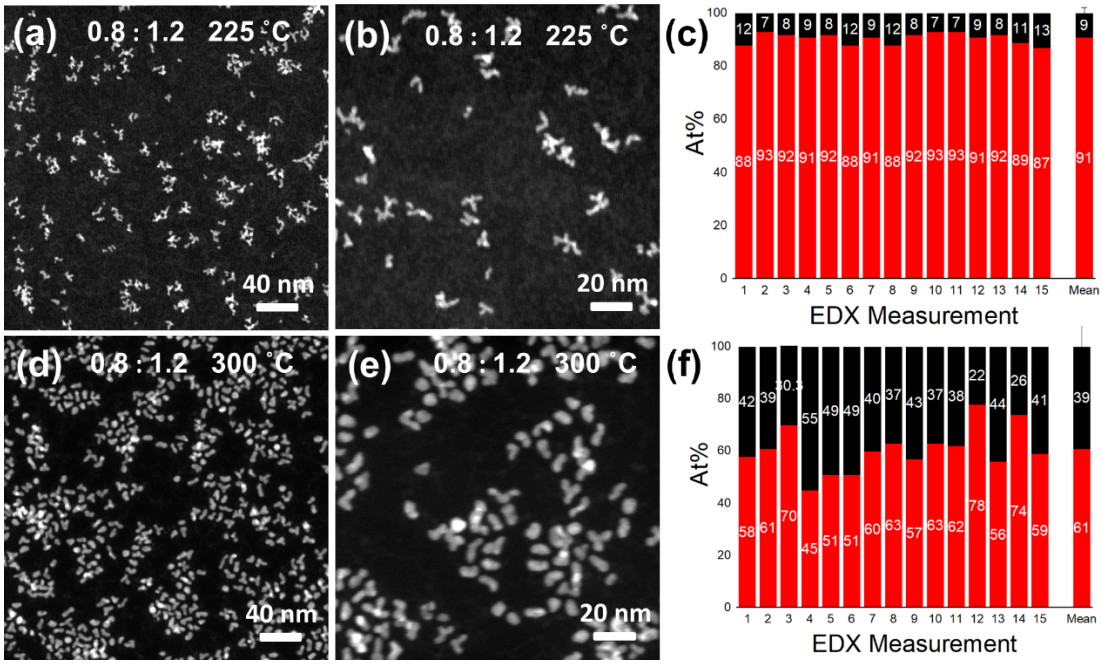

Fig. S11. Representative HAADF images of Pt/Fe NPs synthesized at (a)-(b) 225 ˚C and (d)-(e) 300 ˚C using OA:OAm volume ratios of 0.8:1.2; (c), (f) STEM EDX analysis of 15 randomly selected regions in each sample, alongside the corresponding mean composition (including the standard deviation in the 15 readings), in At% (Fe red, Pt black).

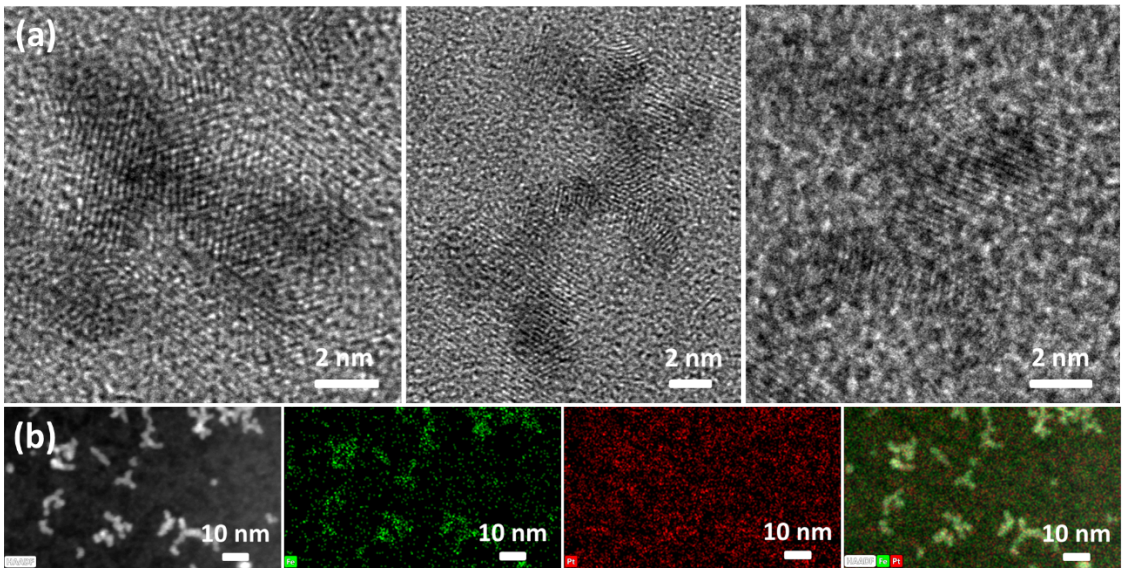

Fig. S12. (a) Representative HRTEM analyses of Pt/Fe NPs synthesized at 225 ˚C using an OA:OAm volume ratio of 0.8:1.2; (b) Corresponding STEM HAADF and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps.

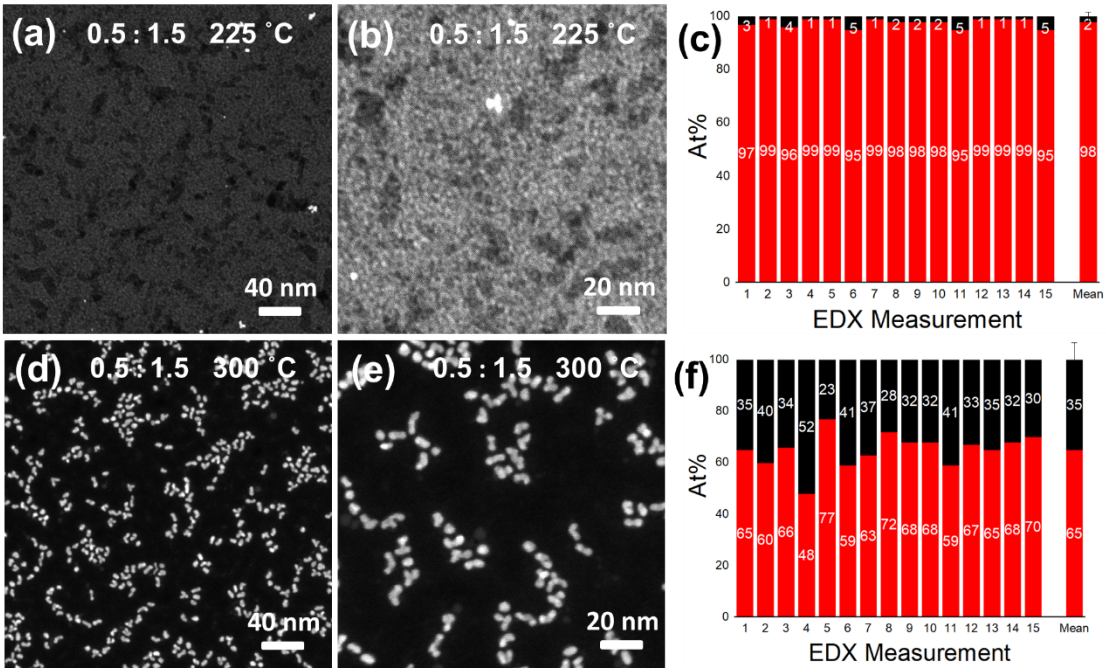

Fig. S13. Representative HAADF images of Pt/Fe NPs synthesized at (a)-(b) 225 ˚C and (d)-(e) 300 ˚C using OA:OAm volume ratios of 0.5:1.5; (c), (f) STEM EDX analysis of 15 randomly selected regions in each sample, alongside the corresponding mean composition (including the standard deviation in the 15 readings), in At% (Fe red, Pt black).

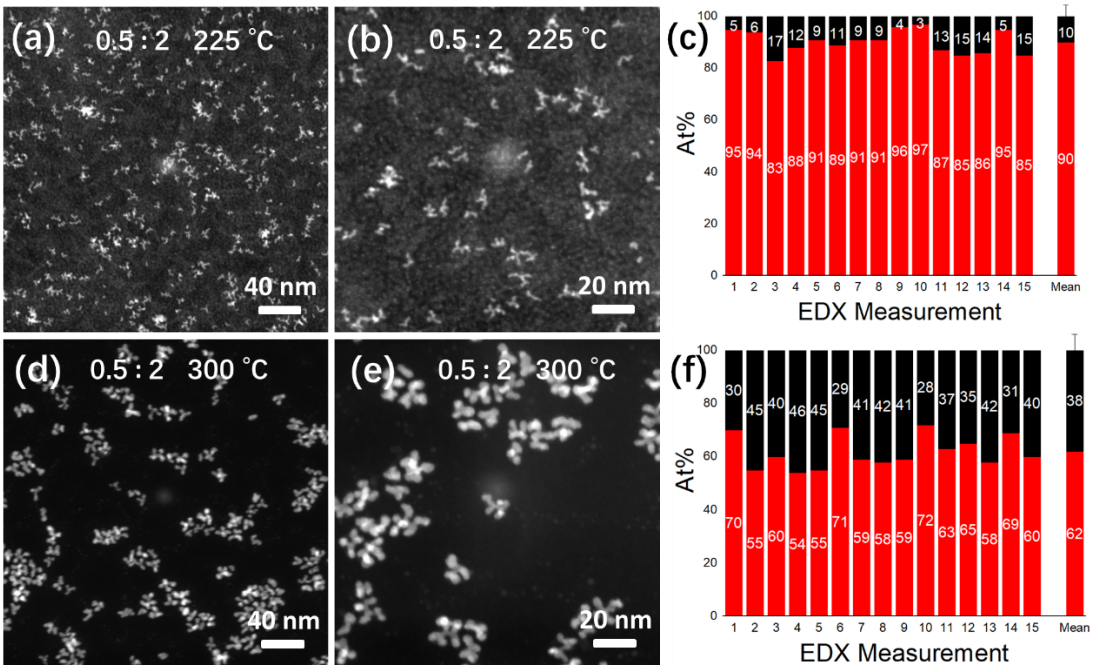

Fig. S14. Representative HAADF images of Pt/Fe NPs synthesized at (a)-(b) 225 ˚C and (d)-(e) 300 ˚C using OA:OAm volume ratios of 0.5:2; (c), (f) STEM EDX analysis of 15 randomly selected regions in each sample, alongside the corresponding mean composition (including the standard deviation in the 15 readings), in At% (Fe red, Pt black).

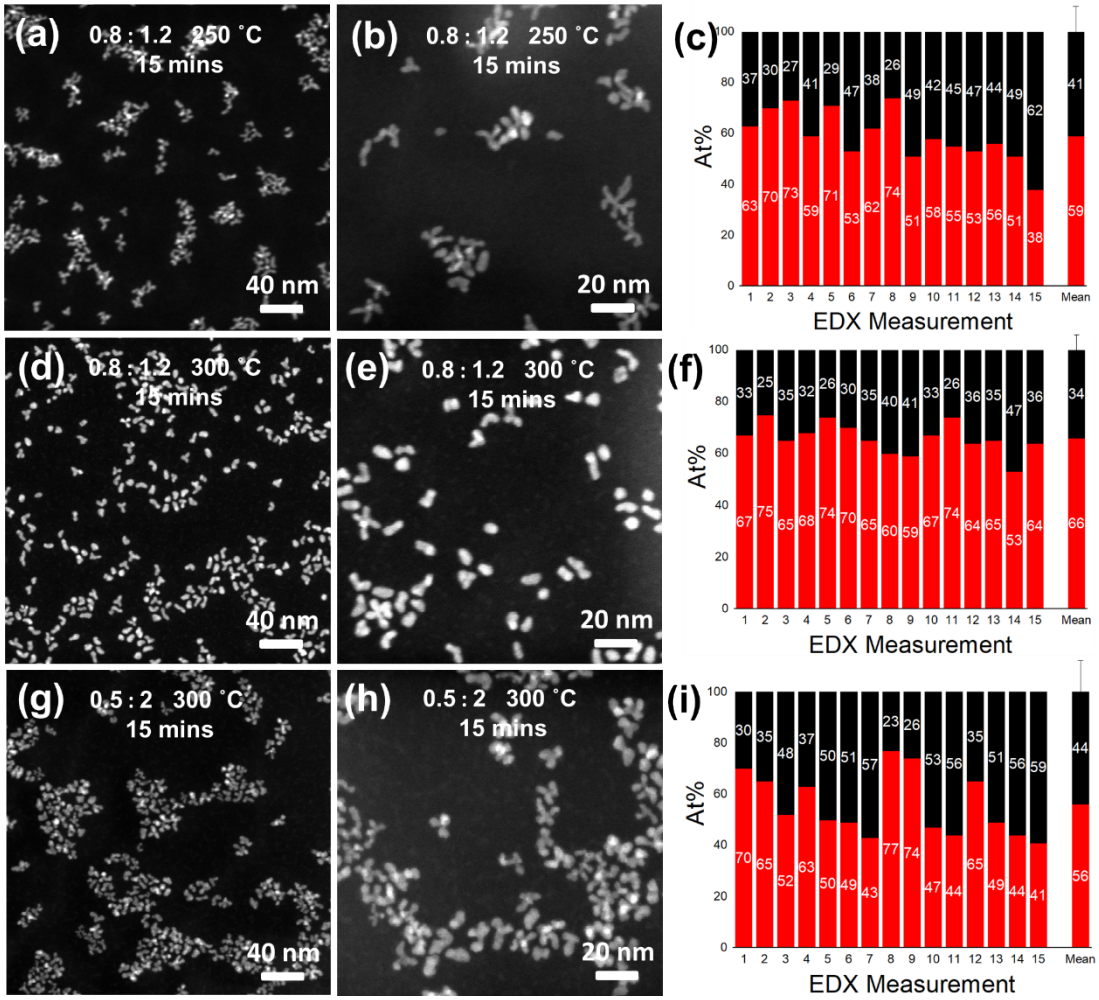

Fig. S15. Representative HAADF images of Pt/Fe NPs synthesized by heating to high temperature for only 15 mins. OA:OAm volume ratios and temperatures were (a)-(b) 0.8:1.2, 250 ˚C, (d)-(e) 0.8:1.2, 300 ˚C, (g)-(h) 0.5:2, 300 ˚C; (c), (f), (i) STEM EDX analysis of 15 randomly selected regions in each sample, alongside the corresponding mean composition (including the standard deviation in the 15 readings), in At% (Fe red, Pt black).

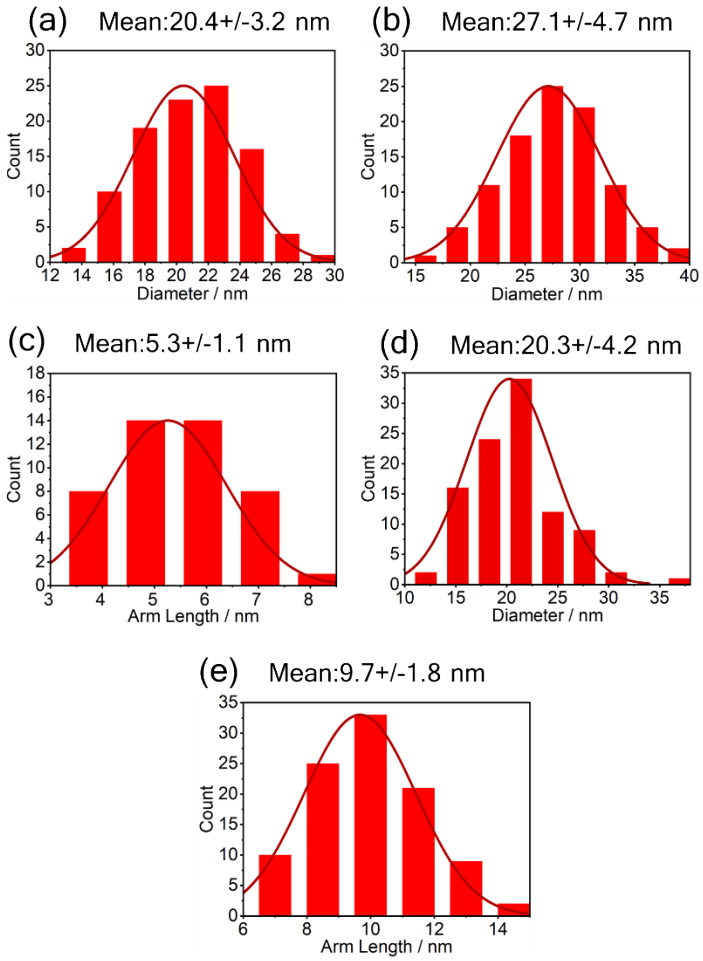

Fig. S16. Size distributions and mean sizes with standard deviations for Pt/Fe NPs synthesized using 2:1 Pt:Fe precursors at 250 ˚C using OA:OAm volume ratios of 0.5:1.5 (a), 0.5:2 (b), 0.5:2.5 (nanopods only, $N = 45$; c), 0.5:2.5 (nanodendrites only; d) and at 300 ˚C ˚C with an OA:OAm volume ratio of 0.5:2 where only nanopods were seen (e).

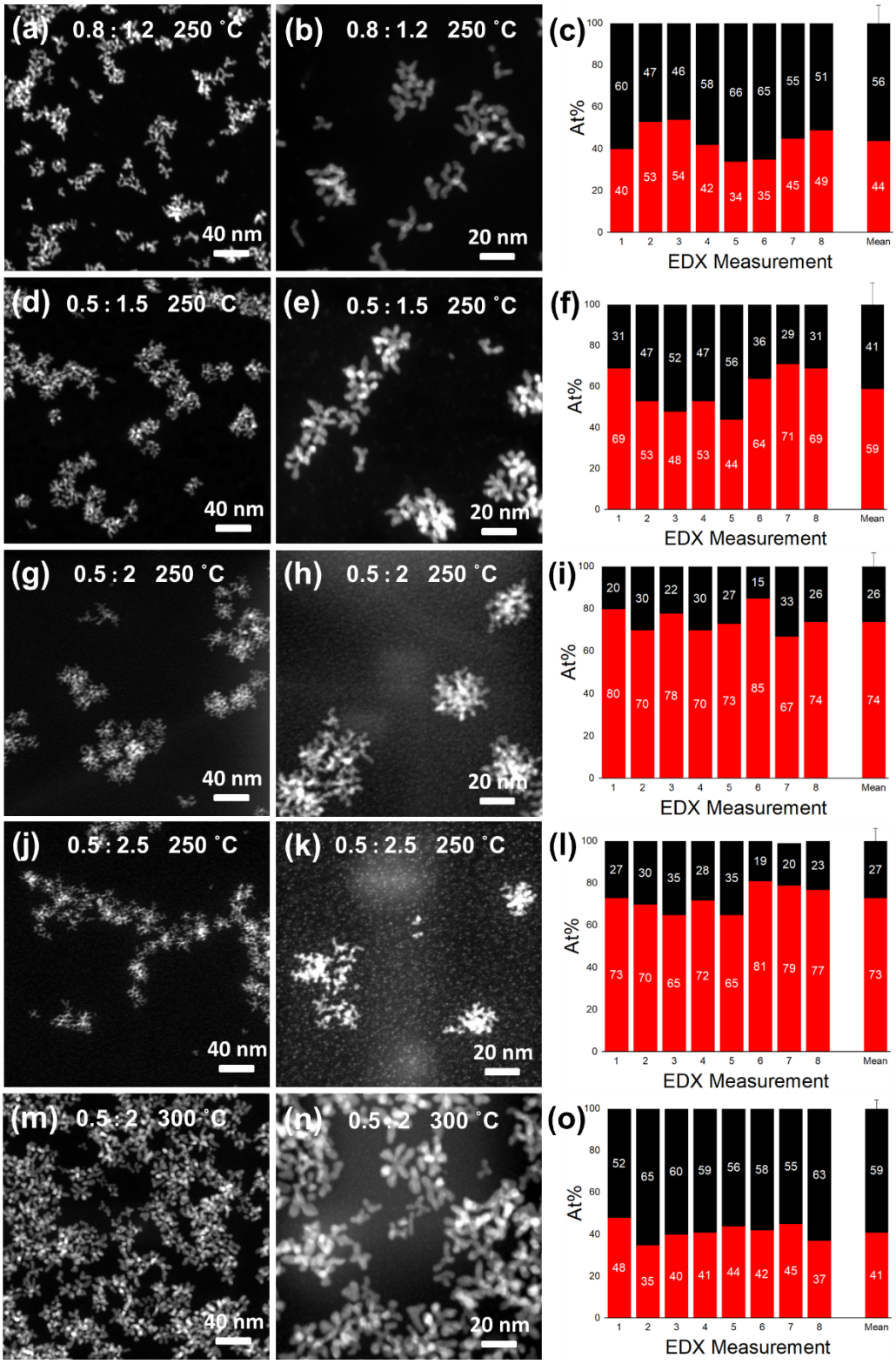

Fig. S17. Representative HAADF images of Pt/Fe NPs synthesized using 2:1 Pt:Fe precursors at 250 ˚C using OA:OAm volume ratios of (a)-(b) 0.8:1.2, (d)-(e) 0.5:1.5, (g)-(h) 0.5:2, (j)-(k) 0.5:2.5. For (m)-(n) conditions were OA:OAm 0.5:2.5, 300 ˚C; (c), (f), (i), (l), (o) STEM EDX analysis of 8 randomly selected regions in each sample, alongside the corresponding mean composition (including the standard deviation in the 8 readings), in At% (Fe red, Pt black).

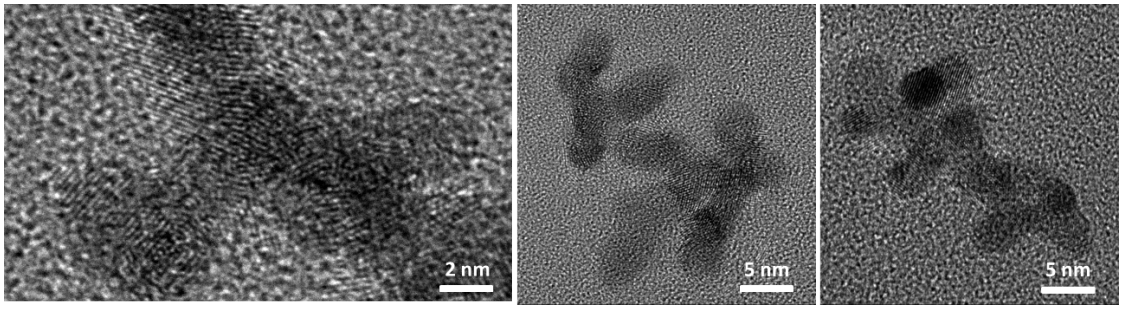

Fig. S18. Representative HRTEM analyses of Pt/Fe NPs synthesized using 2:1 Pt:Fe precursors at 250 ˚C and an OA:OAm volume ratio of 0.8:1.2.

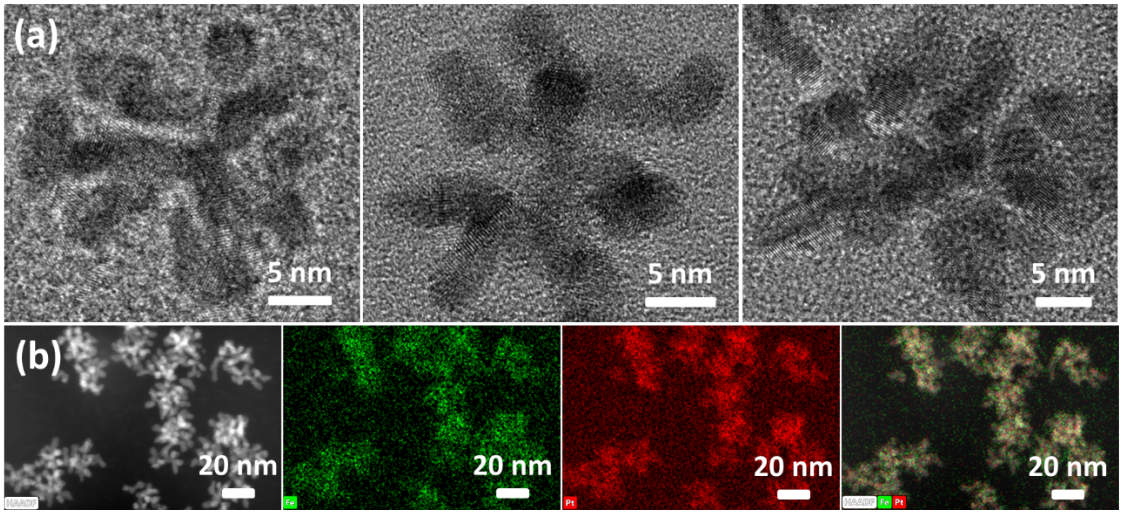

Fig. S19. (a) Representative HRTEM analyses of Pt/Fe NPs synthesized using 2:1 Pt:Fe precursors at 250 ˚C and OA:OAm volume ratio of 0.5:1.5; (b) Corresponding HAADF imaging and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps.

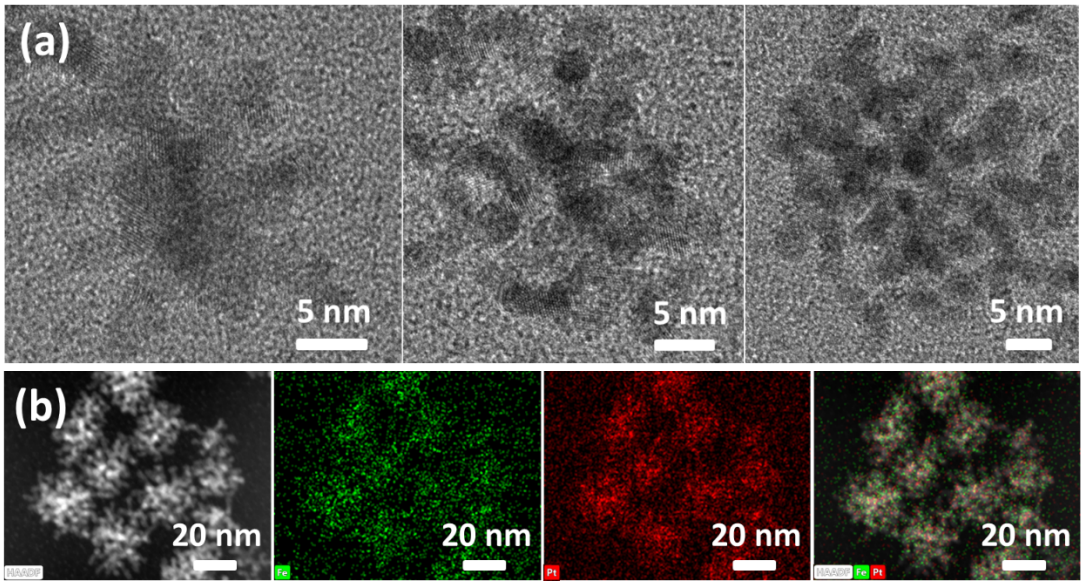

Fig. S20. (a) Representative HRTEM analyses of Pt/Fe NPs synthesized using 2:1 Pt:Fe precursors at 250 ˚C and an OA:OAm volume ratio of 0.5:2; (b) Corresponding HAADF imaging and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps.

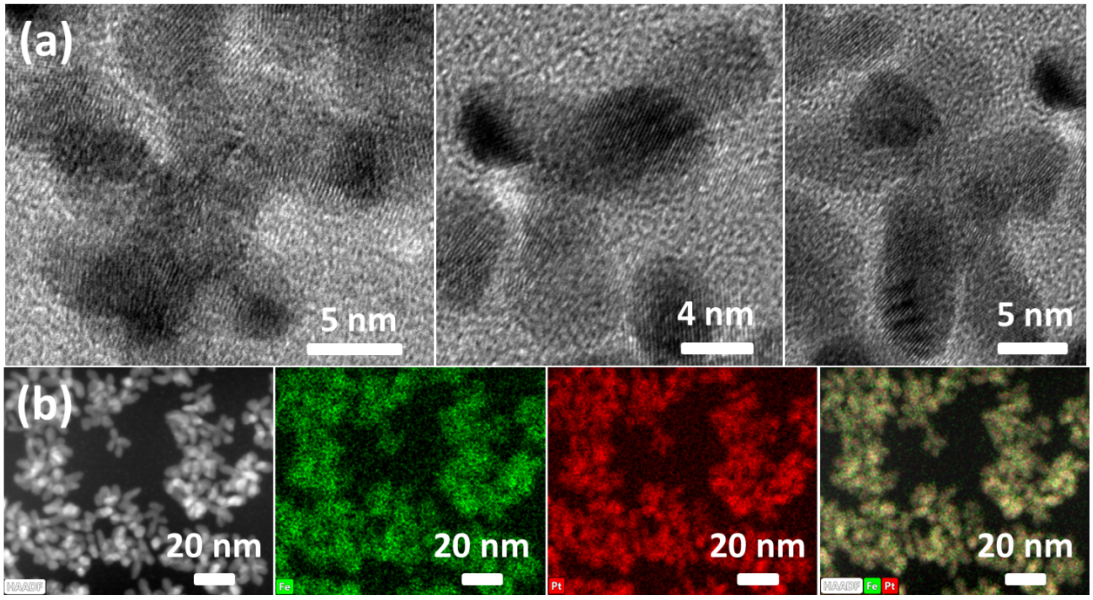

Fig. S21. (a) Representative HRTEM analyses of Pt/Fe NPs synthesized using 2:1 Pt:Fe precursors at 300 ˚C using an OA:OAm volume ratio of 0.5:2; (b) Corresponding STEM HAADF and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps.

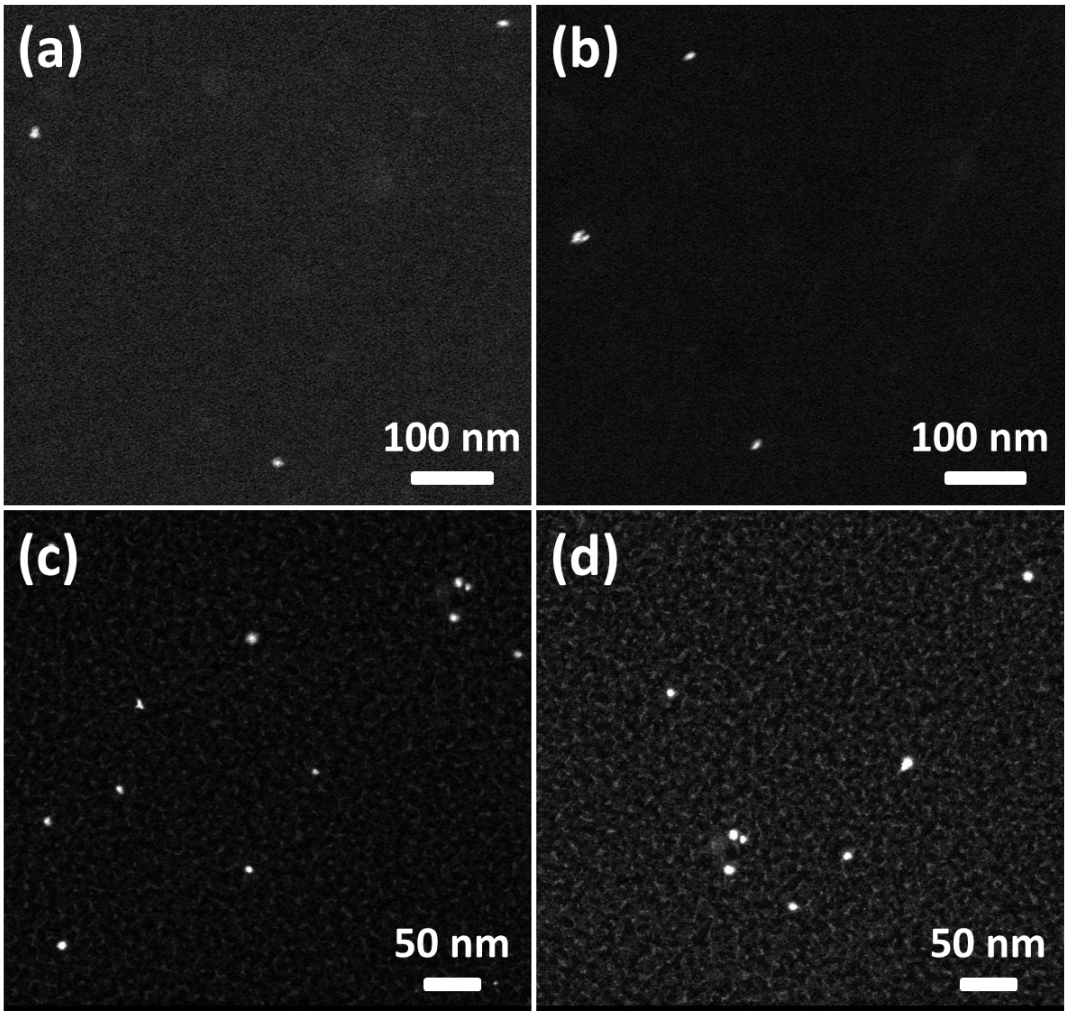

Fig. S22. Representative HAADF images of (a)-(b) Pt/Fe seeds synthesized using 2:1 Pt:Fe and 0.8:1.2 mL OA:OAm at 200 ˚C for 10 min. and (c)-(d) Pt/Ni seeds synthesized using 1:1 Pt:Ni and 0.4:1.2 mL OA:OAm at 200 ˚C for 40 mins.

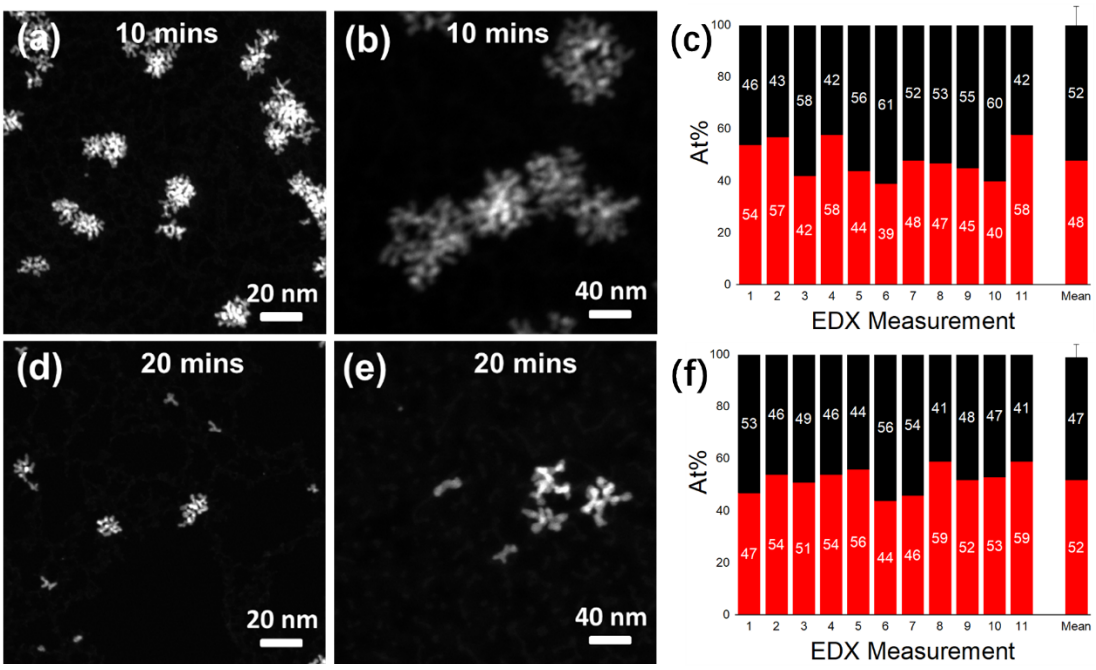

Fig. S23. Representative HAADF images of Pt/Fe NPs synthesized using 2:1 Pt:Fe and 0.8:1.2 mL OA:OAm at 250 ˚C for 30 mins after mixing at 200 ˚C for 10 mins in (a)-(b) and 20 mins in (d)-(e); (c) and (f), corresponding STEM EDX analysis of 11 randomly selected regions in each sample, alongside the corresponding mean composition (including the standard deviation in the 11 readings), in At% (Fe red, Pt black).

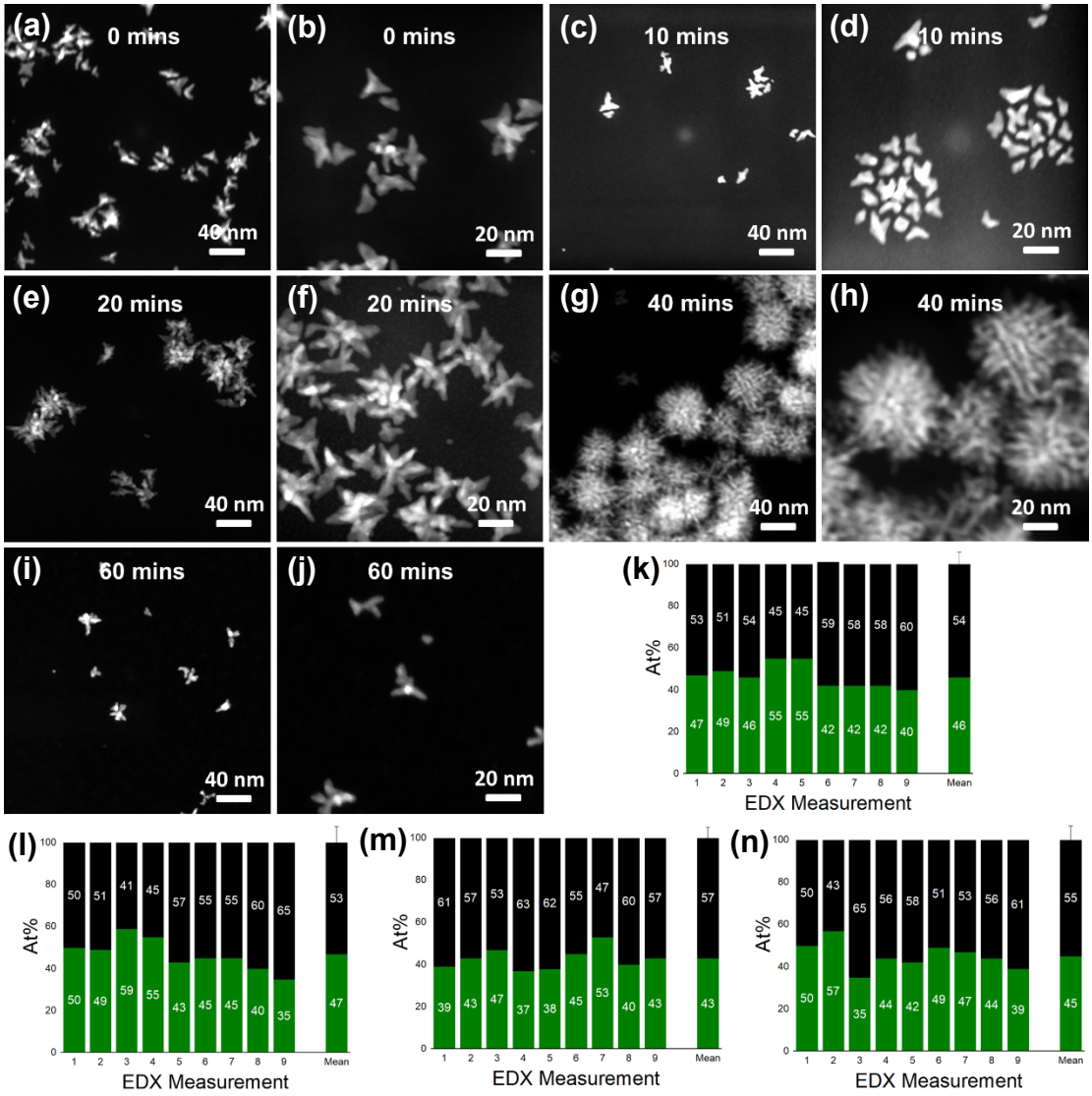

Fig. S24. Representative HAADF images of Pt/Ni NPs synthesized using 1:1 Pt:Ni precursors and a 0.4:1.2 OA:OAm volume ratio at 250 ˚C for 30 mins after mixing at 200 ˚C for 0 mins (a)-(b), 10 mins (c)-(d), 20 mins (e)-(f), 40 mins (g)-(h), and 60 mins (i)-(j); (k), (l), (m) and (n) STEM EDX analysis of 9 randomly selected regions in each sample (corresponding to 0, 20, 40, 60 mins mixing time, respectively), alongside the corresponding mean composition (including the standard deviation in the 9 readings), in At% (Ni green, Pt black).

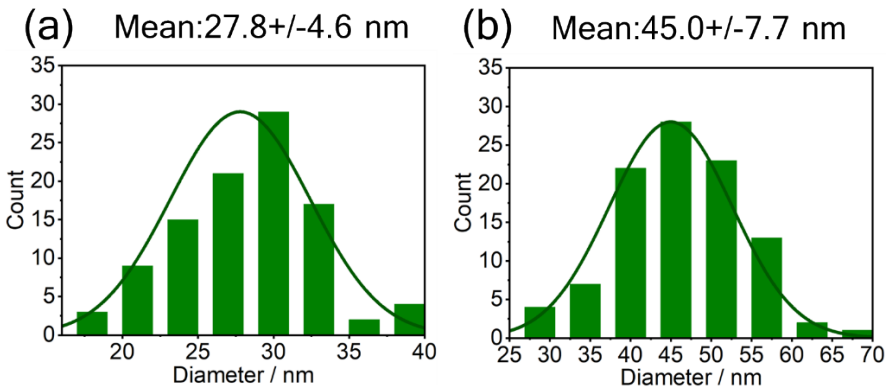

Fig. S25. Size distributions and mean sizes for Pt/Ni nanodendrites synthesized using 1:1 Pt:Ni precursors and a 0.4:1.2 OA:OAm volume ratio at 250 ˚C for 30 mins after mixing at 200 ˚C for 20 min (a) (see also Fig. S24(e), (f), (l)) and 40 mins (b) (see also Fig. S24(g), (h), (m)).

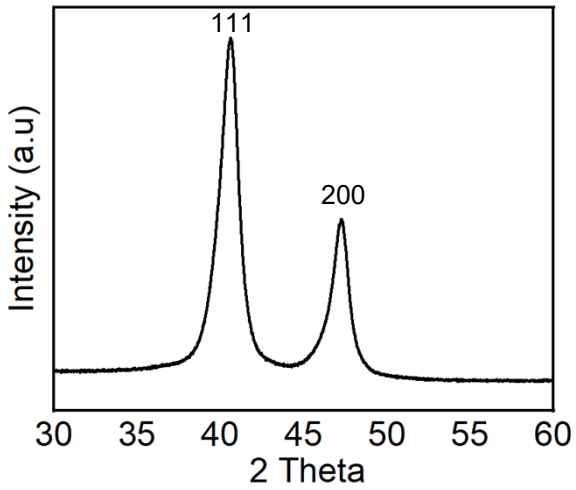

Fig. S26. Powder X-ray diffraction pattern of Pt/Ni NPs synthesized using 1:1 Pt:Ni and 0.4:1.2 mL OA:OAm at 200 ˚C for 40 mins and then 250 ˚C for 30 mins.

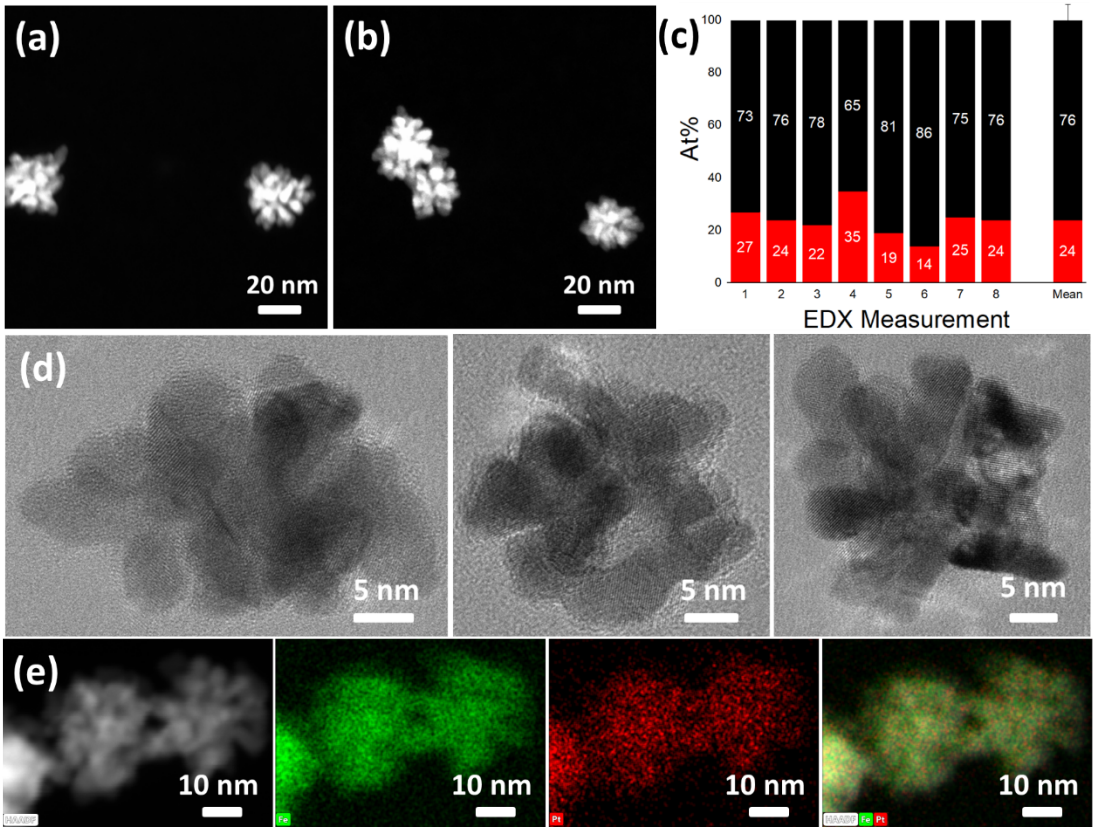

Fig. S27. (a)-(b) Representative HAADF images of Pt/Fe NPs synthesized using 1:0.2 Pt:Fe precursors at 250 ˚C using an OA:OAm volume ratio of 0.8:1.2; (c) STEM EDX analysis of 8 randomly selected regions, alongside the corresponding mean composition (including the standard deviation for the 8 readings), in At% (Fe red, Pt black); (d) corresponding HRTEM analyses and (e) HAADF imaging and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps.

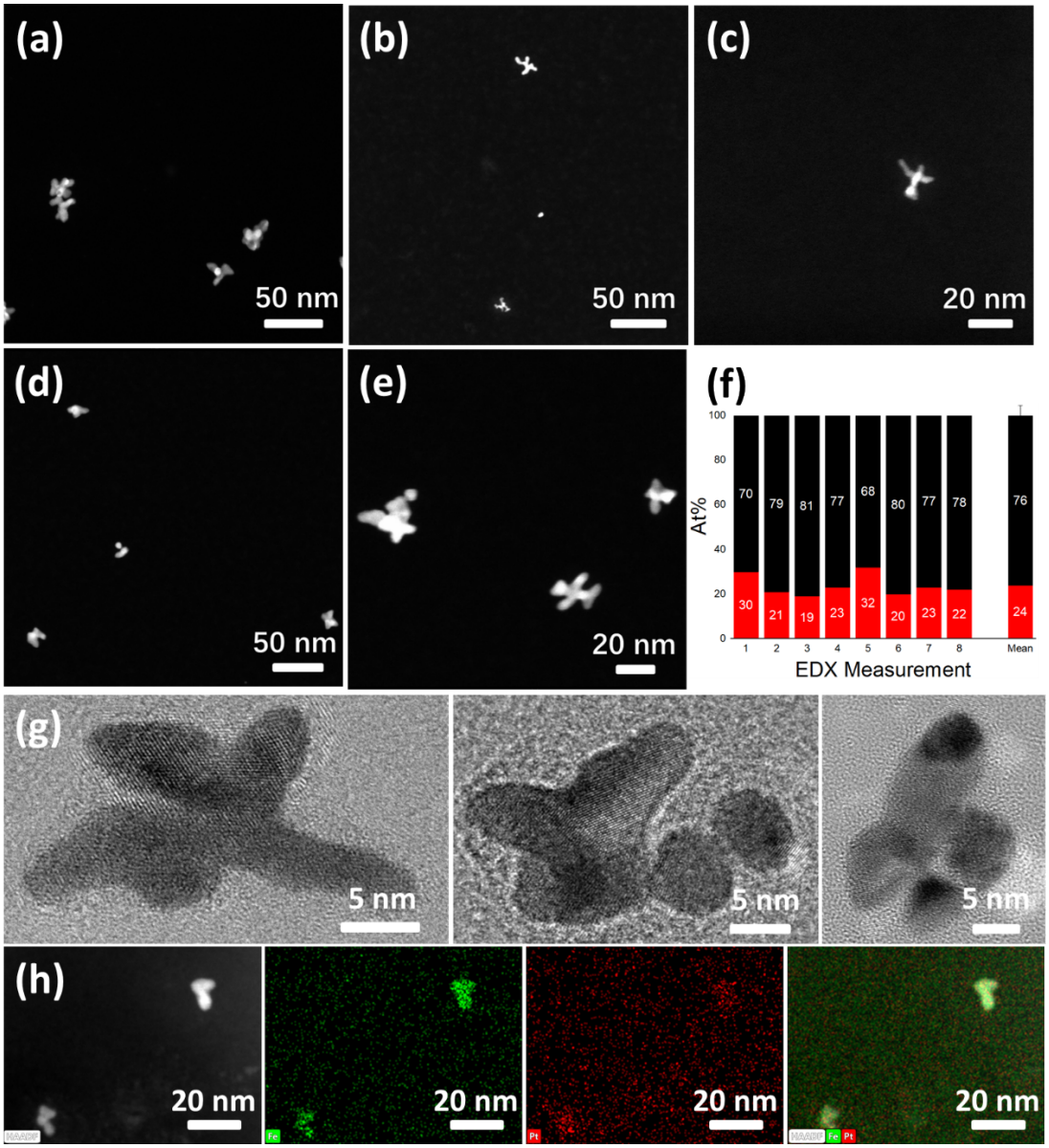

Fig. S28. (a)-(e) Representative HAADF images of Pt/Fe NPs synthesized using 1:0.2 Pt:Fe precursors at 300 ˚C using an OA:OAm volume ratio of 0.5:2; (f) STEM EDX analysis of 8 randomly selected regions, alongside the corresponding mean composition (including the standard deviation in the 8 readings), in At% (Fe red, Pt black); (g) corresponding HRTEM analyses and (h) HAADF imaging and STEM EDX maps showing Fe (green), Pt (red), and their overlapped maps.