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

Supplementary materials

A New Insight into Thermodynamical Criterion for Preparation of Semiconductor and Metal Nanocrystals using Polymerized Complexing method

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Table S1. Experimental conditions for preparation of different NCs

Product	Initial chemical agents
Ni	$Ni(NO_3)_2 \cdot 6H_2O$, gelatin, PVP, DW
Ni	$Ni(NO_3)_2 \cdot 6H_2O$, arabinose, PVP, DW
Ni	$Ni(NO_3)_2 \cdot 6H_2O$, trehalose, PVP, DW
Ni	$Ni(NO_3)_2 \cdot 6H_2O$, inulin, PVP, DW
Ni	$Ni(NO_3)_2 \cdot 6H_2O$, raffinose, PVP, DW
Ag	$AgNO_3$, gelatin, Tween20, DW
Cu	$Cu(CH_3COO)_2 \cdot 6H_2O$, gelatin, PVP, DW
Te	H_6TeO_6, gelatin, PVP, DW
Te	H_6TeO_6, CA, PVP, DW
Te	H_6TeO_6, starch, PVP, DW
Te	H_6TeO_6, Coca-Cola, PVP, DW
Te	H_6TeO_6, Sprite, PVP, DW
Bi	$Bi(NO_3)_3 \cdot 5H_2O$, gelatin, PVP, EG
Bi	$Bi(NO_3)_3 \cdot 5H_2O$, CA, PVP, EG
Bi	$Bi(NO_3)_3 \cdot 5H_2O$, acrylamide, PVP, EG
Bi	$Bi(NO_3)_3 \cdot 5H_2O$, nitric acid, glucose, PVP, DW
Sb	$Sb(CH_3COO)_3$, gelatin, PVP, EG
Sb	$Sb(CH_3COO)_3$, CA, PVP, EG
Co	$Co(NO_3)_2 \cdot 6H_2O$, CA, PVP, DW
Co	$Co(NO_3)_2 \cdot 6H_2O$, starch, PVP, DW

Co	$Co(NO_3)_2 \cdot 6H_2O$, EDTA, PVP, DW
Co	$Co(NO_3)_2 \cdot 6H_2O$, ascorbic acid, PVP, DW
Co	$Co(NO_3)_2 \cdot 6H_2O$, glucose, PVP, DW
Co	$Co(NO_3)_2 \cdot 6H_2O$, sucrose, PVP, DW
Co	$Co(NO_3)_2 \cdot 6H_2O$, sucrose, PVP, DW
Co	$Co(NO_3)_2 \cdot 6H_2O$, EG, PVP, DW
Cd	$Cd(CH_3COO)_2 \cdot 3H_2O$, glucose, PVP, DW
Sn	$SnCl_4 \cdot 5H_2O$, glucose, PVP, DW
CdTe	$Cd(CH_3COO)_2 \cdot 3H_2O$, H_6TeO_6, gelatin, PVP, DW
CdTe	$Cd(CH_3COO)_2 \cdot 3H_2O$, H_6TeO_6,CA, PVP, DW
CdTe	$Cd(CH_3COO)_2 \cdot 3H_2O$, H_6TeO_6, gelatin, Tween20, EG
Bi-Sb	$Bi(NO_3)_3 \cdot 5H_2O$, $Sb(CH_3COO)_3$, CA, PVP, EG
Bi-Sb	$Bi(NO_3)_3 \cdot 5H_2O$, $Sb(CH_3COO)_3$, gelatin, PVP, EG
$NiTe_{1.5}$	$Ni(NO_3)_2 \cdot 6H_2O$, H_6TeO_6, gelatin, PVP, DW
$NiTe_{1.5}$	$Ni(NO_3)_2 \cdot 6H_2O$, H_6TeO_6, CA, PVP, DW
$NiTe_{1.5}$	$Ni(NO_3)_2 \cdot 6H_2O$, H_6TeO_6, CA, PVP, EG
Ag_2Te	$AgNO_3$, H_6TeO_6, gelatin, Tween 20, DW
CuTe	$Cu(CH_3COO)_2 \cdot 6H_2O$, H_6TeO_6, CA, PVP, DW
Sb_2Te_3	$Sb(CH_3COO)_3$, H_6TeO_6, CA, PVP, EG
Bi_2Te_3	$Bi(NO_3)_3 \cdot 5H_2O$, CA, PVP, EG
Bi_2Te_3	$Bi(NO_3)_3 \cdot 5H_2O$, H_6TeO_6, gelatin, PVP, EG
In_2Te_3	$In(NO_3)_3$, H_6TeO_6, CA, PVP, DW

$CoTe_{1.5}$	$Co(NO_3)_2·6H_2O$, H_6TeO_6,gelatin, PVP, DW
SnSb	$SnCl_4·5H_2O$, $Sb(CH_3COO)_3$, CA, PVP, EG
SnTe	$SnCl_4·5H_2O$, H_6TeO_6, CA, PVP, DW
SnTe	$SnCl_4·5H_2O$, H_6TeO_6, gelatin, PVP, DW
CdS	$Cd(CH_3COO)_2·3H_2O$, thiocarbamide, CA, PVP, DW
$Ni_{2.9}SnTe_2$	$Ni(NO_3)_2·6H_2O$, $SnCl_4$, H_6TeO_6, CA, PVP, DW
$CuInS_2$	$Cu(CH_3COO)_2·6H_2O$, $In(NO_3)_3$, thiocarbamide, EDTA, PVP, DW
$CuInS_2$	$Cu(CH_3COO)_2·6H_2O$, $In(NO_3)_3$, thiocarbamide, CA, PVP, EG
$CuGaTe_2$	$Cu(CH_3COO)_2·6H_2O$, $Ga(NO_3)_3·H_2O$, H_6TeO_6,CA, PVP, DW

Table S2. Electronegativity of elements (Pauling)

H																
2.18																
Li	Be											B	C	N	O	F
0.98	1.57											2.04	2.55	3.04	3.44	3.98
Na	Mg											Al	Si	P	S	Cl
0.93	1.31											1.61	1.90	2.19	2.58	3.16
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.8	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.82	0.95	1.22	1.33	1.60	2.16	1.9	2.28	2.2	2.20	1.93	1.69	1.78	1.96	2.05	2.10	2.66
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.79	0.89	1.2	1.3	1.5	2.36	1.9	2.2	2.2	2.28	2.54	2.00	2.04	2.33	2.02	2.0	2.2

Table S3. Electronegativity of elements (Allred-Rochow)

H																
2.20																
Li	Be											B	C	N	O	F
0.97	1.47											2.01	2.50	3.07	3.50	3.40
Na	Mg											Al	Si	P	S	Cl
1.01	1.23											1.47	1.74	2.06	2.44	3.61
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.91	1.04	1.20	1.32	1.45	1.56	1.60	1.64	1.75	1.75	1.75	1.66	1.82	2.02	2.20	2.48	3.36
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.89	0.99	1.11	1.22	1.23	1.30	1.36	1.42	1.14	1.35	1.42	1.46	1.49	1.72	1.82	2.01	3.06
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.86	0.97	1.08	1.23	1.33	1.40	1.46	1.52	1.44	1.44	1.42	1.44	1.44	1.55	1.67	1.76	2.80

Table S4. Electrode Potential of metallic ions at room temperature (Unit: Voltage)

$2H^{+}+2e^{-} = H_2$	0.0000
$Cd^{2+}+2e^{-} = Cd$	-0.403
$In^{3+}+3e^{-} = In$	-0.338
$Co^{2+}+2e^{-} = Co$	-0.282
$Ni^{2+}+2e^{-} = Ni$	-0.257
$Sn^{2+}+2e^{-} = Sn$	-0.138
$Sn^{4+}+4e^{-} = Sn$	0.008
$SbO^{+}+2H^{+}+3e^{-} = Sb+H_2O$	0.204
$Bi^{3+}+3e^{-} = Bi$	0.317
$Cu^{2+}+2e^{-} = Cu$	0.340
$TeO_2(s)+4H^{+}+4e^{-} = Te(s)+2H_2O$ (l)	0.5285
$Rh^{3+}+3e^{-} = Rh$	0.6
$Ag^{+}+e^{-} = Ag$	0.7991
$Pd^{2+}+2e^{-} = Pd$	0.951
$Pt^{4+}+4e^{-} = Pt$	1.118
$Ir^{3+}+3e^{-} = Ir$	1.156
$Au^{3+}+3e^{-} = Au$	1.52

Table S5. Thermodynamical data of pure substances

Substance	$\Delta_f H_m^{\emptyset}$ (kJ·mol^{-1})	$S_m^{\emptyset}$ (J·mol^{-1}·K^{-1})	Substance	$\Delta_f H_m^{\emptyset}$ (kJ·mol^{-1})	$S_m^{\emptyset}$ (J·mol^{-1}·K^{-1})
H_2	0	130.680	H_2O (g)	-241.826	188.959
			H_2O(l)	-285.83	69.950
Ag	0	42.677	Ag_2O	-31.049	121.298
As	0	35.706	As_2O_3	-654.796	117.001
Au	0	47.497	Au_2O_3	-3.347	130.332
Bi	0	56.735	Bi_2O_3	-573.883	151.499
C(s)	0	5.740	CH_4	-74.387	186.214
CO	-110.541	197.661	CO_2	-393.505	213.77
Cd	0	51.798	CdO	-258.99	54.810
Co	0	30.041	Co_3O_4	-910.02	114.307
CoO	-237.944	52.969	Cu	0	33.164
CuO	-156.063	42.593	Fe	0	27.28
Fe_2O_3	-824.248	87.404	Fe_3O_4	-1118.383	146.147
Ga	0	40.828	Ga_2O_3	-1089.095	84.977
Hg	0	65.898	HgO	-90.789	70.27
In	0	57.823	In_2O_3	-929.789	104.198
Ir	0	35.505	IrO_2	-242.672	58.948
Ni	0	29.874	NiO	-239.701	37.991
Os	0	32.635	OsO_4	-394.099	143.900

OsO_2	-294.972	51.882			
Pb	0	64.785	PbO_2	-274.47	71.797
Pb_3O_4	-718.686	211.961	PbO	-218.062	68.999
Pd	0	37.823	PdO	-115.478	38.911
Pt	0	51.631	PtO_2	170.707	259.517
Rh	0	31.505	Rh_2O_3	-355.64	106.274
Ru	0	28.535	RuO_2	-305.014	58.158
Sb	0	45.522	Sb_2O_3	-720.305	110.449
Se	0	42.258	SeO_2	-225.350	66.693
Sn	0	51.195	SnO_2	-580.823	52.342
Te	0	32.056	TeO_2	-323.423	74.057
Ag_2Se	-37.999	150.712	Ag_2Te	-35.982	153.553
Bi_2Se_3	-140.164	239.743	Bi_2Te_3	-77.404	260.914
CdSe	-144.766	83.262	CdTe	-101.797	92.885
CuSe	-41.84	78.241	CuTe	-25.104	86.609
Cu_2Sb	-12.134	126.482	Ga_2Te_3	-274.889	213.384
In_2Te_3	-191.627	234.304	Ni_3Sn	-93.701	131.378
$NiTe_{1.1}$	-58.158	84.057	$NiSe_2$	-108.784	103.512
Sb_2Se_3	-127.612	212.129	Sb_2Te_3	-56.484	246.438
SnSe	-115.397	89.539	SnTe	-61.923	99.998

$\Delta_f H_m^{\emptyset}$: *standard enthalpy change, and* $S_m^{\emptyset}$: *standard entropy*

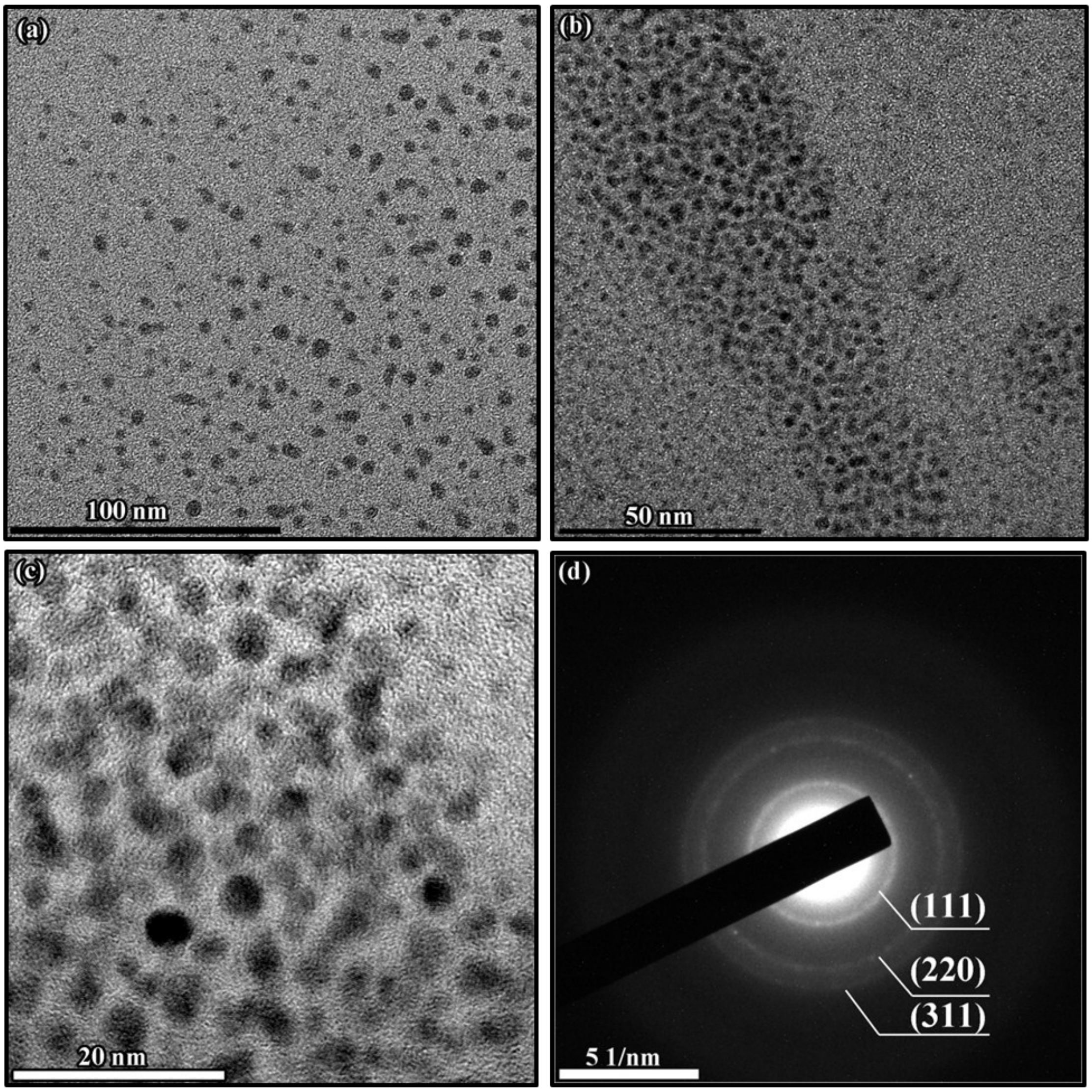

Figure S1. TEM analysis results of CdTe NCs being calcined at 723 K by using gelatin as bonding agent and EG as solvent.

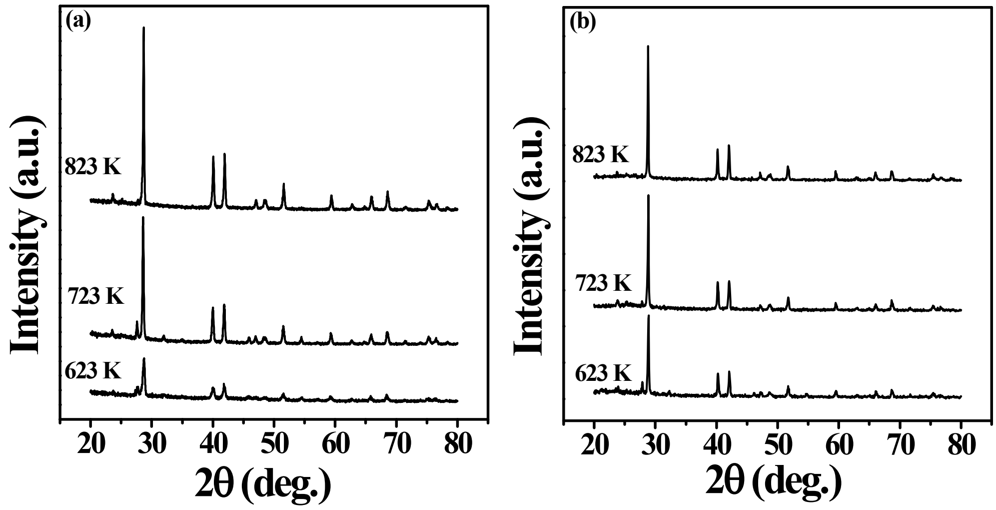

Figure S2. XRD profiles of Sb products being calcined at different temperatures by using CA (a) and gelatin (b) as bonding agent.

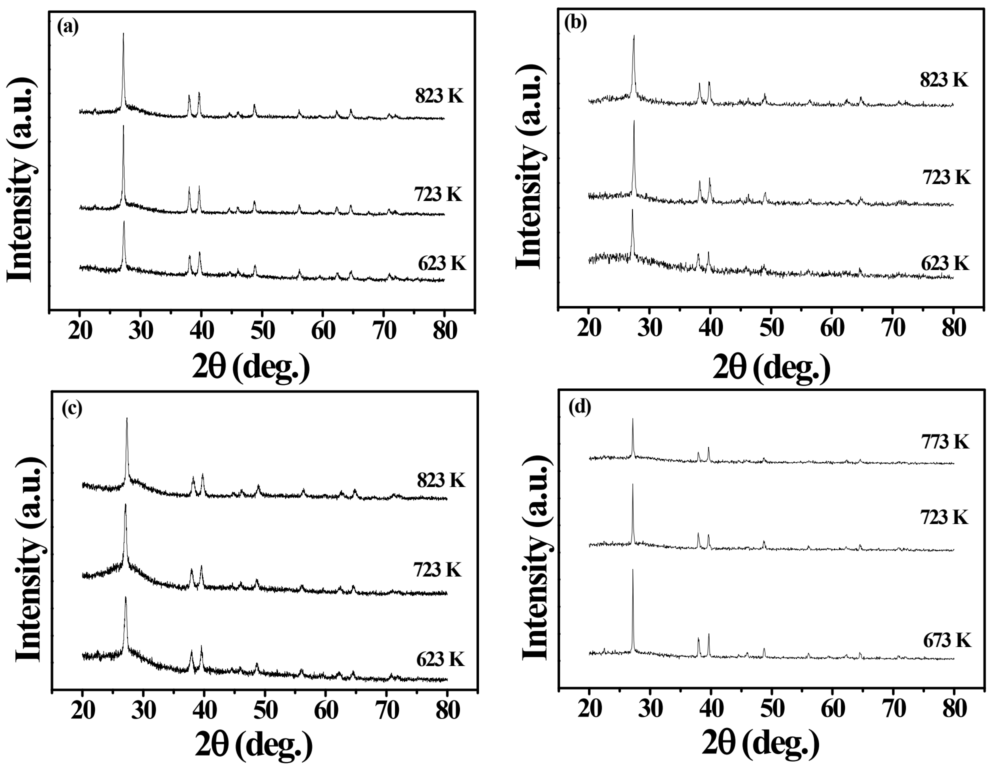

Figure S3. XRD profiles of Bi products being calcined at different temperatures by using CA (a), gelatin (b), acrylamide (c), and glucose (d) as bonding agent. The solvents are EG (a-c) and DW (d), respectively.

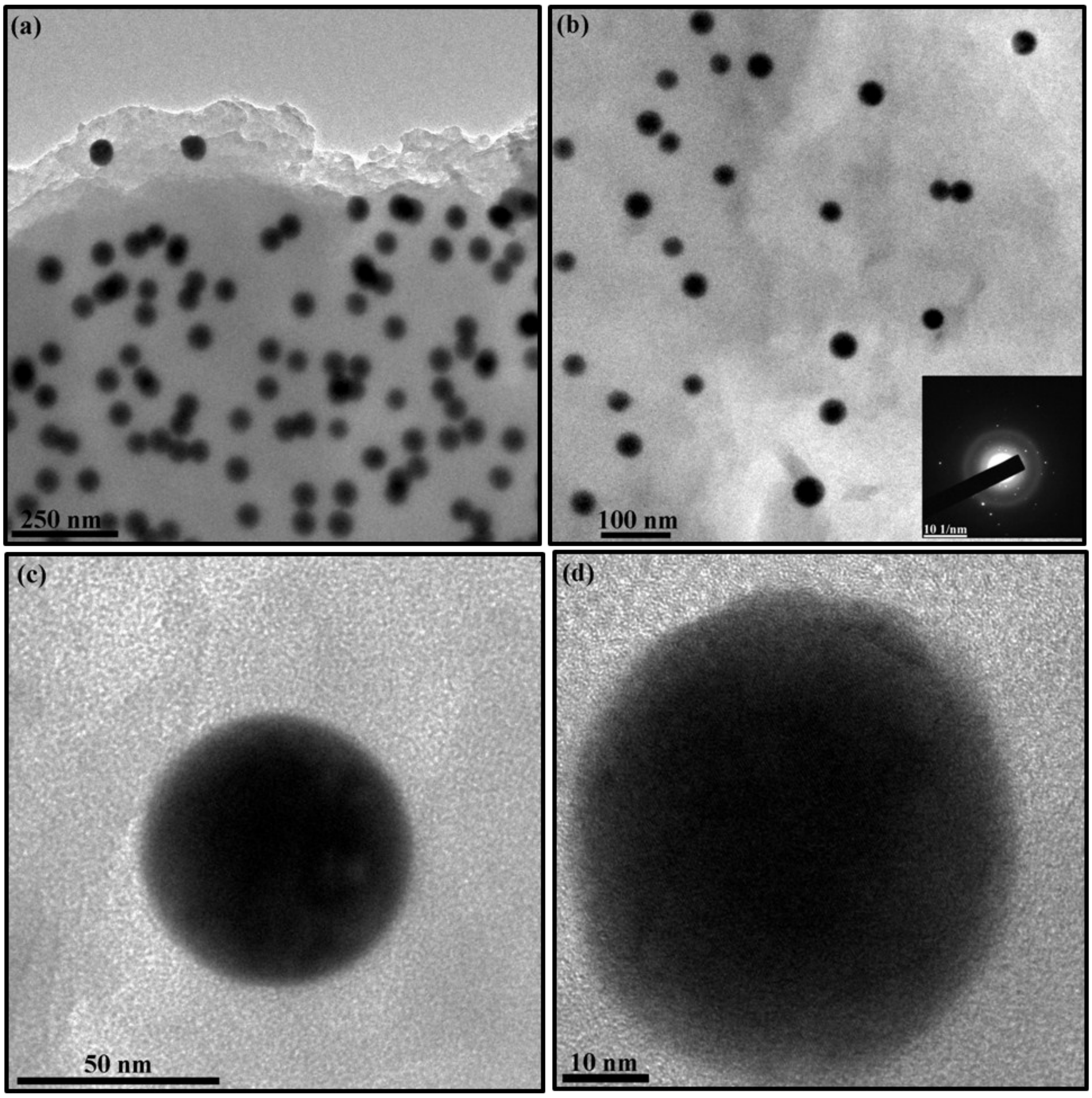

Figure S4. TEM images of Bi NCs being calcined at 723 K by using acrylamide as bonding agent, PVP as surfactant and EG as solvent.

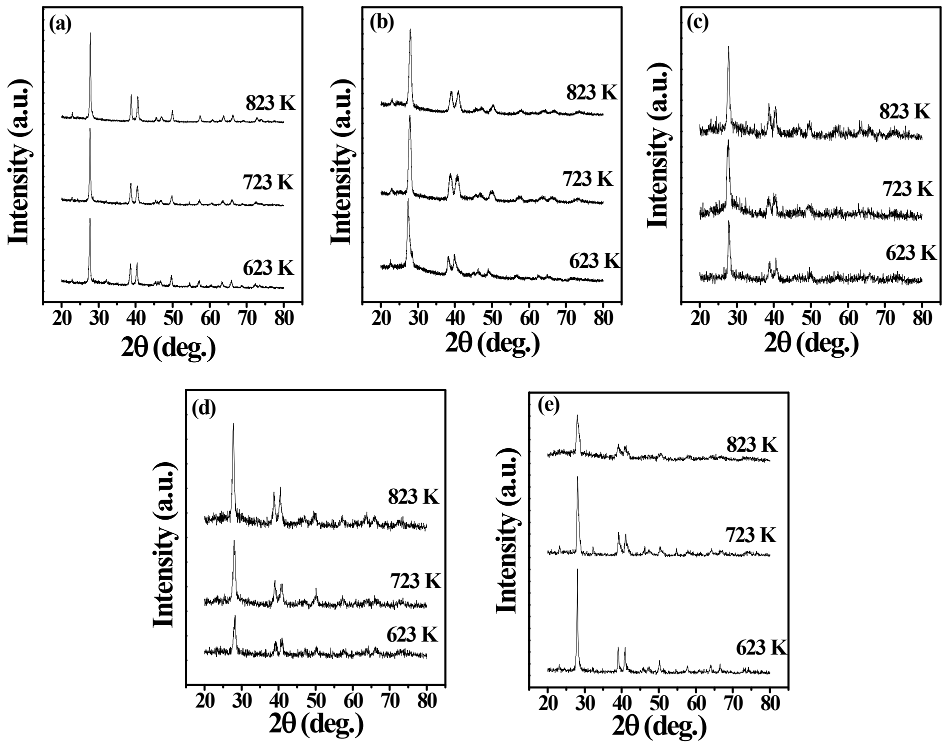

Figure S5. XRD patterns of Bi-Sb solid solution products by using CA (a, d, e) and gelatin (b, c) as bonding agents, PVP as surfactant and EG as solvent. The atomic ratio of Bi:Sb in the solid solution NCs with initial atomic ratio of 50:50 is 49.92:50.08 as determined by XRF, which is close to the starting composition.

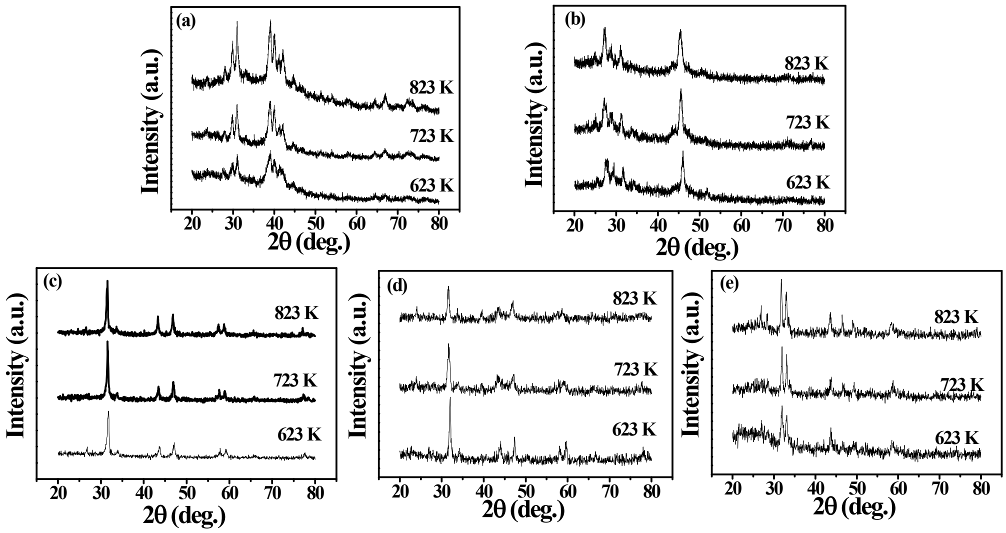

Figure S6. XRD profiles of Ag_2Te (a), CuTe (b), $NiTe_{1.5}$ (c and d), $CoTe_{1.5}$ (e) products where the solvents for $NiTe_{1.5}$ products are DW (c) and EG (d), respectively.

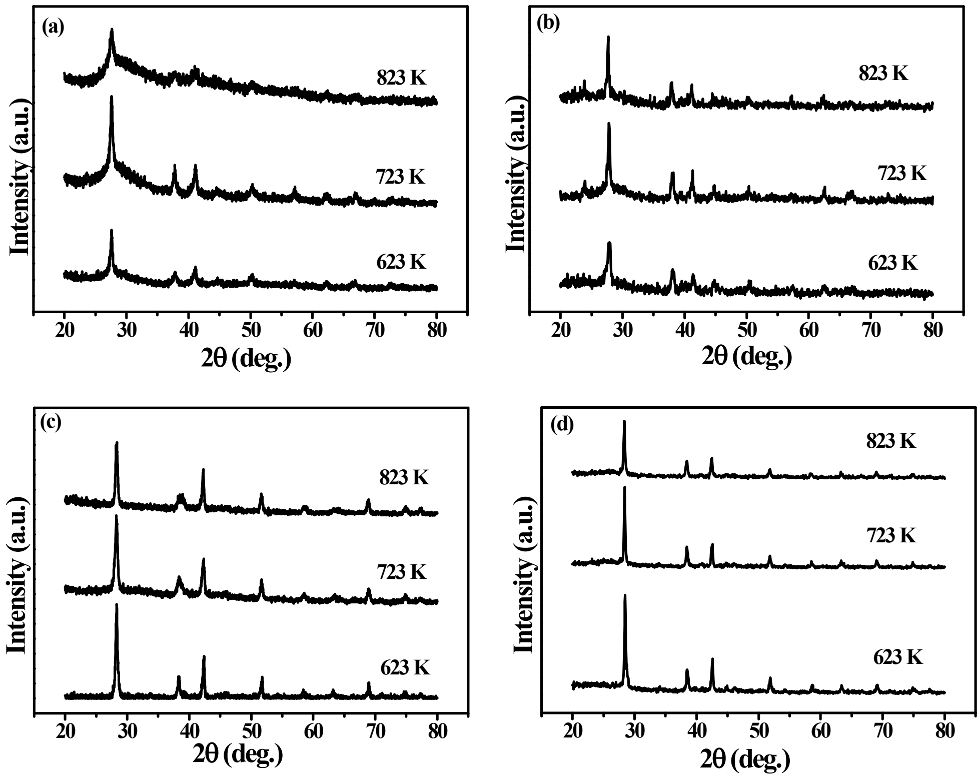

Figure S7. XRD profiles of Bi_2Te_3 (a, b) and Sb_2Te_3 (c, d) products by employing CA (a, c) and gelatin (b, d) as bonding agents.

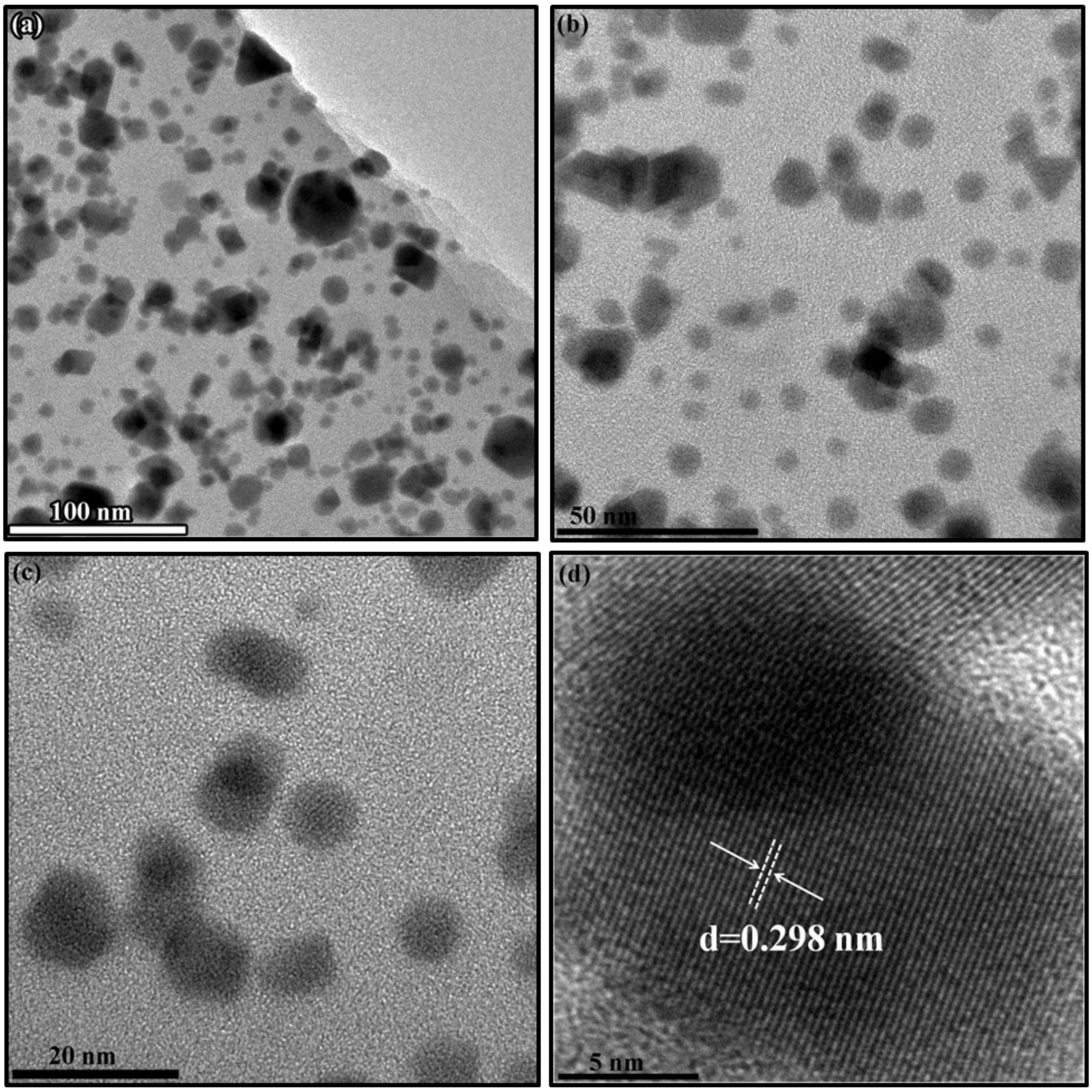

Figure S8. TEM images of Ag_2Te NCs being calcined at 823 K under N_2 protecting atmosphere.

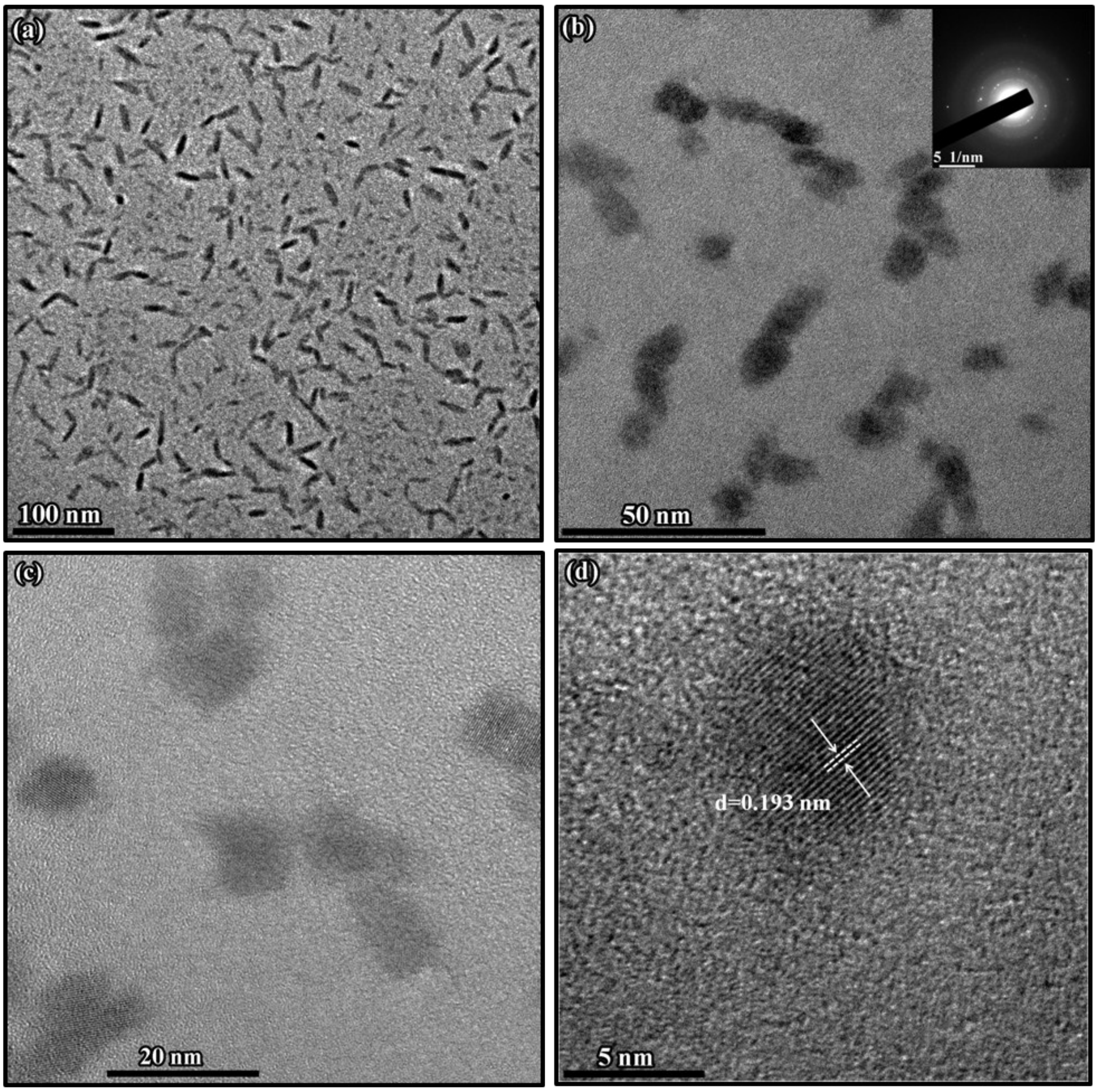

Figure S9. TEM images of $NiTe_{1.5}$ NCs being calcined at 823 K under N_2 protecting atmosphere.

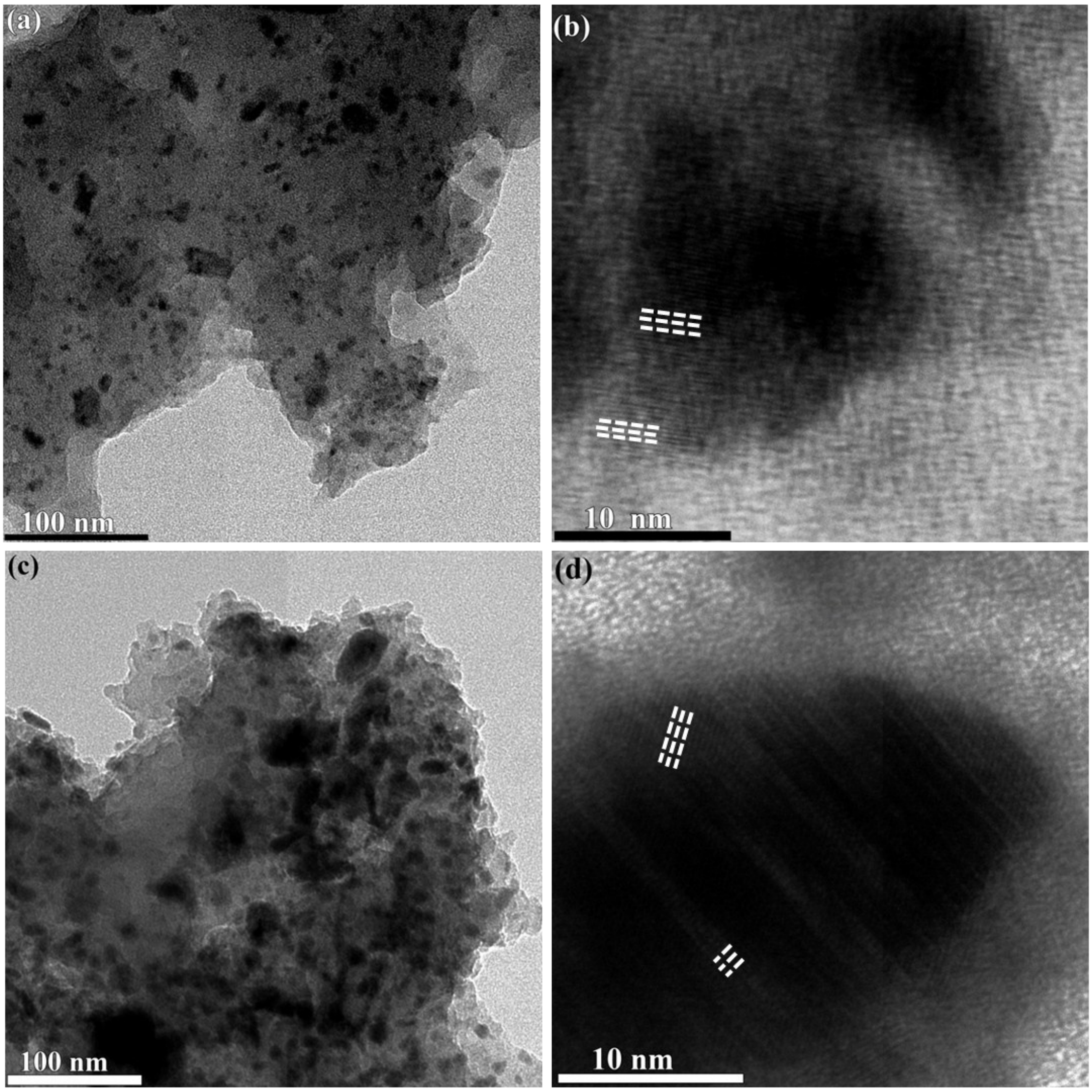

Figure S10. TEM images of Sb_2Te_3 (a, b), Bi_2Te_3 (c, d) NCs being calcined at 723 K under N_2 protecting atmosphere by using CA as bonding agent.

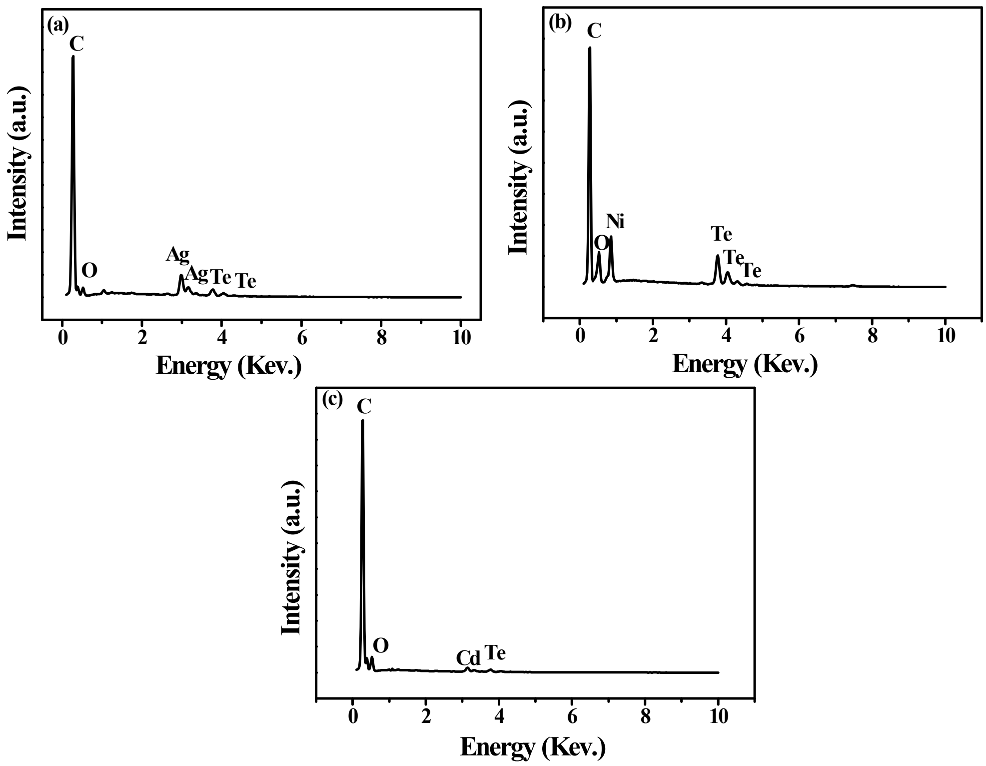

Figure S11. EDX analysis results of Ag_2Te (a) and $NiTe_{1.5}$ (b) products being calcined at 823 K, and CdTe (c) product being calcined at 723 K. The solvents are DW (a, b), EG (c) and bonding agents are gelatin (a), CA (b), gelatin (c) for Ag_2Te, $NiTe_{1.5}$ and CdTe, respectively.

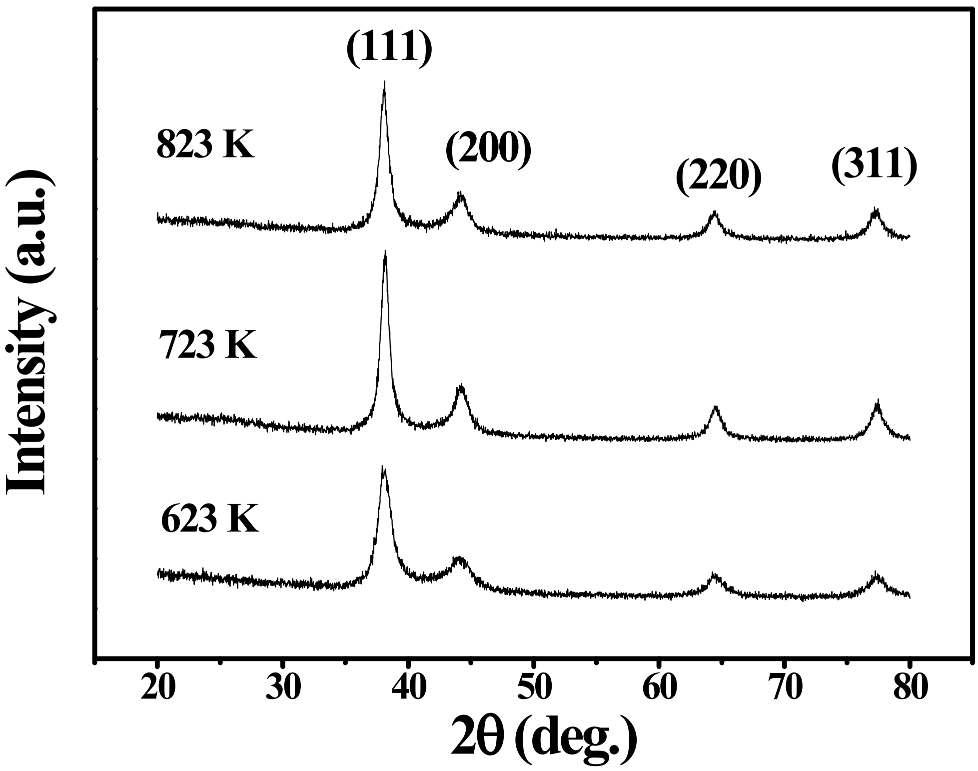

Figure S12. XRD patterns Ag NCs being calcined at different temperatures by using DW as solven, gelatin as bonding agent.

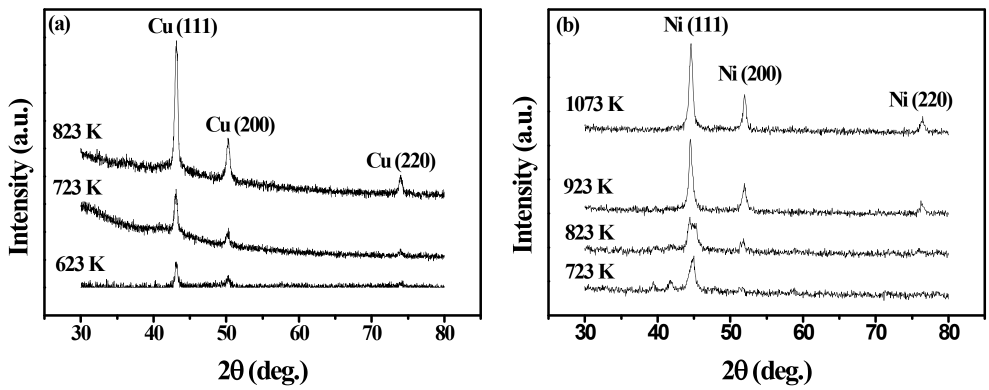

Figure S13. XRD patterns of Cu and Ni NCs being calcined at different temperatures by using gelatin as bonding agent.

Figure S14. Image of Ni NCs being calcined at 1073 K by using gelatin as bonding agent, PVP as surfactant and de-ionized water as solvent. The total weight of the final poduct is 16.53 g. This product contains metallic Ni NCs and supporting material, which is considered to be amorphous carbon. Then a certain selected part of the product has been calcined at 1473 K in air to transform the Ni NCs completely to NiO and to eliminate amorphous carbon. From the mass of NiO and the mass of the selected product, the mass of Ni NCs in the product being calcined at 1073 K can then be calculated to be 4.8 g, meaning that this method can prepare Ni NCs in large scale. The yield of nickel can then be determined to be 97.1% from the initial mass of nickel nitrate and the final mass of NiO.

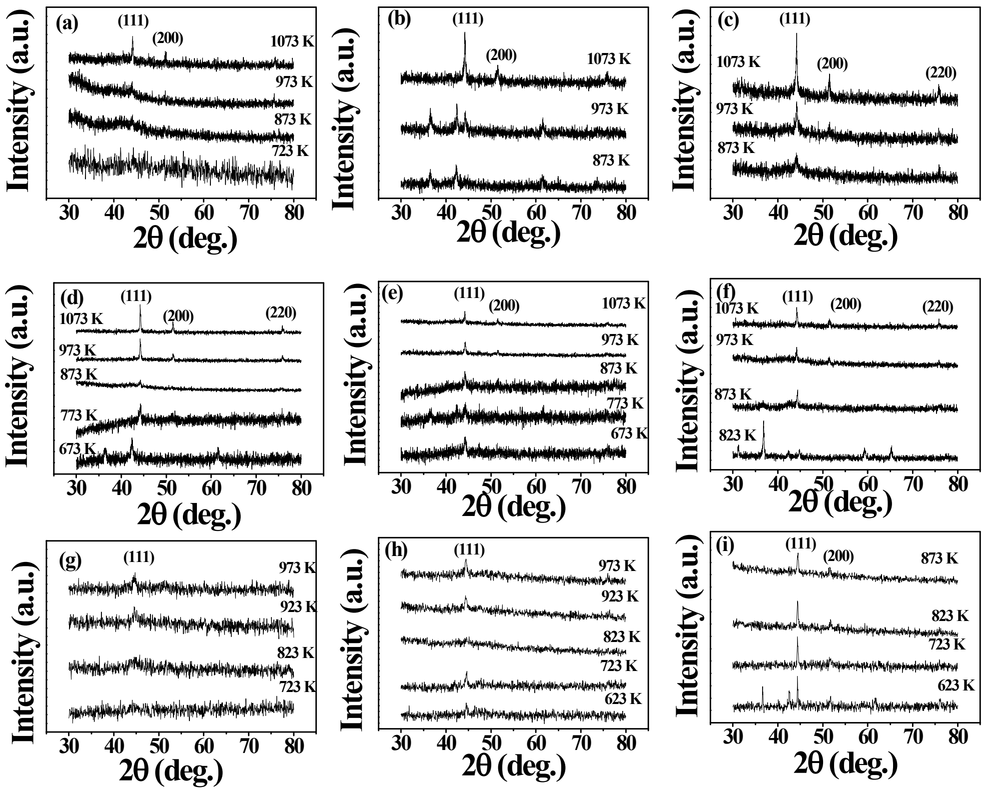

Figure S15. XRD analysis results of Co products being calcined at different temperatures by using cobalt nitrate, PVP, DW, and CA (a), starch (b), EDTA (c), ascorbic acid (d), glucose (e), sucrose (f), lactose (g), EG (h, i). The molar concentration ratios of Co^{2+}: EG are 1: 1 and 1: 2 for (h) and (i).

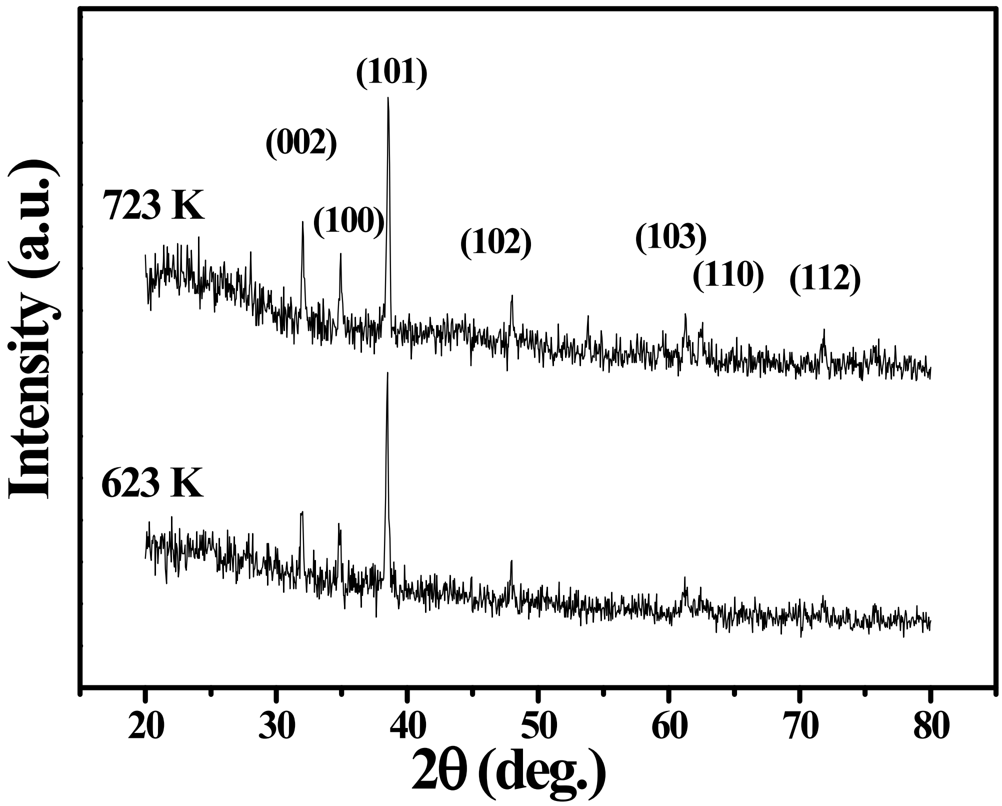

Figure S16. XRD patterns of Cd products by using $Cd(CH_3COO)_2·3H_2O$, glucose, PVP and DW as raw materials.

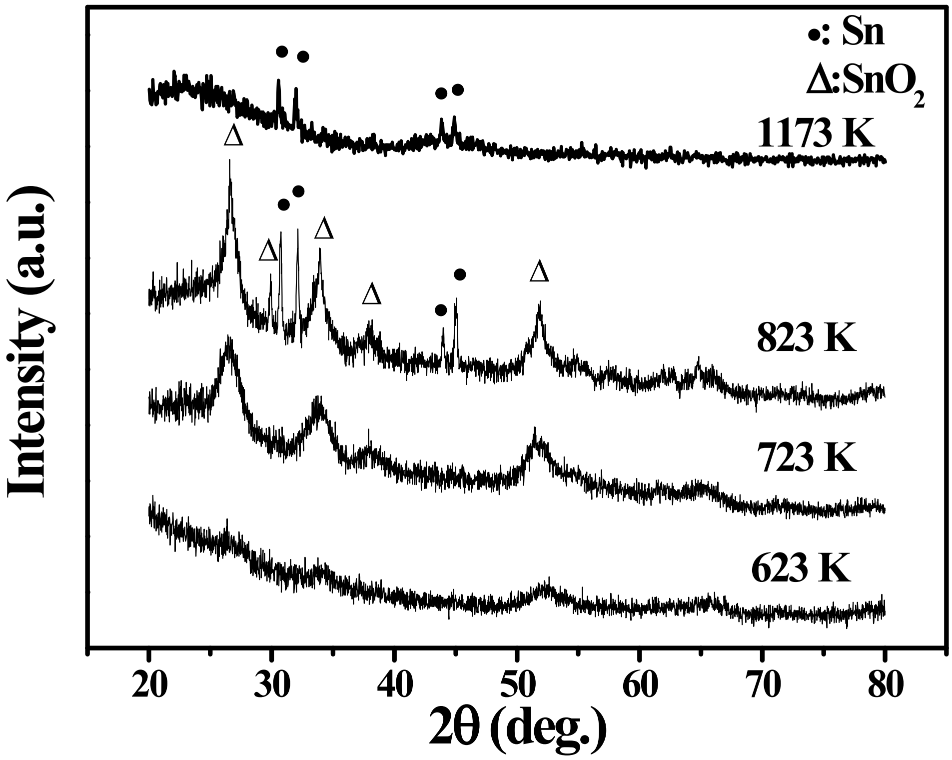

Figure S17. XRD patterns of the products by using $SnCl_4 \cdot 4H_2O$, glucose, PVP and DW as raw materials.

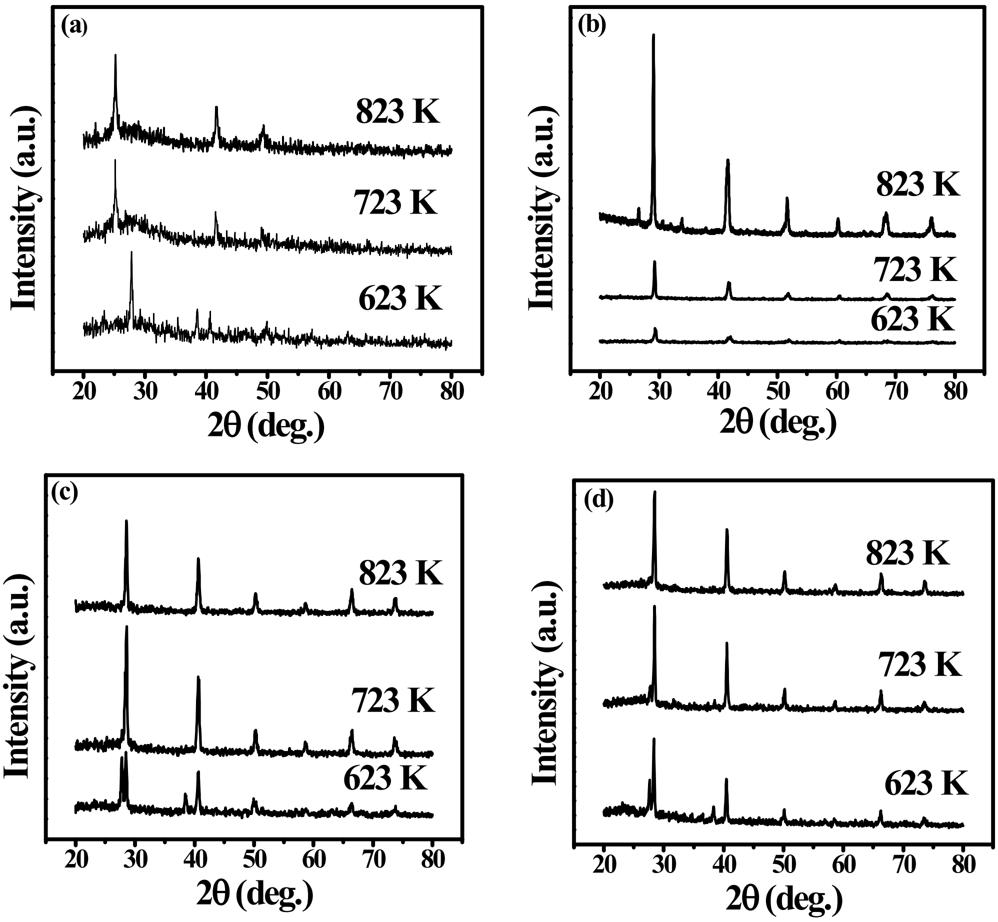

Figure S18. XRD patterns of In_2Te_3 (a), SnSb (b), SnTe (c, d) products being calcined at different temperatures where the bonding agents are CA (a-c) and gelatin (d) and solvents are DW (a, c, d) and EG (b).

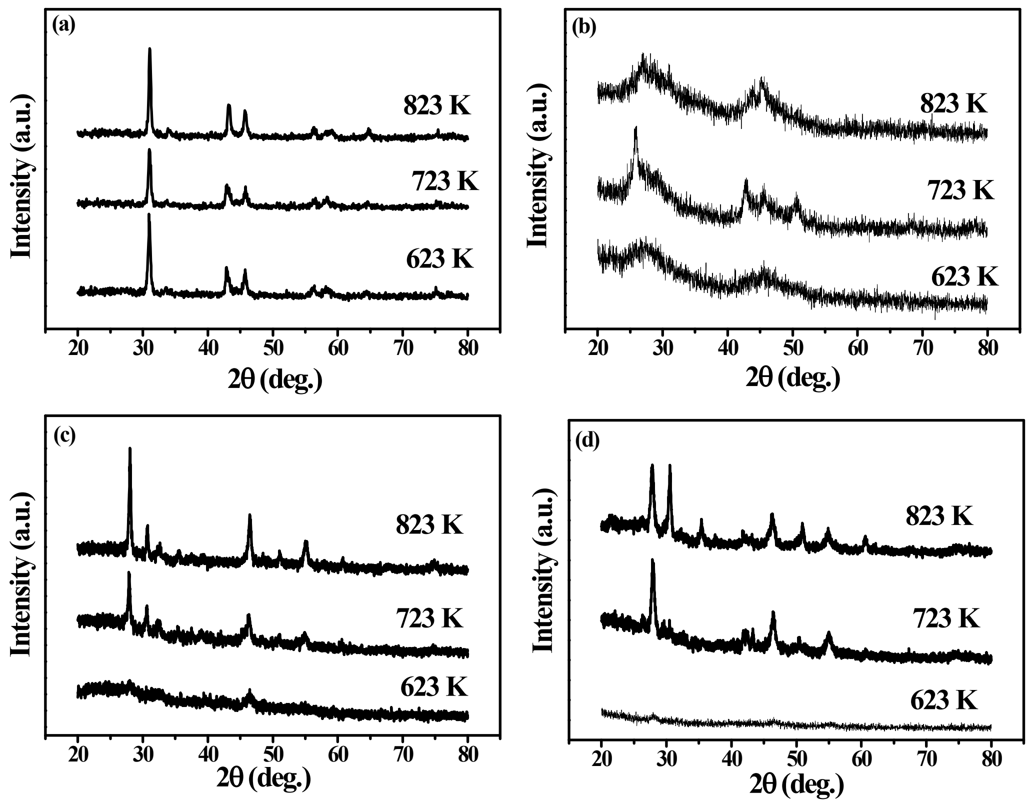

Figure S19. XRD analysis results of $Ni_{2.9}SnTe_2$ (a), $CuGaTe_2$ (b), $CuInS_2$ (c and d) products. The solvents are DW (a-c), EG (d) and the bonding agents are CA (a, b, d), and EDTA (c), respectively.

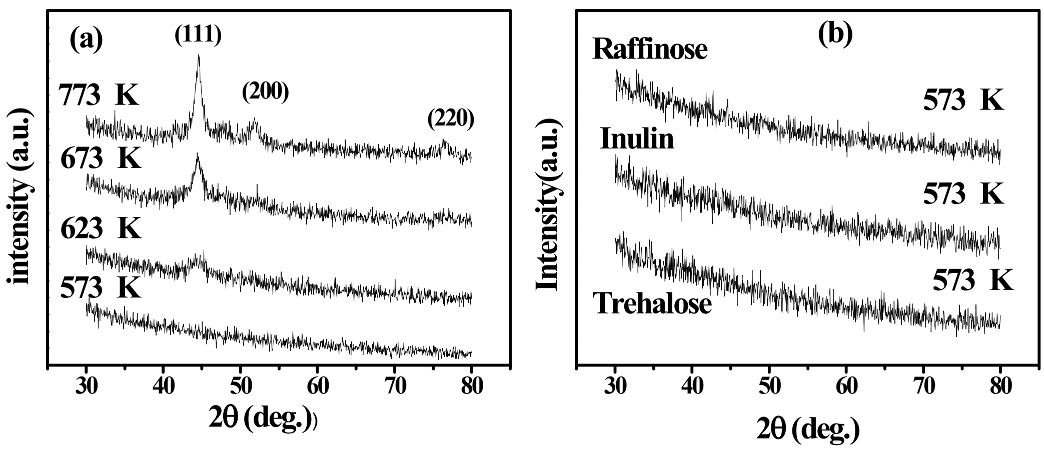

Figure S20. XRD patterns of the products being calcined at different temperatures by using $Ni(NO_3)_2 \cdot 6H_2O$, PVP, DW and Arabinose (a), Trehalose (b), Inulin (b), Raffinose (b).

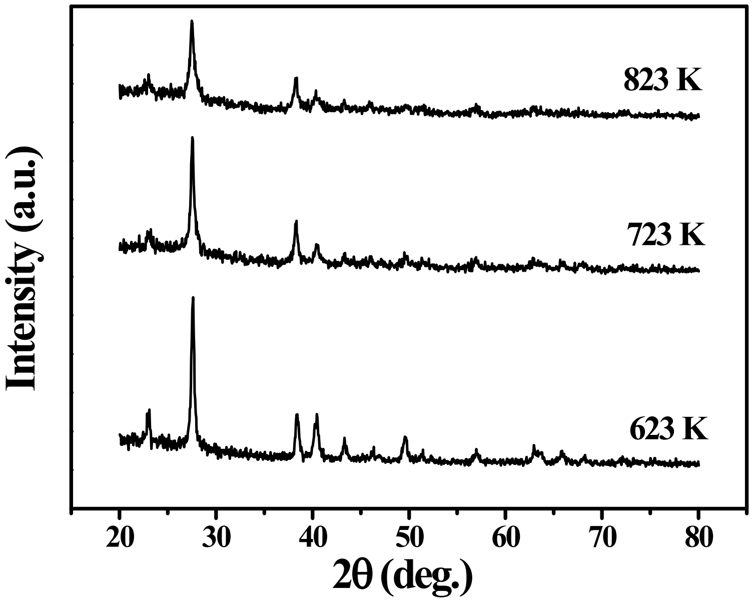

Figure S21. XRD analysis results of Te products by using H_6TeO_6 as Te source, Coca-Cola as bonding agent, PVP as surfactant and DW as solvent.

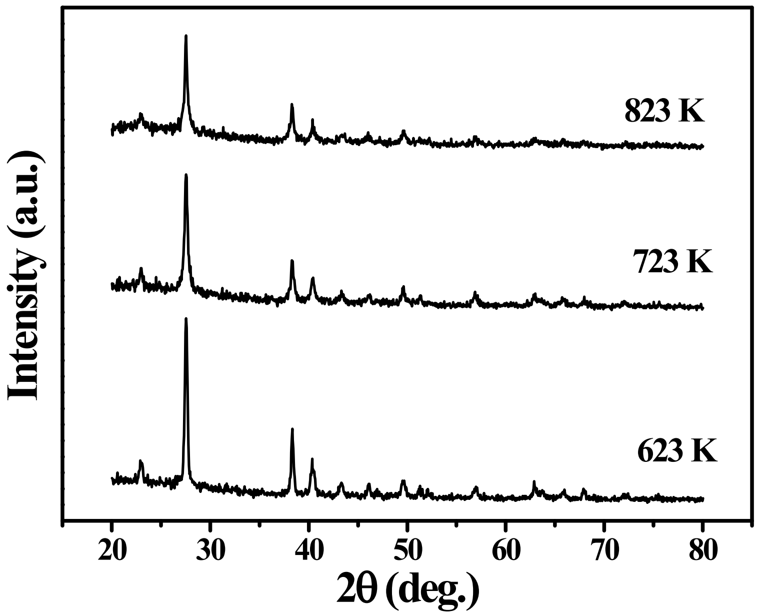

Figure S22. XRD analysis results of Te products by using H_6TeO_6 as Te source, sprite as bonding agent, PVP as surfactant and DW as solvent.