Supplementary Information for ***Acta Phys. -Chim. Sin.*****, 2010, 26(11): 3113-3119**

一种新型纺锤状 α-Fe_2O_3 纳米晶的合成、表征及其表面性能

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Synthesis, Characterization and Surface Functionalization of Novel Spindle-Like α-Fe_2O_3 Nanocrystals

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Supporting Information

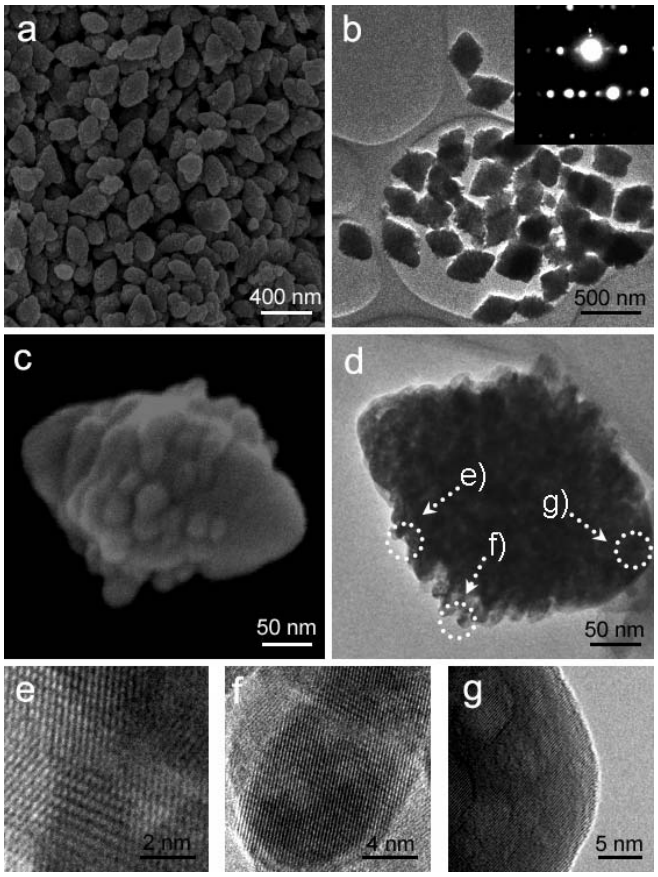

Fig.S1 SEM, TEM and HRTEM images of NFO-1

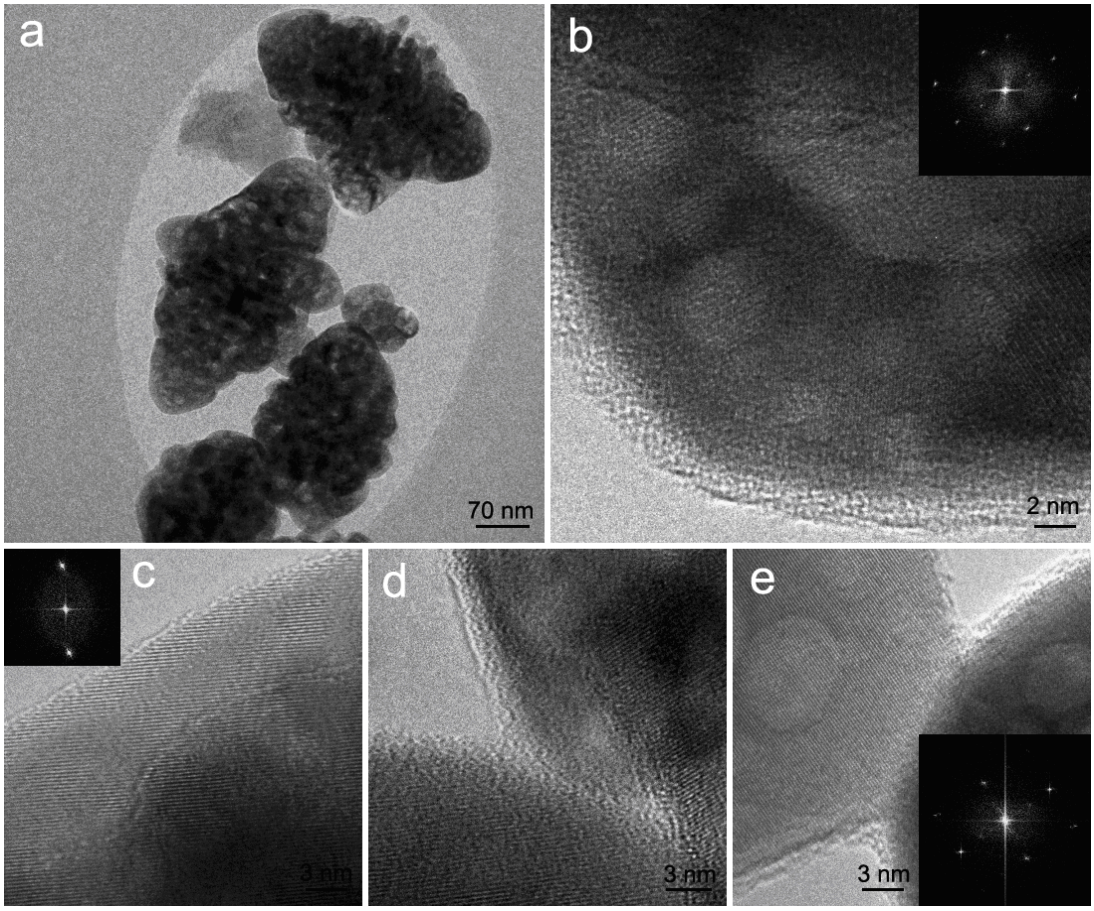

Fig.S2 TEM and HRTEM images of NFO-11

Insets are the corresponding FFT diffractograms

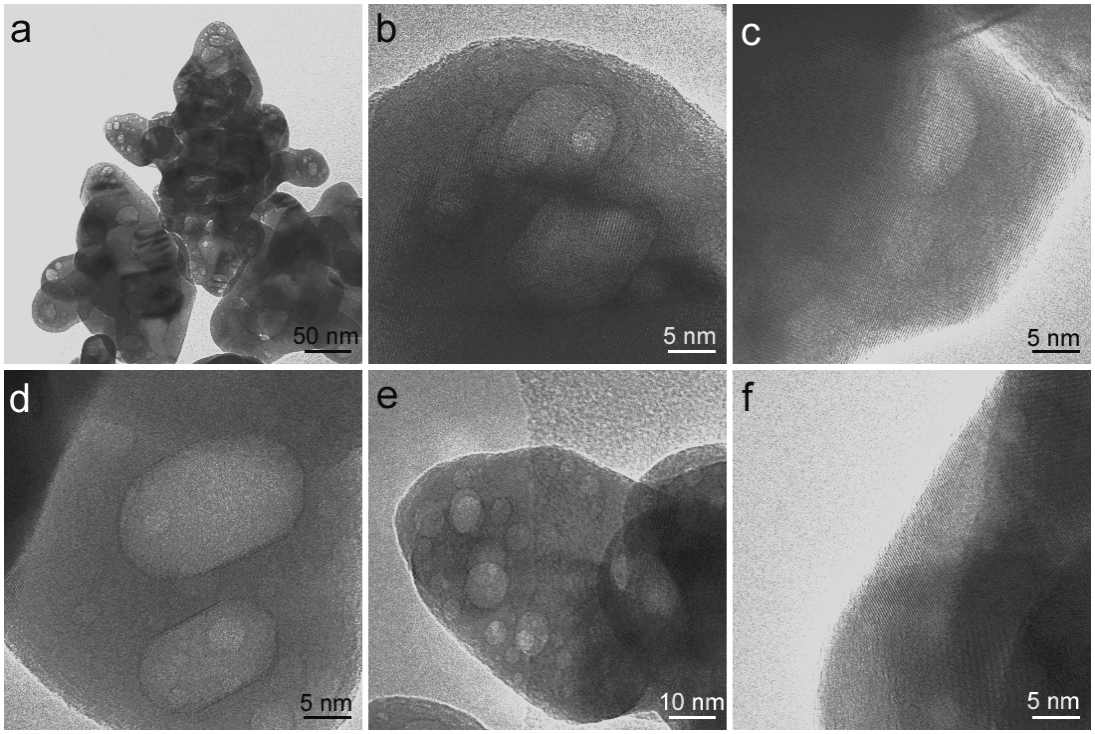

Fig.S3 TEM and HRTEM images of NFO-12

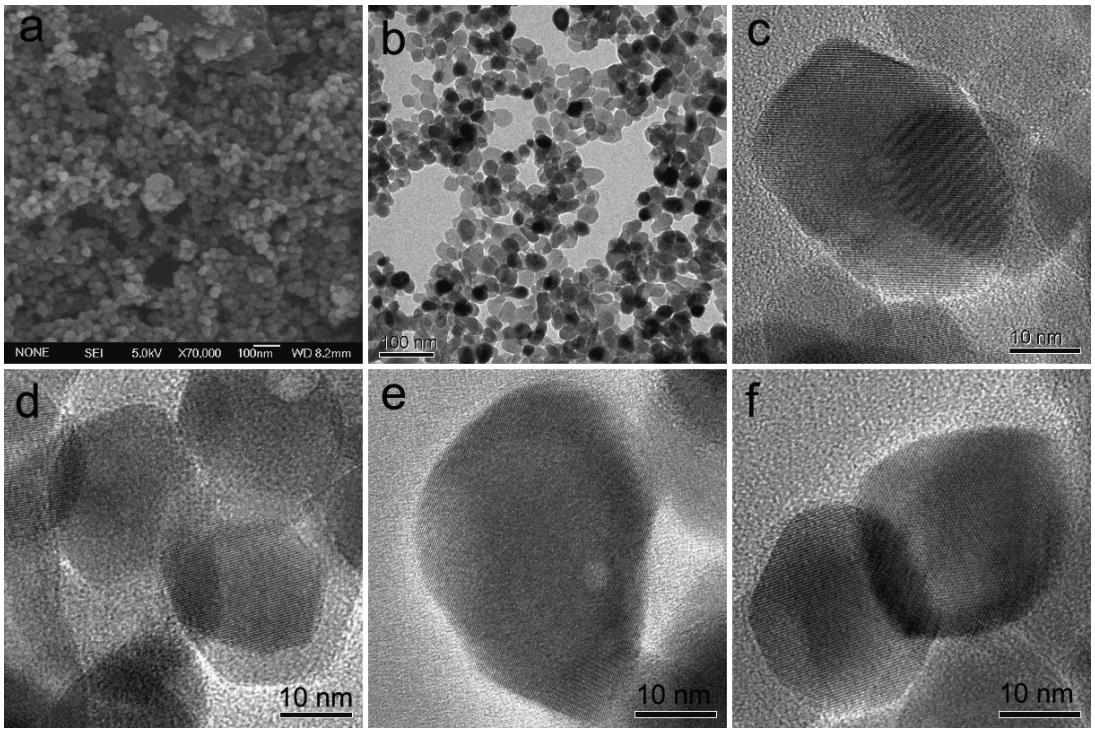

Fig.S4 SEM, TEM and HRTEM images of NFO-2

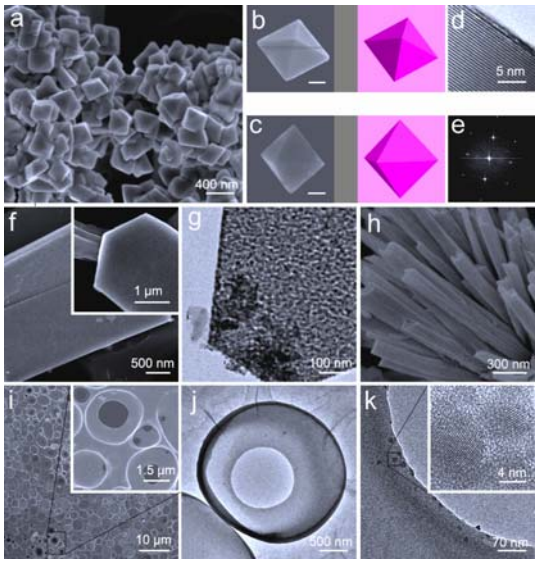

Fig.S5 SEM and TEM images of synthesized transition metal oxides nanocrystals and Fe_2O_3/SiO_2 complex oxides in the NFO-2 synthesis system

(a)-(e) Mn_3O_4 nanocrystals. Scale bars in inset are 100 nm. (f) - (g)CuO nanocrystals. (h) Co_3O_4 nanocrystals arrays. (i) - (k) Fe_2O_3/SiO_2 complex oxides. Because of different structure units, although the resulted materials are synthesized by uniform methods, their morphologies are different from each other. Mn_3O_4 is uniform octahedron shape with a diameter ~300 nm, whereas Co_3O_4 nanocrystals arrays are characterized as having rod-like shape with a diameter ~150 nm and length ~2.4 μm and CuO nanocrystals are sheet-like morphology. SiO_2/Fe_2O_3 complex oxides are round-like morphology and Fe_2O_3 nanocrystals are uniformly dispersed in the silica matrix.

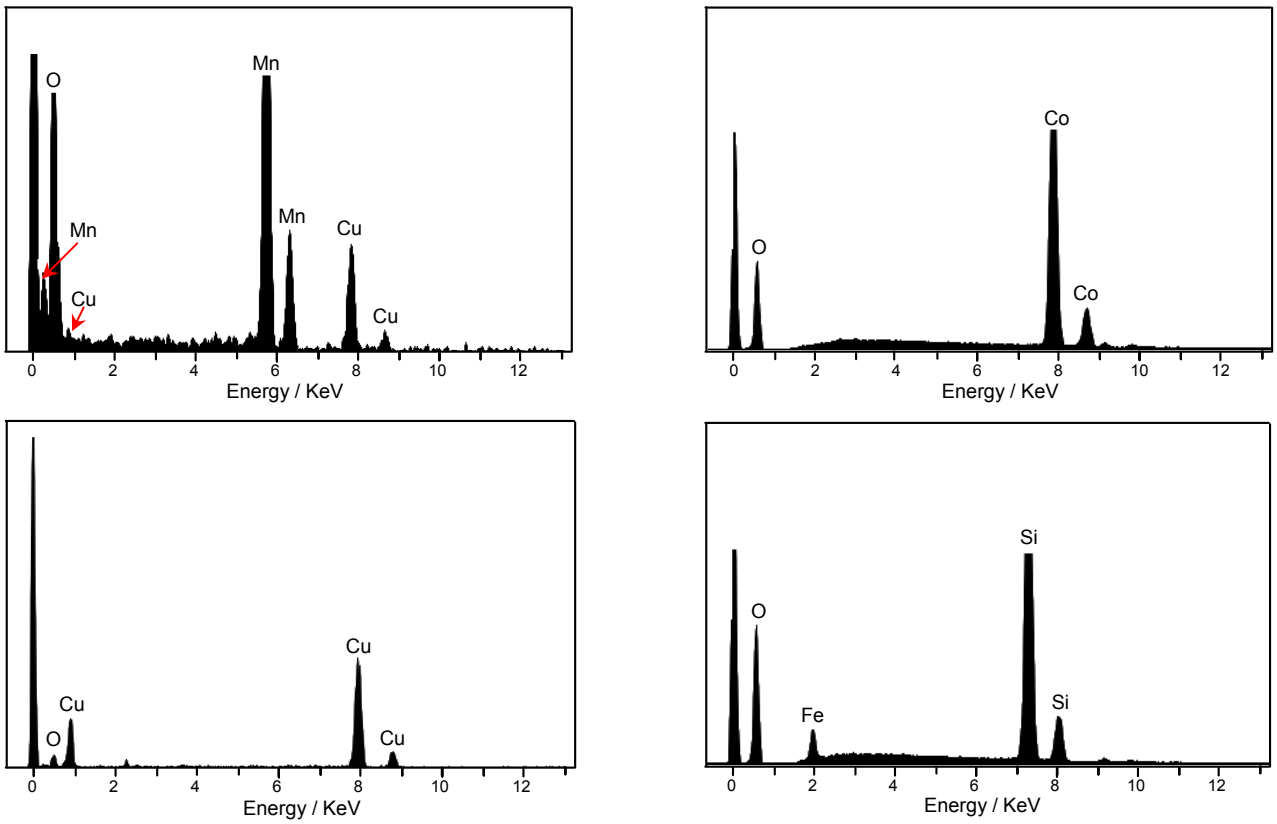

Fig.S6 The presence of carbon and copper element is owing to the use of the copper grids covered with carbon films for EDX analysis

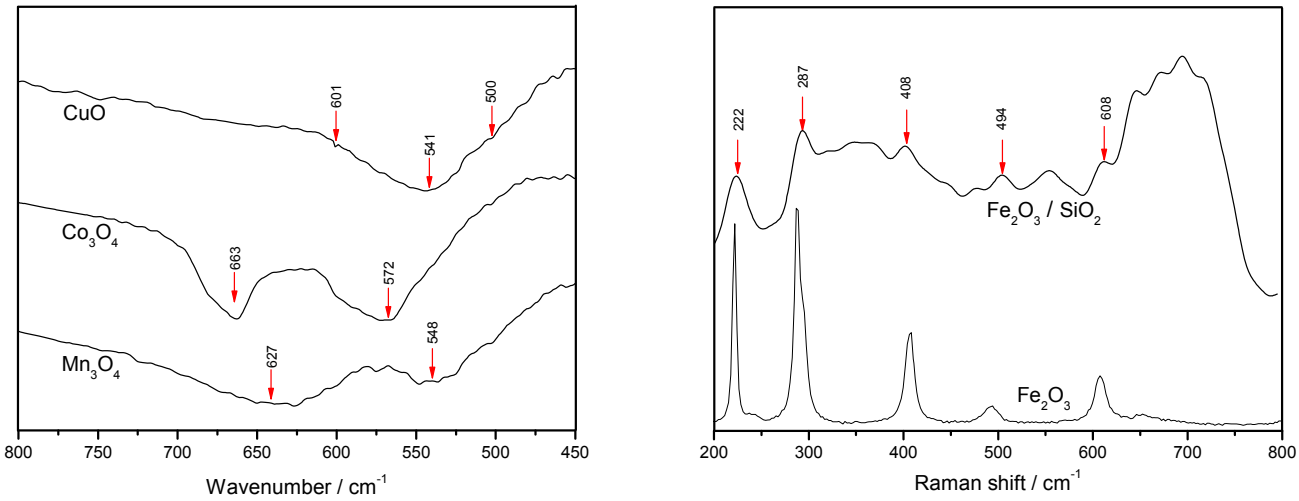

Fig.S7 The FT-IR spectrum of the synthesized transition metal oxide nanocrystals (a) and Raman spectroscopy of the synthesized complex oxides (b)

The synthesis procedure of Fe_2O_3/SiO_2: 4.76 g CTAB was dissolved in 50 ml deionizer water at 60 ^oC with vigorous stirring to form a clear solution. 1.50 g SS and 4.4 ml EA were added to the clear solution with vigorous

stirring for 5min, and the mixture was kept static at 23 ^{o}C for 8 h in the airproofed. Then the precipitation was collected by centrifugation and dried at 60 ^{o}C in the airproofed. The obtained SiO_2 by the above method was dispersed in 50ml deionizer water by ultrasonic 2h. The turbidity liquid was added to another solution that 0.1845 g of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 150 ml deionizer water followed by addition of 1.0983 g CTAB and 1.1926 g urea stirring at room temperature for 10 min. The mixture system was sealed to a Teflon flask and aged in the airproofed at 85 ^{o}C for 24 h. After the flask cooled down, the resulting synthesis red solid was collected and washed with absolute alcohol two times to remove the surfactants and dry at 60 ^{o}C in the airproofed. Finally the products calculated at 650 ^{o}C for 1 h.

The synthesis process of single MOx (Mn_3O_4, Co_3O_4 and CuO) nanocrystals follows that of NFO-2: 1.11 mmol precursor ($MnSO_4 \cdot H_2O$, $Co(NO_3)_2 \cdot 5H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$) was dissolved in deionized water (200 ml) before adding CTAB (3.33 mmol) and urea (22.2 mmol) under stirring for 10 min to form a clear solution. The reaction mixture was kept static reaction for 24 h at room temperature (23 ^{o}C). The mixture was then allowed to age in the airproofed Teflon flask at 85 ^{o}C under static conditions for 24 h. After aged, the resulting solid was washed with ethanol (100 ml × 2) to remove the surfactants and collected though centrifugation and dried at room temperature. The leftover surfactants were removed by calcinations at 240 ^{o}C for 5 h.

The FT-IR spectrum (Fig. S7a) shows characteristic absorption bands at 628 and 548 cm^{-1}, 663 and 572 cm^{-1}, 601, 542 and 501 cm^{-1}, respectively, corresponding to Mn_3O_4, Co_3O_4, CuO, which have been documented by the literatures[1-3]. And Raman spectroscopy obtained for Fe_2O_3/SiO_2 is presented in Fig. S7b, for comparison the Raman spectrum of Fe_2O_3 is also recorded, which exhibits five resonant peaks at about 222, 287, 408, 494, and 608 cm^{-1} in the range of 200-700 cm^{-1}. The positions of the peaks are in good agreement with the typical frequencies observed from α-Fe_2O_3[4].

References

1. Vázquez-Olmos, A. *et al.* One-step synthesis of Mn_3O_4 nanoparticles: structural and magnetic study. *J. Colloid Interf. Sci.* **291,** 175–180 (2005).
2. Meng, Y. D., Chen, D. R. & Jiao, X. L. Fabrication and characterization of mesoporous Co_3O_4 core/mesoporous silica shell nanocomposites. *J. Phys. Chem. B* **110,** 15212–15217 (2006).
3. Vaseem, M. *et al.* Flower-shaped CuO nanostructures: structural, photocatalytic and XANES studies. *Catal. Commun.* **10,** 11–16 (2008).
4. Li, S. Z., Zhang, H., Wu, J. B., Ma, X. Y. & Yang, D. R. Shape-control fabrication and characterization of the airplane-like FeO(OH) and Fe_2O_3 nanostructures. *Cryst. Growth Des.* **6,** 351–353 (2006).

Table S1 The particle sizes statistics of NFO-1 estimated from SEM images

Paticle	Long axis /nm	Short axis / nm	Long axis /Short axis
1	456	325	1.4
2	447	300	1.5
3	425	269	1.6
4	497	325	1.5
5	490	320	1.5
6	440	310	1.4
7	510	350	1.5
8	470	320	1.5
9	370	270	1.4
10	380	260	1.5
11	430	290	1.5
12	440	310	1.4
13	360	240	1.5
14	400	280	1.4
15	500	330	1.5
16	440	290	1.5
17	430	290	1.5
18	390	290	1.3
19	480	320	1.5
20	460	320	1.4
21	430	300	1.4
22	420	270	1.6
23	450	310	1.5
24	430	290	1.5
	439.3	**299.1**	**1.5**

Long axis: 370-510 nm; Short axis: 260-350 nm.

Table S2 The particle sizes statistics of NFO-2 estimated from SEM images

particle	particle size/nm	particle	particle size/nm	particle	particle size/nm
1	35.04×27.27	44	28.57×28.57	87	32.48×33.77
2	32.48×31.17	45	37.66×38.96	88	37.66×42.86
3	37.66×36.36	46	28.57×28.57	89	35.04×41.56
4	32.48×31.17	47	28.57×29.87	90	36.36×36.36
5	32.48×31.17	48	32.48×33.77	91	36.36×32.48
6	31.17×33.77	49	35.04×35.04	92	31.17×36.36
7	35.04×32.48	50	32.48×41.56	93	33.77×28.57
8	35.04×35.04	51	40.26×36.36	94	33.77×32.48
9	38.96×37.66	52	29.87×33.77	95	35.04×37.66
10	41.56×41.56	53	31.17×35.04	96	37.66×42.86
11	36.36×35.04	54	37.66×38.96	97	44.16×38.96
12	37.66×40.26	55	38.96×44.16	98	38.96×36.36
13	32.48×29.87	56	37.66×35.04	99	36.36×36.36
14	31.17×32.48	57	44.16×44.16	100	41.56×31.17
15	41.56×40.26	58	33.77×37.66	101	32.48×37.66
16	31.17×28.57	59	33.77×28.57	102	33.77×38.96
17	25.97×29.87	60	32.48×28.57	103	27.27×29.87
18	33.77×35.04	61	29.87×31.17	104	38.96×28.57
19	33.77×38.96	62	33.77×36.36	105	44.16×40.26
20	35.04×37.66	63	32.48×41.56	106	35.04×27.27
21	40.26×42.86	64	36.36×37.66	107	31.17×29.87
22	35.04×32.48	65	35.04×33.77	108	41.56×40.26
23	29.87×29.87	66	36.36×37.66	109	46.75×33.77
24	32.48×32.48	67	42.86×35.04	110	32.48×37.66
25	31.17×28.57	68	31.17×32.48	111	35.04×33.77
26	35.04×32.48	69	45.45×36.36	112	38.96×32.48
27	28.57×29.87	70	32.48×37.66	113	35.04×37.66
28	31.17×31.17	71	35.04×41.56	114	35.04×36.36

29	31.17×36.36	72	36.36×37.66	115	44.16×33.77
30	32.48×36.36	73	40.26×41.56	116	32.48×41.56
31	37.66×35.04	74	38.96×33.77	117	36.36×32.48
32	28.57×29.87	75	31.17×36.36	118	37.66×38.96
33	36.36×37.66	76	33.77×41.56	sample average	35.24×35.18