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Remarkable Difference in Pre-Cation Exchange Reactions of Inorganic Nanoparticles in Cases with Eventual Complete Exchange

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Table S1. The elemental composition of the nanoparticles (NPs) studied in the pre-cation exchange reaction condition.[a]

		[Zn(Tb)S] : [Hg^{2+}] = 1:10^{M} [M = –12 to –2]										
		M										
	Zn(Tb)S	**–12**	**–11**	**–10**	**–9**	**–8**	**–7**	**–6**	**– 5**	**–4**	**–3**	**–2**
Zn	35.5 ± 0.9 (35.9 ± 0.4)	33.9 ± 2.9	35.0 ± 2.5	35.0 ± 3.7	34.7 ± 2.5	31.2 ± 1.7	35.2 ± 2.1	38.5 ± 2.4	44.0 ± 0.2	33.1 ± 3.9	42.8 ± 0.7	27.9 ± 3.0
Tb	3.1 ± 0.2 (6.3 ± 0.2)	3.3 ± 0.2	3.2 ± 0.3	3.4 ± 0.1	3.1 ± 0.4	5.0 ± 0.4	4.5 ± 0.6	4.6 ± 0.2	5.8 ± 1.1	4.6 ± 0.9	5.9 ± 0.3	5.4 ± 0.5
S	61.4 ± 0.8 (57.8 ± 0.4)	61.7 ± 3.0	60.5 ± 2.5	60.5 ± 3.5	60.8 ± 2.0	62.1 ± 1.9	58.8 ± 2.2	54.2 ± 2.6	46.3 ± 2.1	58.3 ± 2.8	47.8 ± 0.9	61.9 ± 3.2
Hg	----	1.2 ± 0.1	1.3 ± 0.1	1.2 ± 0.2	1.4 ± 0.2	1.7 ± 0.1	1.5 ± 0.1	2.7 ± 0.1	4.0 ± 0.9	4.0 ± 0.3	3.5 ± 0.1	4.8 ± 0.3
		[Zn(Tb)S] : [Pb^{2+}] = 1:10^{M} [b]										
		M										
	Zn(Tb)S	**–12**	**–11**	**–10**	**–9**	**–8**	**–7**	**–6**	**–5**	**–4**	**–3**	**–2**
Zn	35.5 ± 0.9 (35.9 ± 0.4)	40.7 ± 0.4	36.6 ± 1.9	39.5 ± 0.7	36.6 ± 3.0	31.2 ± 3.3	30.7 ± 4.2	31.1 ± 4.8	35.1 ± 3.3 (28.3 ± 5.3)	29.3 ± 2.2 (32.3 ± 3.1)	30.0 ± 3.3 (19.6 ± 3.2)	30.2 ± 0.8 (32.2 ± 2.1)
Tb	3.1 ± 0.2 (6.3 ± 0.2)	2.7 ± 0.3	3.6 ± 0.3	3.2 ± 0.3	3.5 ± 0.3	4.3 ± 0.4	4.4 ± 0.7	4.7 ± 0.9	3.6 ± 0.8 (4.5 ± 0.4)	3.8 ± 0.3 (5.4 ± 0.1)	4.3 ± 0.4 (4.7 ± 0.5)	4.8 ± 0.6 (6.0 ± 1.0)
S	61.4 ± 0.8 (57.8 ± 0.4)	54.9 ± 0.3	58.1 ± 2.1	55.4 ± 0.8	58.0 ± 2.7	62.8 ± 3.6	63.1 ± 3.9	62.2 ± 4.6	59.7 ± 2.7 (66.6 ± 5.6)	65.8 ± 2.4 (61.5 ± 3.1)	64.5 ± 3.3 (74.4 ± 3.8)	62.6 ± 0.9 (59.8 ± 2.3)
Pb	----	1.7 ± 0.2	1.7 ± 0.1	1.9 ± 0.1	1.8 ± 0.2	1.7 ± 0.1	1.7 ± 0.2	2.0 ± 0.1	1.7 ± 0.2 (0.5 ± 0.1)	1.2 ± 0.1 (0.8 ± 0.5)	1.2 ± 0.2 (1.3 ± 0.4)	2.5 ± 0.2 (2.0 ± 0.1)

[a] The values were obtained from multiple areas of the sample and are reported as average and standard deviations.

[b] The values within parentheses are taken from our previous work on Zn(Tb)S/Pb NPs. [RSC Adv. 2018, 8, 18093-18108]

Table S2. The elemental composition of the nanoparticles (NPs) studied in the cation exchange reaction condition.[a]

		[Zn(Tb)S] : [Hg^{2+}] = 1:10^{M} [M = –1 to 10]		
		M		
	Zn(Tb)S	**–1**	**0**	**1**
Zn	35.5 ± 0.9 (35.9 ± 0.4)	25.2 ± 5.3	----	----
Tb	3.1 ± 0.2 (6.3 ± 0.2)	6.0 ± 0.7	1.3 ± 0.3	2.1 ± 0.4
S	61.4 ± 0.8 (57.8 ± 0.4)	55.8 ± 7.3	50.6 ± 1.0	41.2 ± 1.3
Hg	----	13.0 ± 1.4	48.1 ± 1.3	56.8 ± 1.2
		[Zn(Tb)S] : [Pb^{2+}] = 1:10^{M} [b]		
		M		
	Zn(Tb)S	**–1**	**0**	**1**
Zn	35.5 ± 0.9 (35.9 ± 0.4)	27.0 ± 1.5 (34.1 ± 2.4)	---- (----)	---- (----)
Tb	3.1 ± 0.2 (6.3 ± 0.2)	3.9 ± 0.3 (6.8 ± 1.0)	3.0 ± 0.2 (1.3 ± 0.7)	1.4 ± 0.2 (----)
S	61.4 ± 0.8 (57.8 ± 0.4)	62.8 ± 1.7 (48.1 ± 3.6)	65.7 ± 2.5 (44.8 ± 5.1)	58.4 ± 1.7 (45.9 ± 1.2)
Pb	----	6.3 ± 0.8 (11.1 ± 0.8)	31.2 ± 2.3 (53.8 ± 4.7)	40.2 ± 1.5 (54.2 ± 1.2)

[a] The values were obtained from multiple areas of the sample and are reported as average and standard deviations.

[b] The values within parentheses are taken from our previous work on Zn(Tb)S/Pb NPs. [RSC Adv. 2018, 8, 18093-18108] These values indicate that the elemental compositions in the Zn(Tb)S/Hg and Zn(Tb)S/Pb NPs following the cation exchange reaction is similar. We interpret the variation in the elemental composition in the [Zn(Tb)S] : [Hg^{2+}] / [Pb^{2+}] = 1:1 and 1:10 due to batch to batch variation. For example, a source of such variation can arise from amount of post-synthetically cation addition from solution. Nonetheless, both these data track complete exchange of Zn^{2+} by Hg^{2+} / Pb^{2+}.

Table S3. The elemental composition of the NPs from the inductively coupled atomic emission spectroscopy (ICP-AES).[a]

[Zn(Tb)S] : [Pb^{2+}] = 1:10^{M}	**Concentration of elements (ppb)**	
M	Zn	Pb
–8	44442 ± 176	9.8 ± 0.8
–6	43937 ± 64	21.7 ± 0.9
–4	43440 ± 177	92.0 ± 1.0
–2	42312 ± 226	3871 ± 9

[a] The elemental composition values are reported as average and standard deviations from three measurements, and are corrected for background contributions.

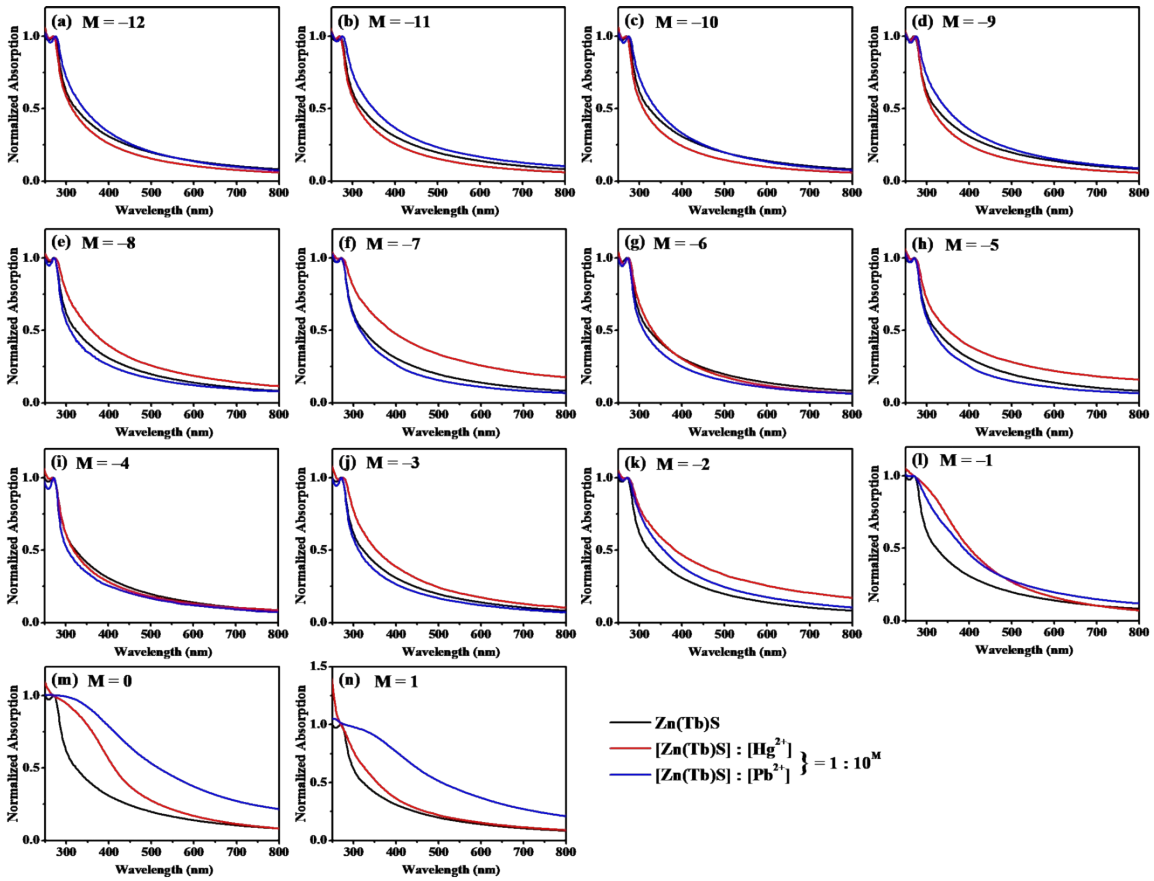


Figure S1. A comparison of the electronic absorption spectra of the Zn(Tb)S/Hg and Zn(Tb)S/Pb NPs are shown. The spectrum of the Zn(Tb)S NPs is included in all the panels for better comparison.

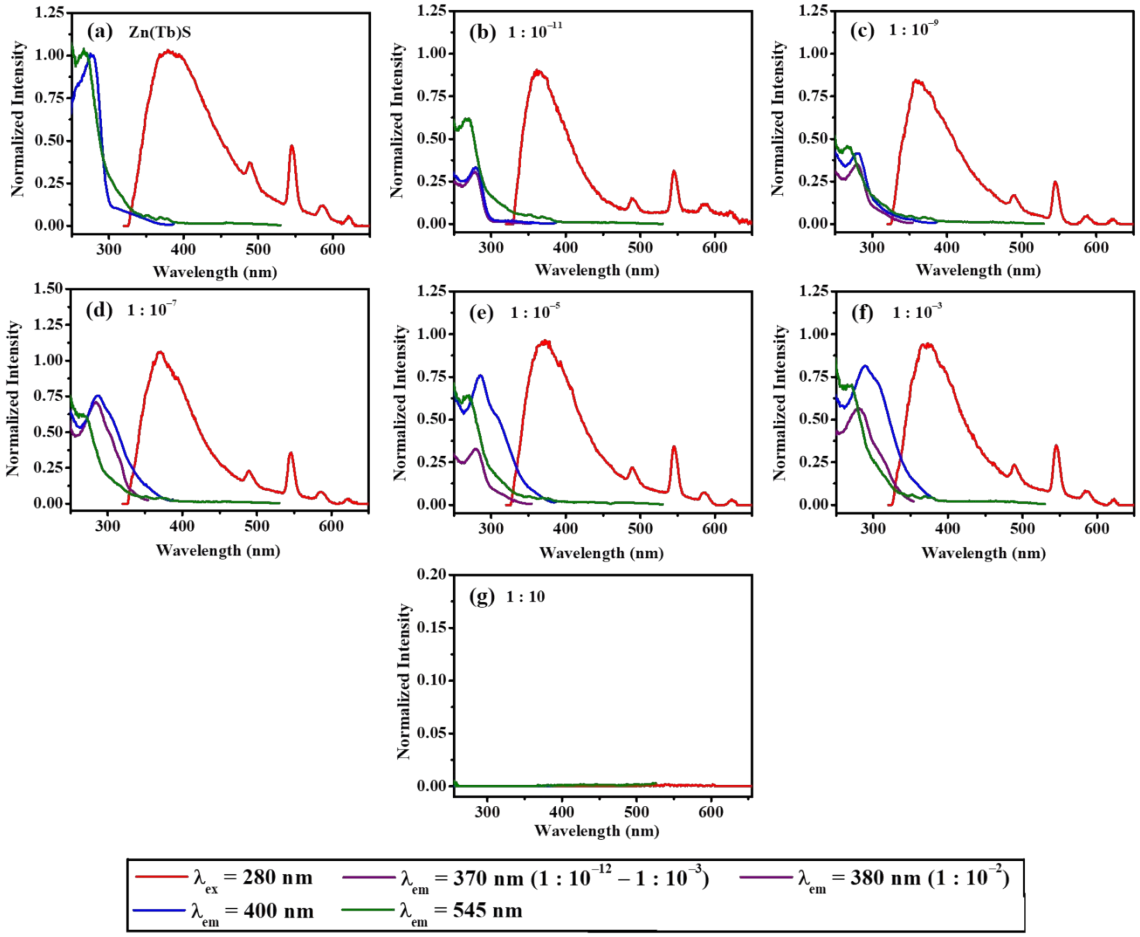


Figure S2. Steady-state photoluminescence spectra of the Zn(Tb)S NPs and the post-synthetically modified NPs with varying ratios of [Zn(Tb)S] : [Hg^{2+}] are shown.

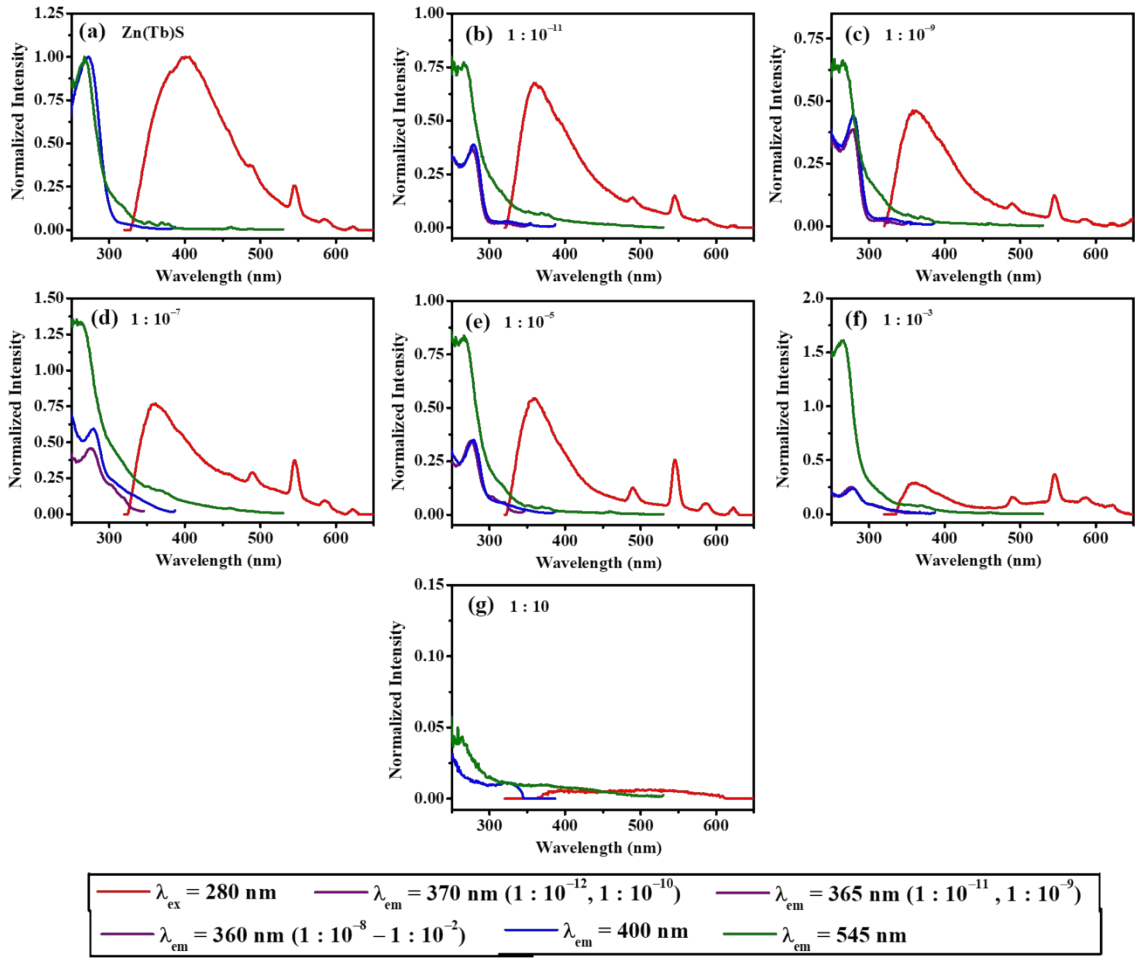


Figure S3. Steady-state photoluminescence spectra of the Zn(Tb)S NPs and the post-synthetically modified NPs with varying ratios of [Zn(Tb)S] : [Pb^{2+}] are shown.

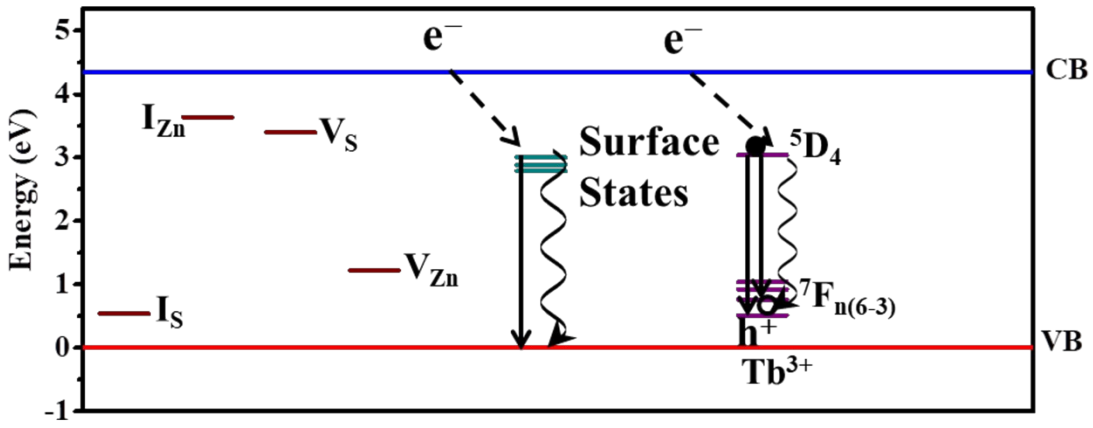


Figure S4. An energy level diagram summarizing key photophysical processes in the Zn(Tb)S NPs is shown.

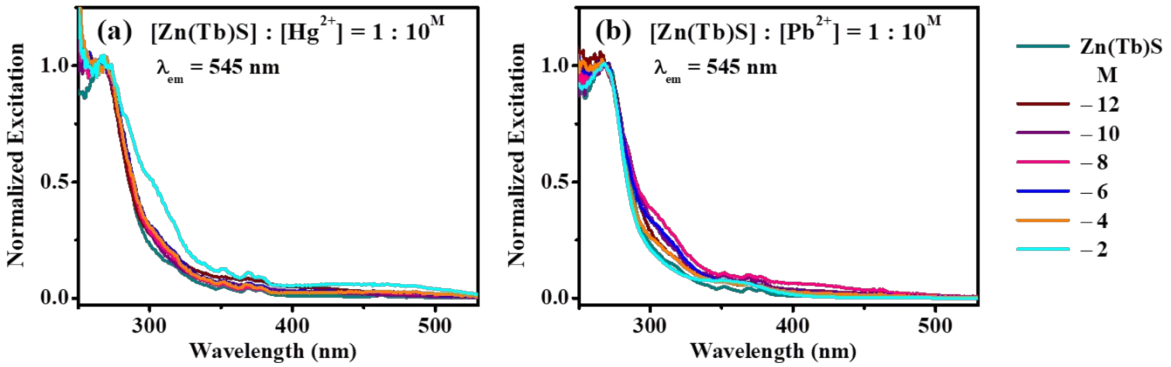


Figure S5. The normalized excitation spectra of the Zn(Tb)S/Hg and Zn(Tb)S/Pb NPs are shown in panels (a) and (b), respectively.

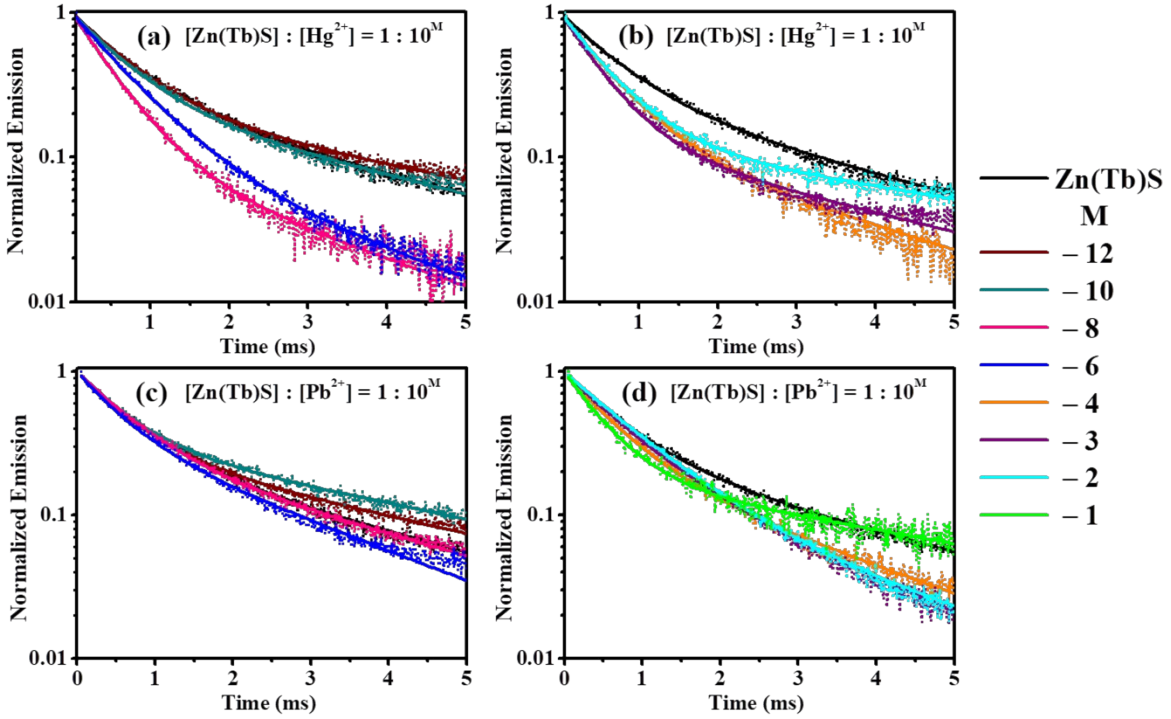


Figure S6. Tb^{3+} emission decay profiles in different NPs are shown.

Table S4. Lifetime Decay Parameters of Tb^{3+} Emission in the Zn(Tb)S/M [M = Hg / Pb] NPs.[a]

	Sample	a_1	τ_1 (ms)	a_2	τ_2 (ms)	$\langle\tau\rangle$ (ms)[b]	R^2
	Zn(Tb)S	0.73 ± 0.05	0.70 ± 0.07	0.27 ± 0.05	3.10 ± 0.03	1.30 ± 0.17	0.997
[Zn(Tb)S] : [Hg^{2+}]	$1 : 10^{-12}$	0.73 ± 0.04	0.62 ± 0.06	0.27 ± 0.04	4.1 ± 0.14	1.60 ± 0.21	0.996
	$1 : 10^{-10}$	0.76 ± 0.01	0.63 ± 0.01	0.24 ± 0.01	2.90± 0.64	1.20 ± 0.16	0.999
	$1 : 10^{-8}$	0.92 ± 0.04	0.51 ± 0.04	0.08 ±0.04	2.10 ± 0.28	0.64 ± 0.09	0.997
	$1 : 10^{-6}$	0.83 ± 0.07	0.61 ± 0.05	0.17 ± 0.07	2.40 ± 0.07	0.90 ± 0.18	0.998
	$1 : 10^{-4}$	0.80 ± 0.05	0.56 ± 0.04	0.20 ± 0.05	2.60 ± 0.07	1.00 ± 0.14	0.997
	$1 : 10^{-3}$	0.86 ± 0.01	0.46 ± 0.01	0.14 ± 0.01	3.30 ± 0.14	0.86 ± 0.04	0.998
	$1 : 10^{-2}$	0.87 ± 0.01	0.54 ± 0.01	0.13 ± 0.01	4.90 ± 0.03	1.11 ± 0.05	0.997
[Zn(Tb)S] : [Pb^{2+}]	$1 : 10^{-12}$	0.69 ± 0.01	0.53 ± 0.09	0.31 ± 0.01	3.9 ± 0.42	1.60 ± 0.15	0.995
	$1 : 10^{-10}$	0.67 ± 0.01	0.49 ± 0.11	0.34 ± 0.01	4.0 ±0.07	1.67 ± 0.09	0.996
	$1 : 10^{-8}$	0.70 ± 0.14	0.55 ± 0.13	0.30 ± 0.01	2.7 ± 0.28	1.20 ± 0.15	0.996
	$1 : 10^{-6}$	0.66 ± 0.04	0.49 ± 0.04	0.34 ± 0.04	2.2 ± 0.07	1.07 ± 0.10	0.996
	$1 : 10^{-4}$	0.72 ± 0.04	0.59 ± 0.01	0.28 ± 0.04	2.3 ± 0.02	1.06 ± 0.10	0.997
	$1 : 10^{-3}$	0.72 ± 0.01	0.72 ± 0.07	0.28 ± 0.01	2.0 ± 0.14	1.08 ± 0.06	0.999
	$1 : 10^{-2}$	0.84 ± 0.01	0.83 ± 0.01	0.16 ± 0.01	2.7 ± 0.07	1.13 ± 0.03	0.999
	$1 : 10^{-1}$	0.78 ± 0.04	0.48 ± 0.01	0.22 ± 0.04	4.7 ± 0.21	1.40 ± 0.19	0.990

[a] The values are reported as the average and standard deviations from multiple measurements.

[b] $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$.

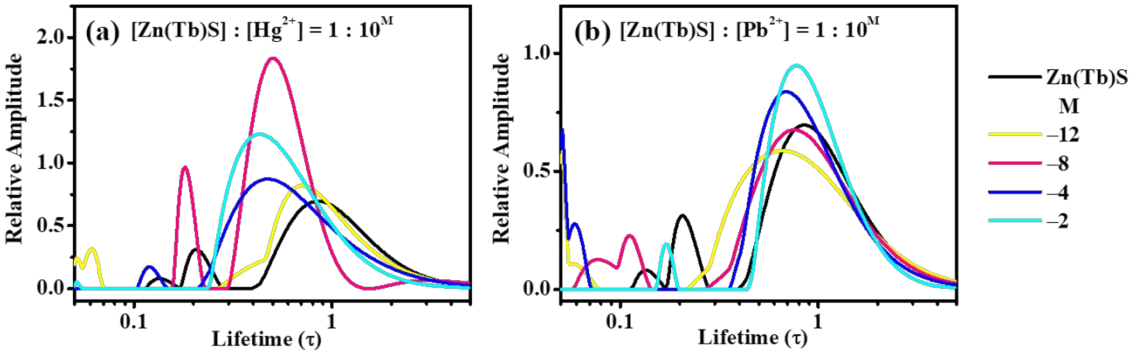
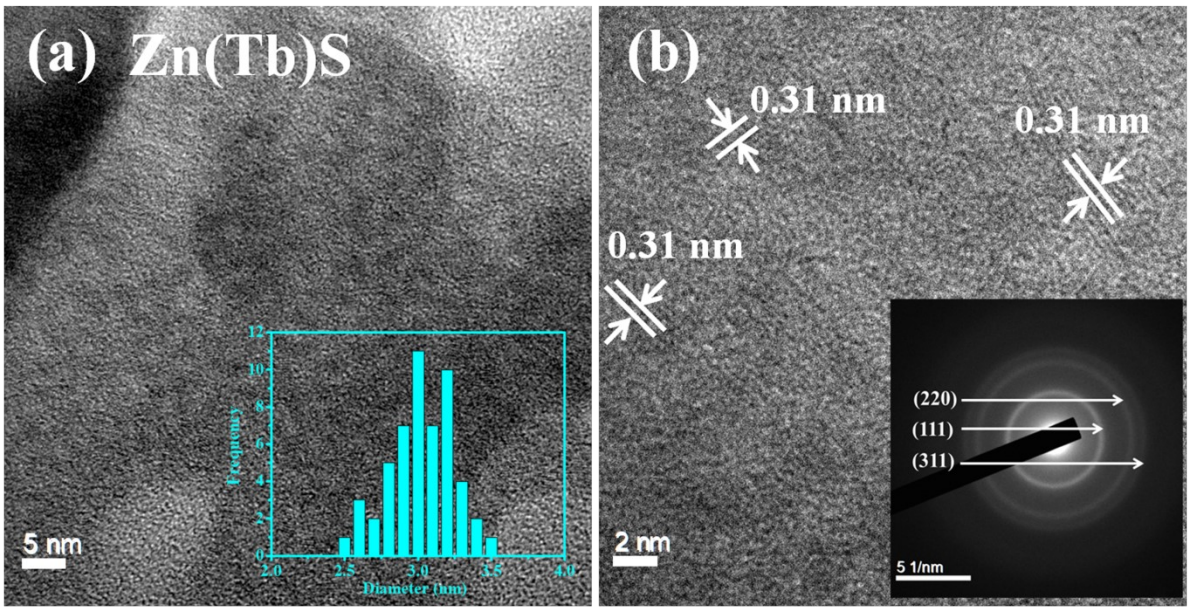
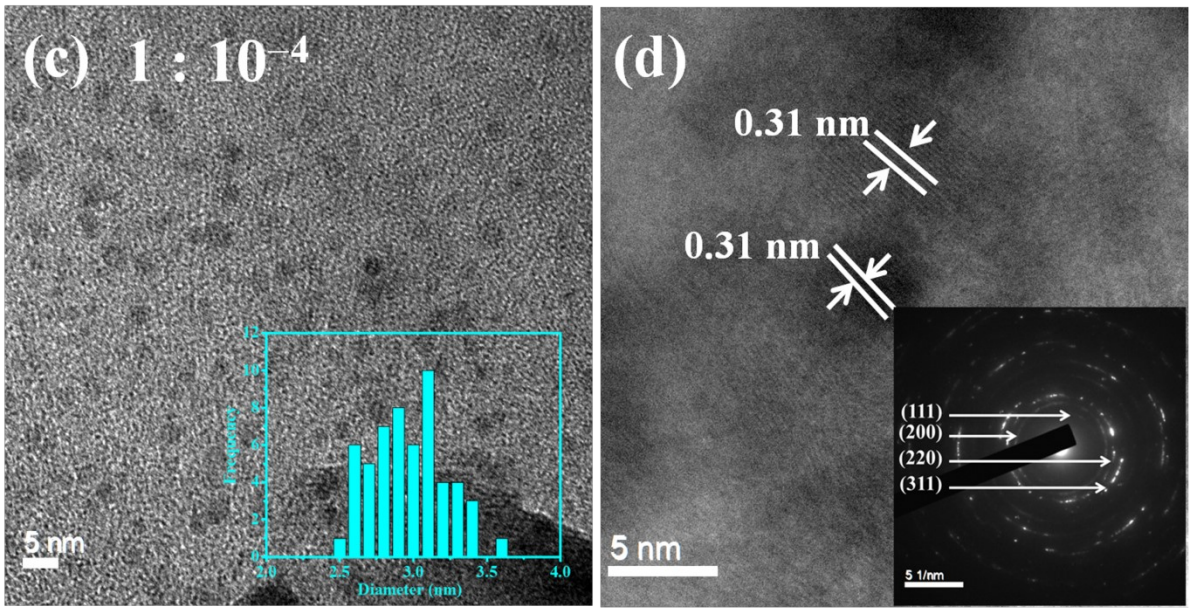


Figure S7. Lifetime distribution profiles of the Zn(Tb)S NPs with post-synthetic addition of Hg^{2+} and Pb^{2+} are shown in panels (a) and (b), respectively.


(a) Zn(Tb)S
5 nm
Frequency
Diameter (nm)
(b)
0.31 nm
0.31 nm
0.31 nm
(220)
(111)
(311)
2 nm
5 1/nm

[Zn(Tb)S] : [Hg^{2+}]


(c) 1 : 10^{-4}
5 nm
Frequency
Diameter (nm)
(d)
0.31 nm
0.31 nm
(111)
(200)
(220)
(311)
5 nm
5 1/nm

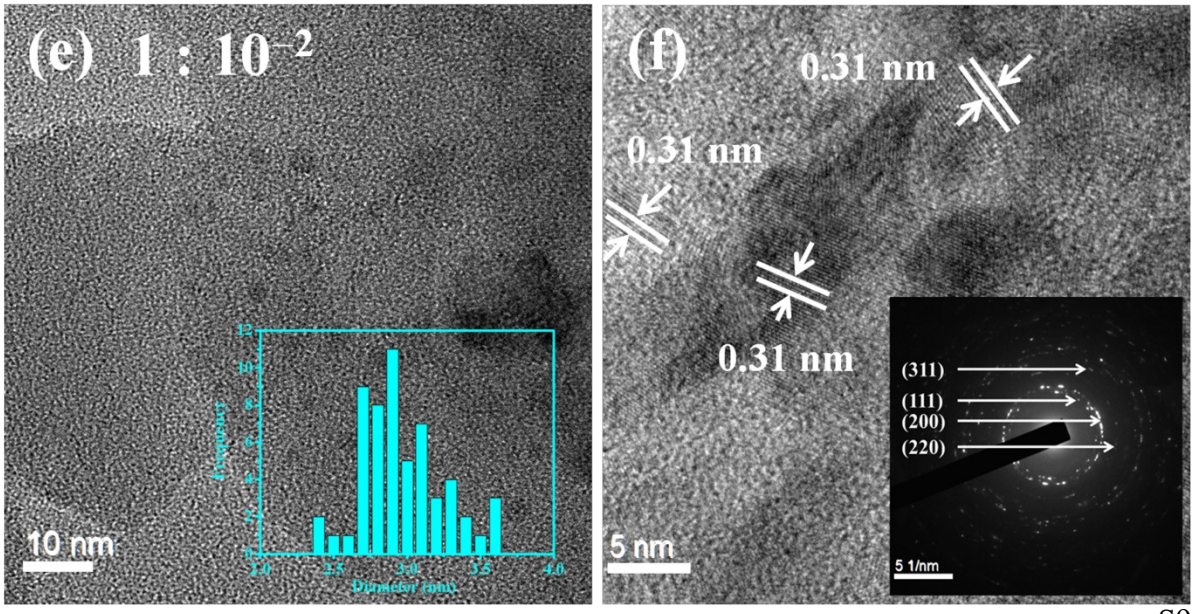

(e) 1 : 10^{-2}
10 nm
Frequency
Diameter (nm)
(f)
0.31 nm
0.31 nm
0.31 nm
(311)
(111)
(200)
(220)
5 nm
5 1/nm

Figure S8. The TEM with size distribution in the inset, HRTEM with SAED pattern in the inset are shown for the Zn(Tb)S, and the samples with [Zn(Tb)S] : [Hg^{2+}] = $1:10^{-4}$ and $1:10^{-2}$.

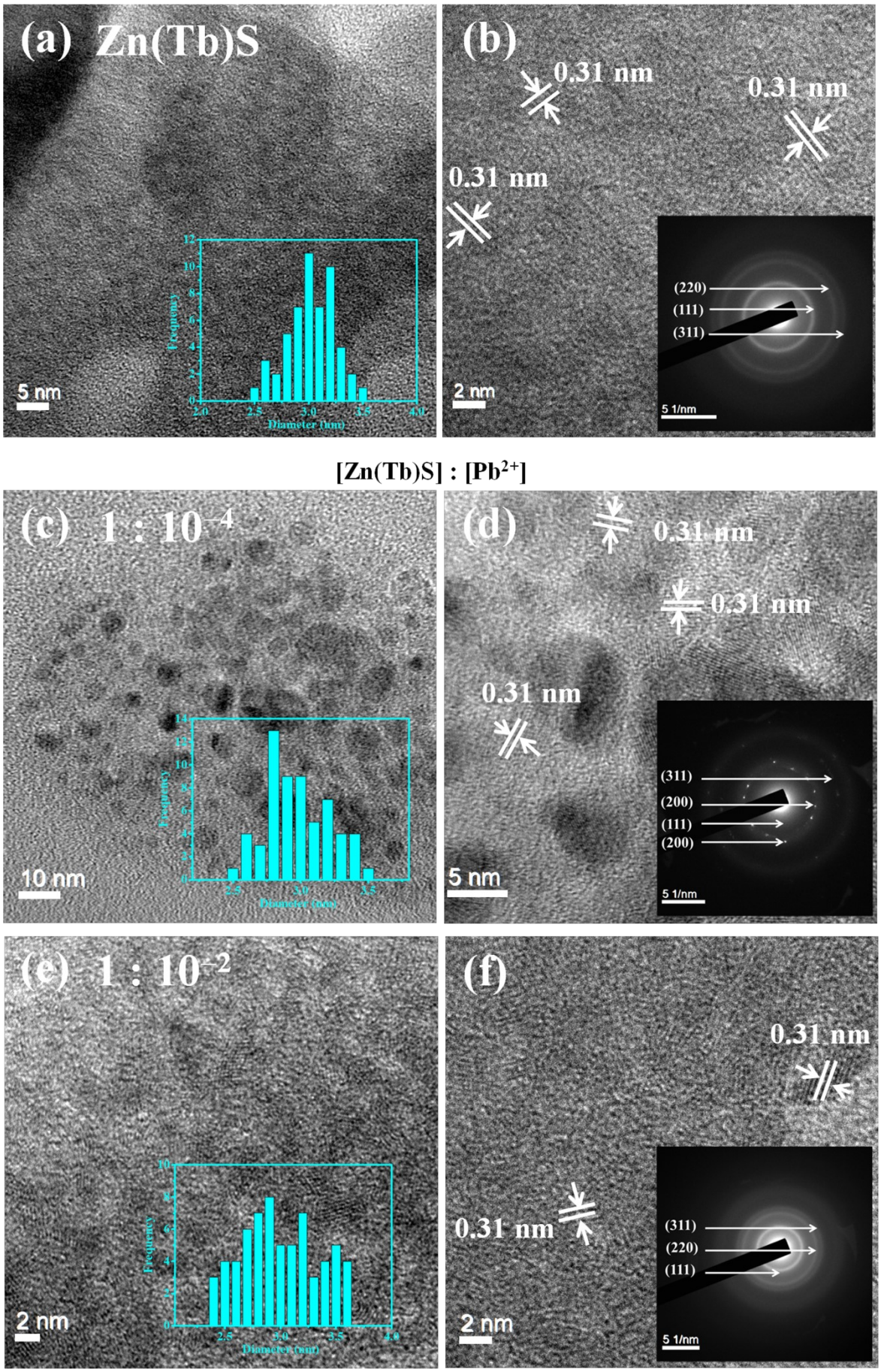
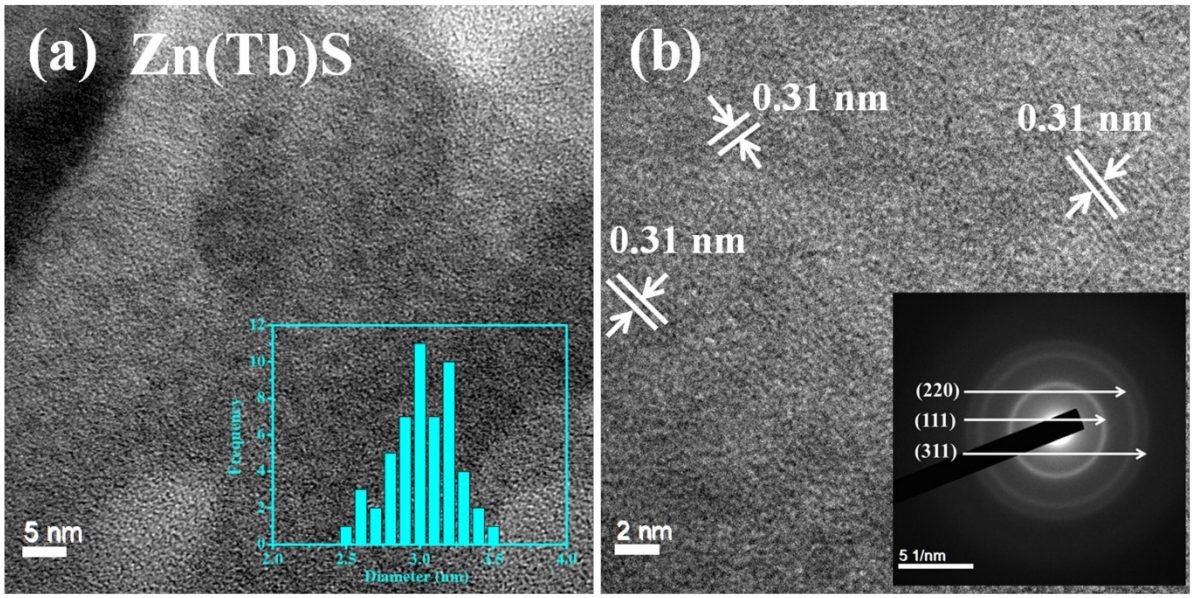

(a) Zn(Tb)S
5 nm
Frequency
Diameter (nm)
(b)
0.31 nm
0.31 nm
0.31 nm
(220)
(111)
(311)
2 nm
5 1/nm
[Zn(Tb)S] : [Pb2+]
(c) 1 : 10−4
10 nm
Frequency
Diameter (nm)
(d)
0.31 nm
0.31 nm
0.31 nm
(311)
(200)
(111)
(200)
5 nm
5 1/nm
(e) 1 : 10−2
2 nm
Frequency
Diameter (nm)
(f)
0.31 nm
0.31 nm
(311)
(220)
(111)
2 nm
5 1/nm

Figure S9. The TEM with size distribution in the inset, HRTEM with SAED pattern in the inset are shown for the Zn(Tb)S, and the samples with [Zn(Tb)S] : [Pb^{2+}] = 1:10^{-4} and 1:10^{-2}.



[Zn(Tb)S] : [Hg^{2+}]

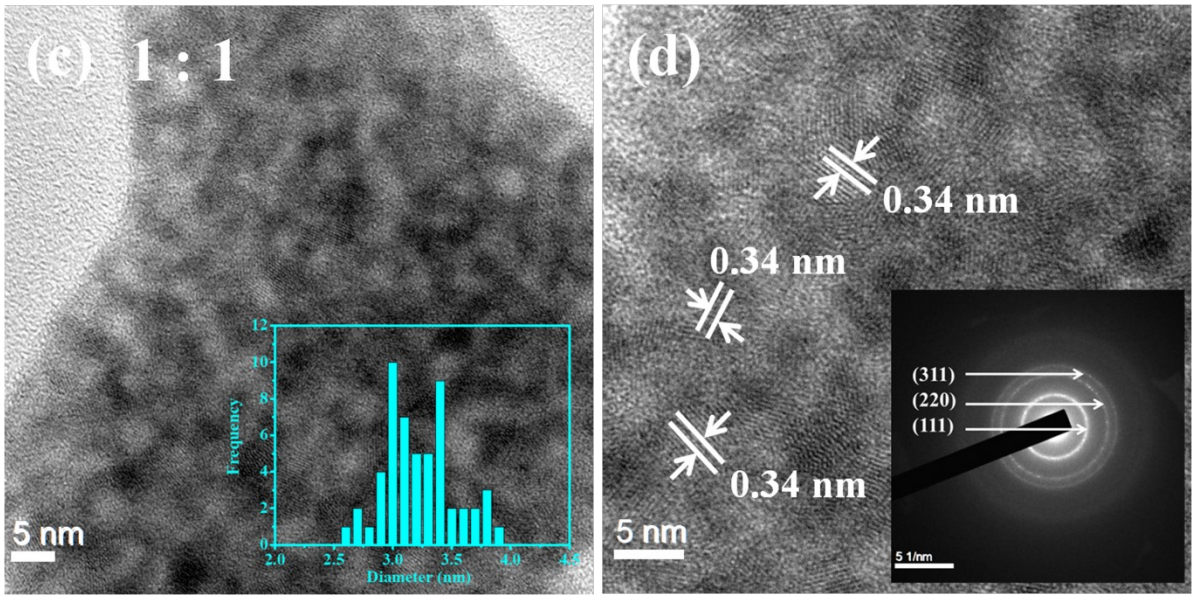


Figure S10. The TEM with size distribution in the inset, HRTEM with SAED pattern in the inset are shown for the Zn(Tb)S, and the samples with [Zn(Tb)S] : [Hg^{2+}] = 1:1.

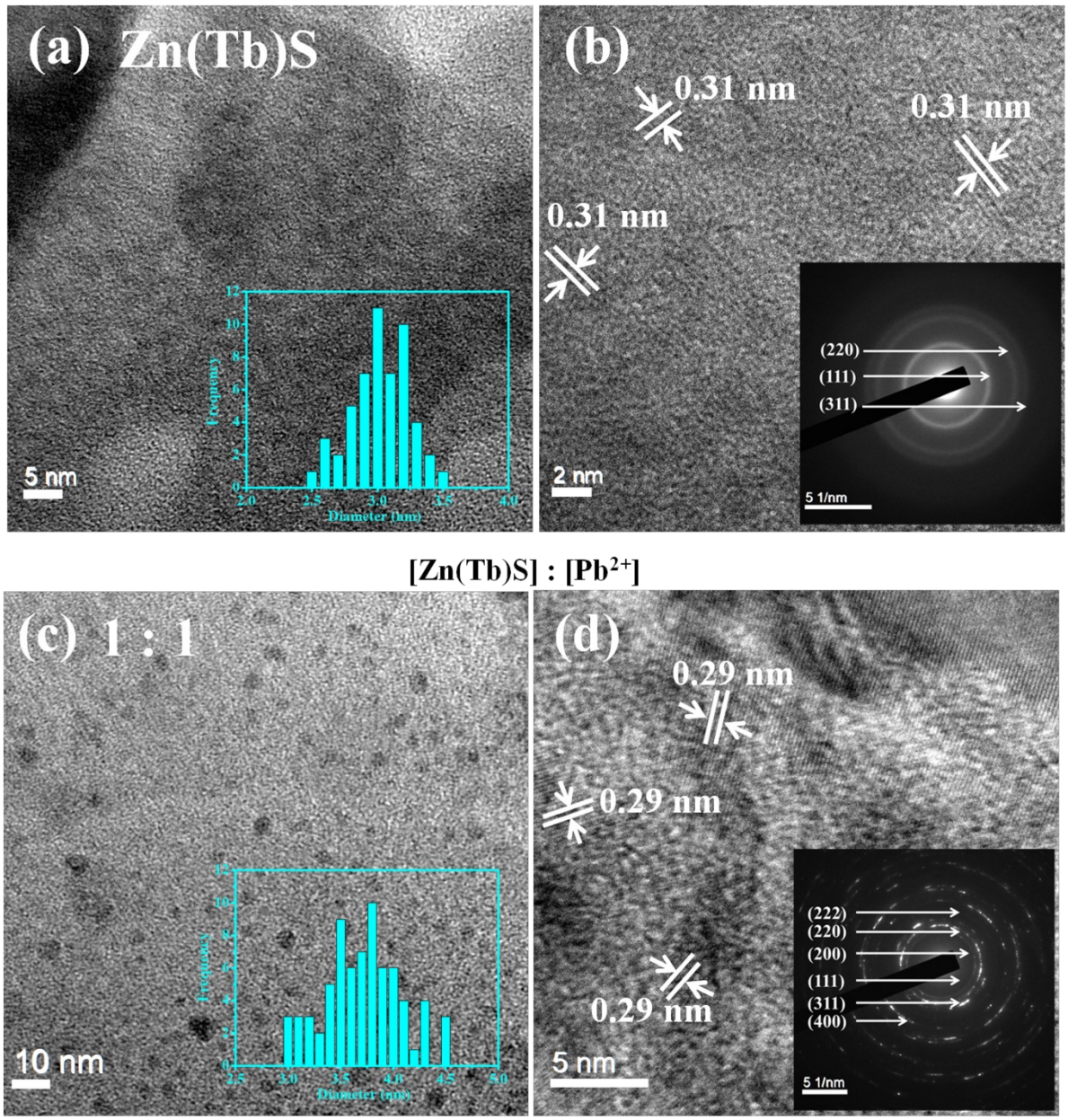


Figure S11. The TEM with size distribution in the inset, HRTEM with SAED pattern in the inset are shown for the Zn(Tb)S, and the samples with [Zn(Tb)S] : [Pb^{2+}] = 1:1.