Supplementary Information

The *in situ* formation of nanoparticles *via* RAFT polymerization-induced self-assembly in a continuous tubular reactor

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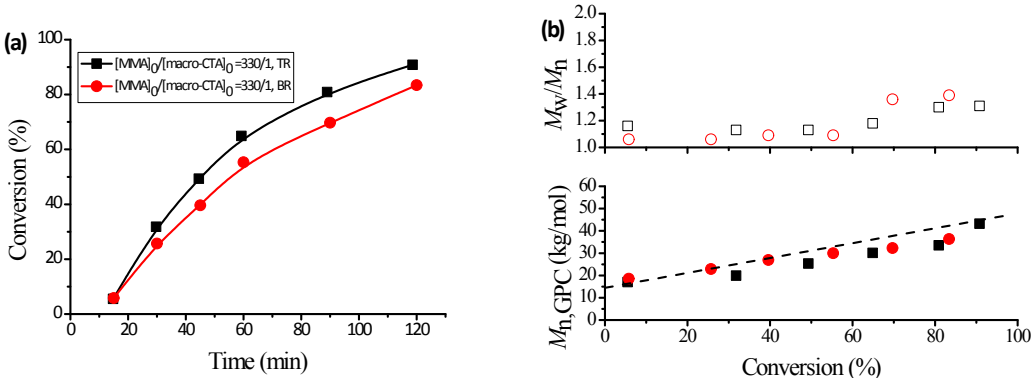


Fig. S1 The evolution of monomer conversion with time (a), and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for the PISA of MMA in batch reactor (BR) and continuous tube reactor (TR). Polymerization conditions: $[PEGMA]_0/[CPADB]_0/[AIBI]_0$ = 40/1/0.2, R_v[1] = $V_{PEGMA}/V_{water}/V_{ethanol}$ = 2/19.9/6.9, $[MMA]_0/[macro\text{-}CTA]_0/[AIBI]_0$ = 330/1/0.3, T = 70 °C.

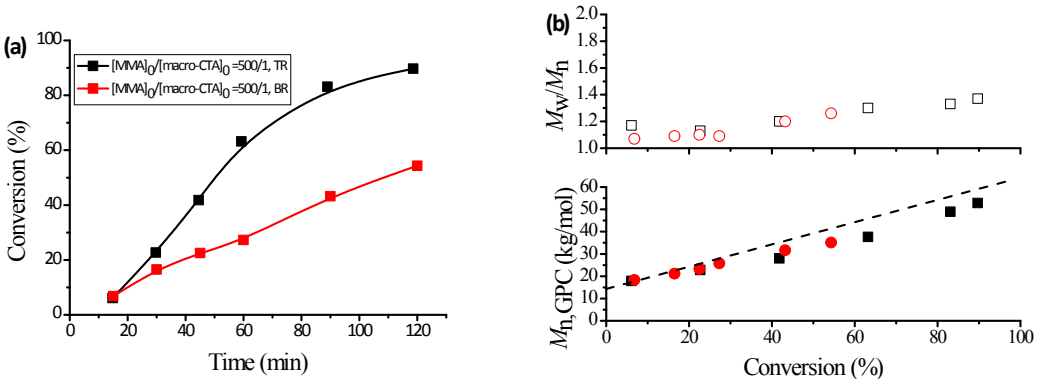


Fig. S2 The evolution of monomer conversion with time (a), and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for the PISA of MMA in batch reactor (BR) and continuous tube reactor (TR). Polymerization conditions: $[PEGMA]_0/[CPADB]_0/[AIBI]_0$ = 40/1/0.2, R_v[1] = $V_{PEGMA}/V_{water}/V_{ethanol}$ = 2/33.9/12.1, $[MMA]_0/[macro\text{-}CTA]_0/[AIBI]_0$ = 500/1/0.3, T = 70 °C.

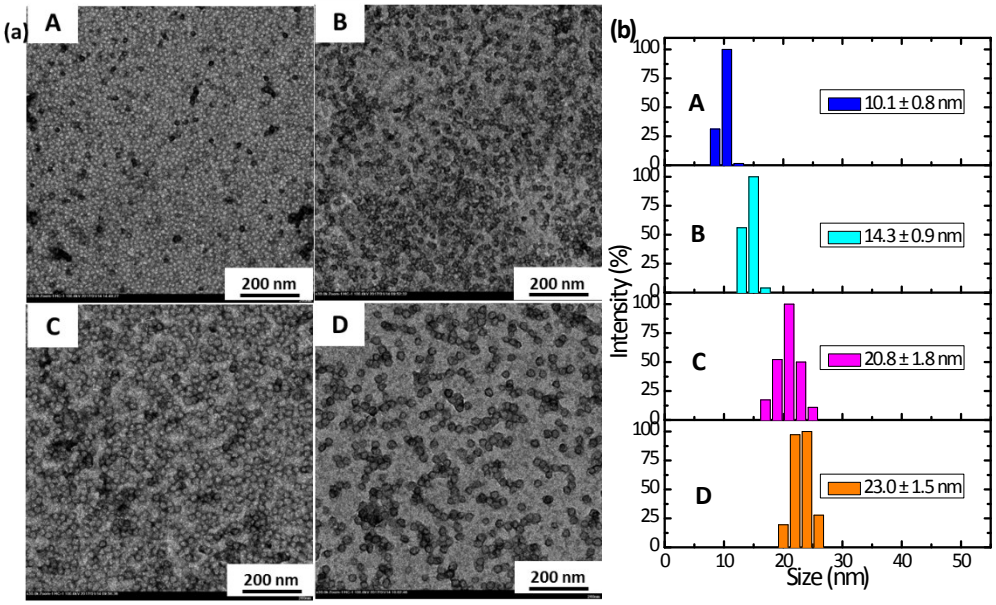


Fig. S3 TEM images of nanoparticles *via* PISA in a batch reactor with molar ratio of $[MMA]_0/[macro\text{-}CTA]_0/[AIBI]_0$ = 330/1/0.3 (a), and size distribution of nanoparticles from TEM images (b) for different polymerization times: (A) 45 min (MMA conv. 39.6%), (B) 60 min (55.3%), (C) 90 min (69.7%), (D) 120 min (83.4%).

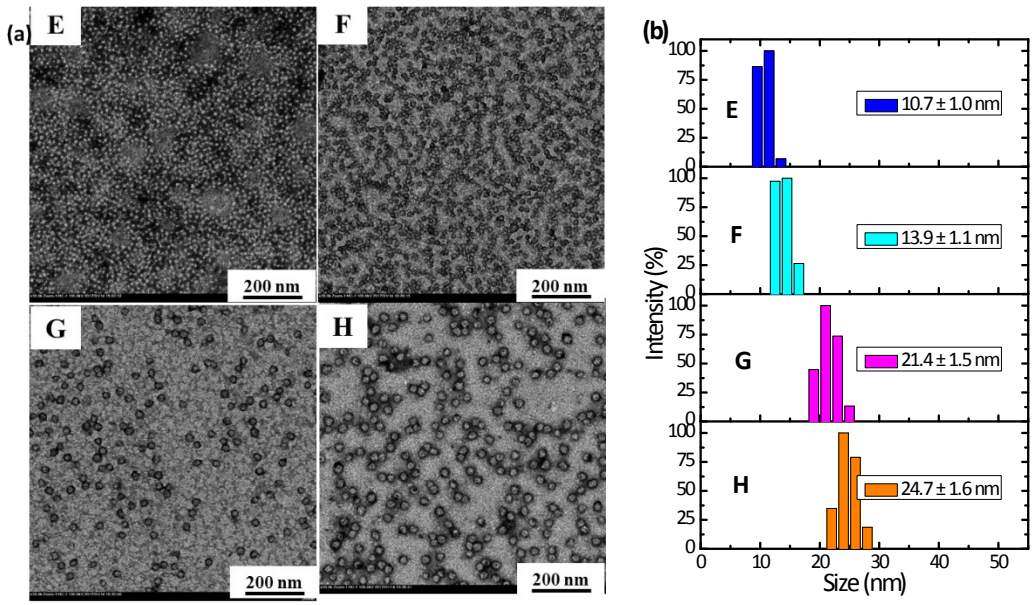
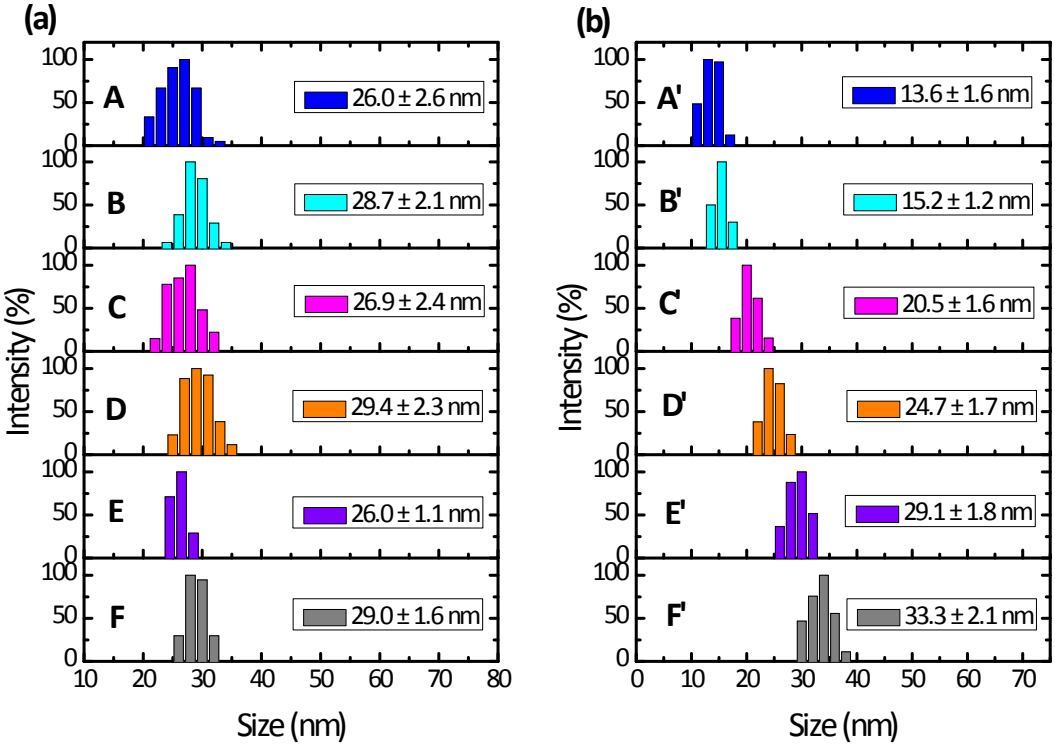


Fig. S4 TEM images of nanoparticles *via* PISA in a batch reactor with molar ratio of $[MMA]_0/[macro\text{-}CTA]_0/[AIBI]_0$ = 500/1/0.3 (a), and size distribution of nanoparticles from TEM images (b) for different polymerization times: (E) 45 min (MMA conv. 22.5%), (F) 60 min (27.3%), (G) 90 min (43.2%), (H) 120 min (54.3%).



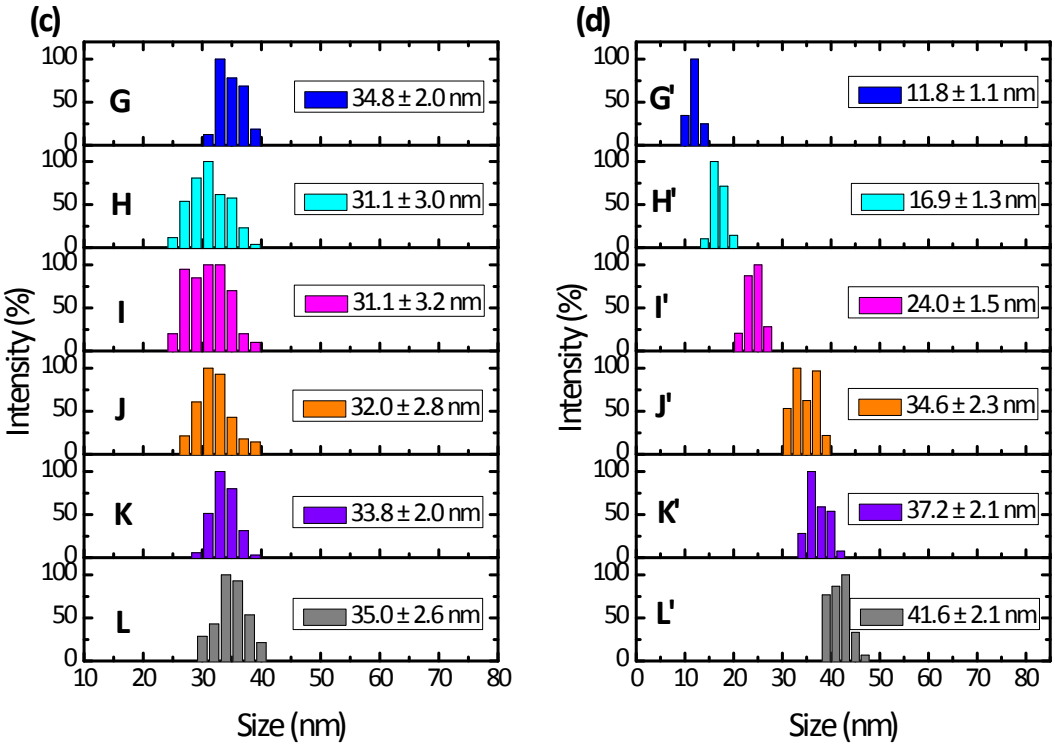


Fig. S5 Size distribution of nanoparticles from TEM images, (a), (b), (c) and (d), corresponding to Fig. 4, Fig. 5, Fig. 7, and Fig. 8, respectively.

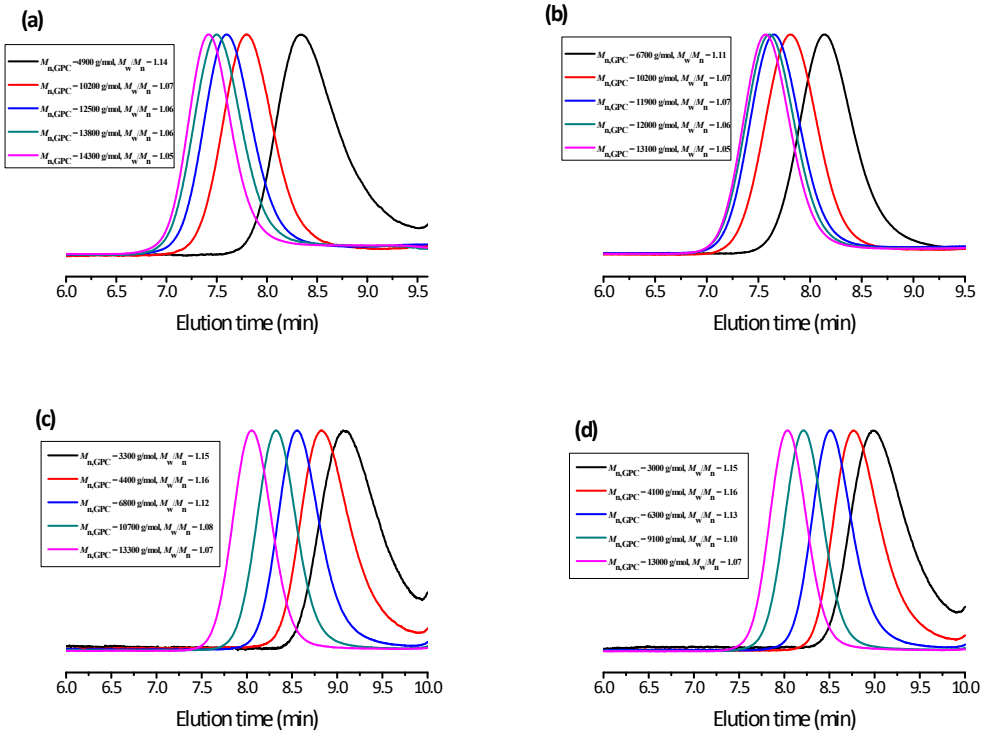


Fig. S6 GPC traces for the polymerization of PEGMA, (a) R_v^1 = 2/19.9/6.9, TR; (b) R_v^1 = 2/33.9/12.1, TR; (c) R_v^1 = 2/19.9/6.9, BR; (d) R_v^1 = 2/33.9/12.1, BR.

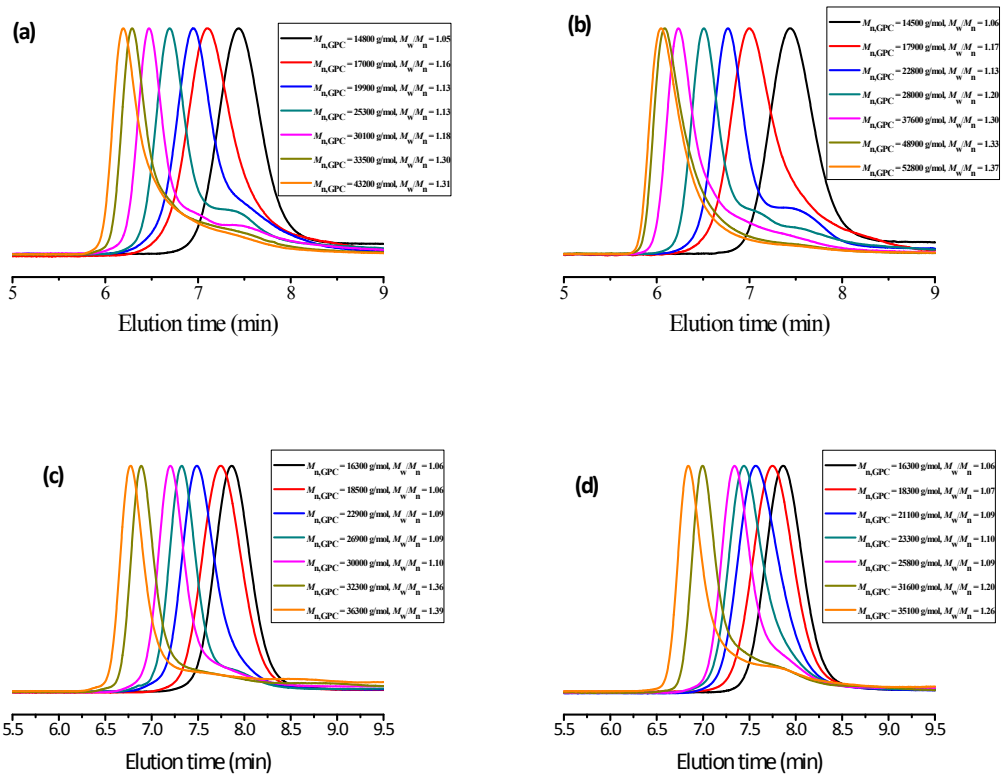


Fig. S7 GPC traces for the polymerization-induced self-assembly of MMA, (a) $[MMA]_0/[macro\text{-}CTA]_0$ =330/1, TR; (b) $[MMA]_0/[macro\text{-}CTA]_0$ =500/1, TR; (c) $[MMA]_0/[macro\text{-}CTA]_0$ =330/1, BR; (d) $[MMA]_0/[macro\text{-}CTA]_0$ =500/1, BR.

Table S1 The conversation and the DP of PPEGMA in different conditions [a]

Entry	R_v^1	Conv. (%)	DP	$M_{n,GPC}$ (g/mol)	M_w/M_n	H_a	H_{b+c}	H_d
1	2/12.9/4.3	96.4	40	14700	1.05	2.00	83.32	3.36
2	2/19.9/6.9	94.2	40	14700	1.05	2.00	51.53	2.04
3	2/26.9/9.5	92.0	39	14400	1.05	2.00	37.59	1.49
4	2/33.9/12.1	90.3	39	14400	1.05	2.00	30.87	1.19
5	2/67.8/24.2	75.9	33	13700	1.05	2.00	12.46	0.48
6	2/135.6/48.4	44.8	19	10500	1.06	2.00	5.43	0.21

[a] Polymerization conditions: R_1 = $[PEGMA]_0/[CPADB]_0/[AIBI]_0$ = 40/1/0.2, R_v^1 = $V_{PEGMA}/V_{water}/V_{ethanol}$, $Length_1$ = 11 m, v_{M1} = 0.262 mL min^{-1}, τ_1 =101.0 min, $[MMA]_0/[macro\text{-}CTAs]_0/[MMA]_0$ =x/1/0.3 (x ≈ 230, 330, 420, 500, 1000, and 2000), T

= 70 °C. H_a, H_{b+c}, and H_d corresponded to integral of the peaks a, b+c, and d (as shown in Fig. S8), respectively.

$$\text{Conv.} = \frac{\text{Hb} + \text{c} - 1.5 \times \text{Ha}}{\text{Hb} + \text{c}} \times 100\,\% \quad ; \quad \text{DP} = \frac{(\text{Hb} + \text{c} - 1.5 \times \text{Ha})/3}{\text{Hd} / 5} \quad .$$

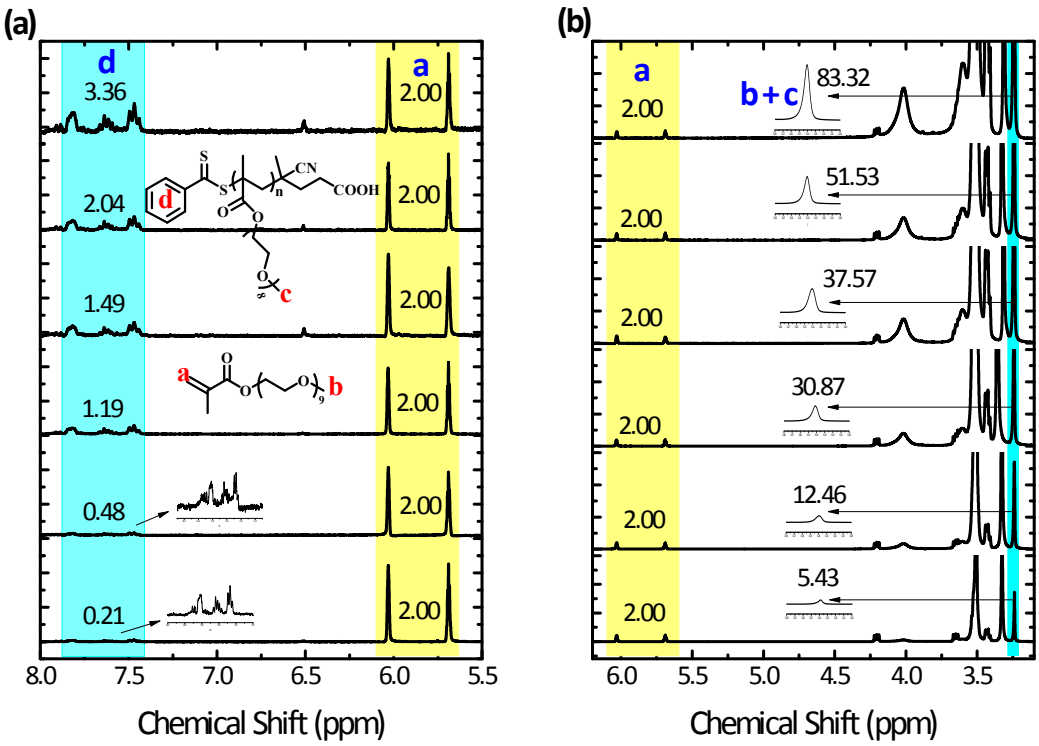


Fig. S8 ^{1}H NMR spectra of unpurified PPEGMA (included unreacted PEGMA) with different DPs in DMSO-d_6.

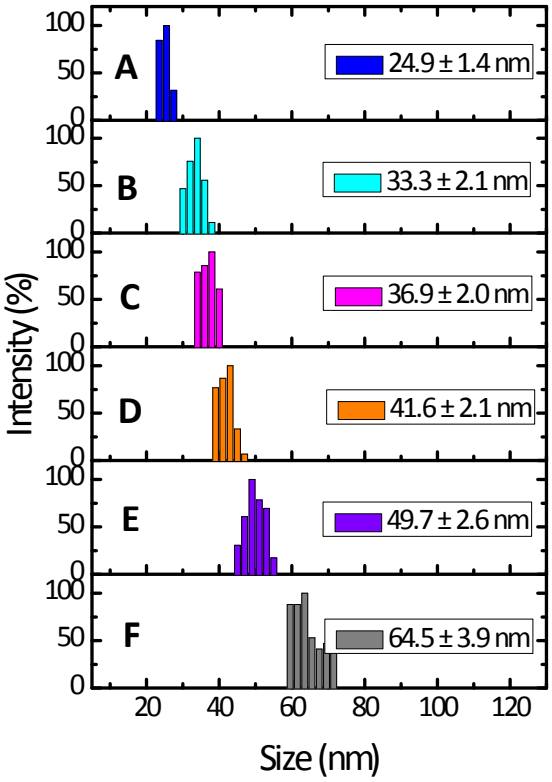


Fig. S9 Size distribution of nanoparticles from TEM images, corresponding to Fig. 10.