

## Electronic Supporting Information

### Polymerized complex method for preparation of supported bimetallic alloy and monometallic nanoparticles

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#### 1. Experimental procedures

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{AgNO}_3$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$  were used as metallic source. Starch, sucrose, glucose, ribose, mannose, trehalose, inulin, galactose, lactose, raffinose, xylose, cyclodextrin, gluconic acid, ascorbic acid, pyrogallol, glyoxylic acid, EDTA, lactic acid, malic acid, pyruvic acid, gelatin and carboxymethyl cellulose (cmc), ethylenediamine, triethanolamine, formamide, N,N-Dimethylformamide (DMF), ethylene glycol, glycerol, diethylene glycol, 1,2-propanediol, maltitol, xylitol, pentaerythritol, inositol, glutaraldehyde, and m-dihydroxybenzene were used as bonding agent. PVP (K-30), tween 20 and tween 80 were used as surfactant. Distilled water was used as solvent, and ammonia was used to mediate the pH value. All the chemical agents were used as received without further purification. In a typical process, 10 ml  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  aqueous solution with molar concentration of  $6.95 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  and 0.1148 g starch were dissolved into 90 ml distilled, then 0.02 g tween 80 was also added into the solution. The molar concentration ratio of  $\text{Pt}^{4+}$ : starch was 1:10. The pH value of the solution was adjusted to 7 by ammonia. Then the brown solution was dried at 363 K. Dried polymerized network structure was formed after the distilled water was evaporated. Heating treatments of the polymerized complex were performed at different temperatures for 3h under  $\text{N}_2$  protecting atmosphere and then cooled down to room temperature. In other experimental processes, starch was replaced by various bonding agents, and the ratios of molar concentrations of  $\text{Pd}^{2+}$ : bonding agent,  $\text{Ag}^+$ : bonding agent,  $\text{Ni}^{2+}$ : bonding agent,  $\text{Cu}^{2+}$ : bonding agent were 1:10, 1:10, 1:5, 1:5, respectively. When surfactant of PVP was used, the ratios of molar concentrations of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ : PVP were 1:1. For the preparation of Ag, Pt and Pd noble NPS, the pH value of the aqueous solution must be maintained in the range of 5.5-7.5. When the pH value was lower than 5.5, the starch hydrolysed as the solvent evaporated, leading to the formation of glucose and reduction of metallic ions. When the pH value was higher than 7.5, precipitation of metal hydroxides took place. For preparation of Ni-Pd alloy NPS,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , starch and tween 20 were used where the molar ratio of  $\text{Ni}^{2+}$ : $\text{Pd}^{2+}$ :starch was 1:1:2 and pH value of the solution was kept at 6.0. For preparation of Cu-Pt alloy NPS,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , starch and tween 20 were used where the molar ratio of  $\text{Cu}^{2+}$ : $\text{Pt}^{4+}$ :starch was 4:1:5.1 and pH value of the solution was kept at 6.0. For preparation of Ni-Pt alloy NPS,  $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , starch and tween 20 were used where the molar ratio of  $\text{Ni}^{2+}$ : $\text{Pt}^{4+}$ :starch was 2:3:5.1 and pH value of the solution was kept at 6.0.

The crystalline phases of the as-obtained metallic particles were examined by XRD with Cu  $K_\alpha$  radiation ( $\lambda=0.15406 \text{ nm}$ ). TEM was used to investigate the microstructures and crystalline phases of the particles. The samples for TEM observation were dispersed in ethanol, and then dropped in copper grid. Mass spectroscopy, TG, and DSC measurements were conducted on the polymerized complex using glucose, PVP, and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  from room temperature to 873 K under  $\text{N}_2$  atmosphere with heating rate being 10 K/min. The elemental analysis of the as-prepared Ni-Pd, Ni-Pt, Cu-Pt NPS were conducted by electron scanning microscope (SEM, S-3400) analysis where an attachment of energy dispersive spectrometer (EDX, Oxford-2500) can determine the composition of NPS. Atomic absorption spectrometer investigation was also performed to investigate the relative concentrations of metallic elements in the bimetallic alloy NPS.

## Figures

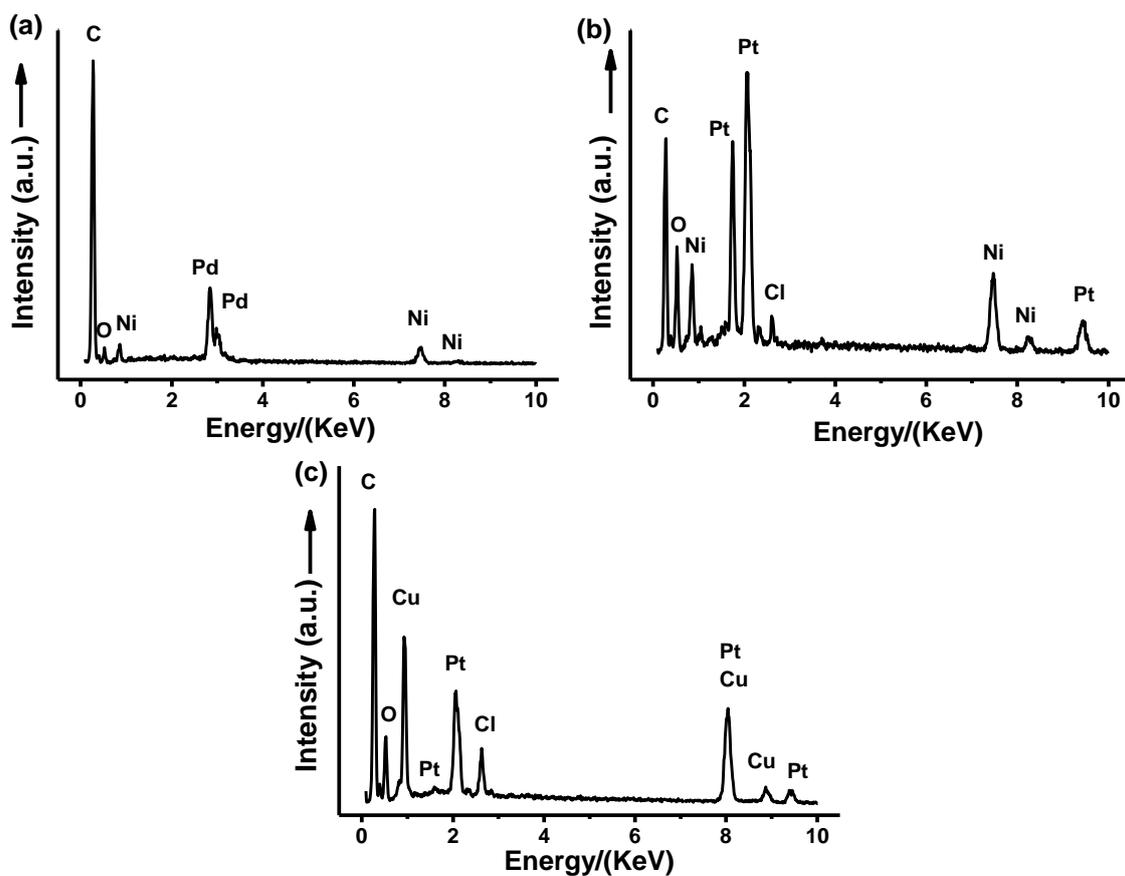


Figure S1. Energy dispersive X-Ray spectroscopy (EDX) analysis results of supported Ni-Pd, Ni-Pt, Cu-Pt NPS being calcined at 773, 723, 623 K, respectively. The atomic ratios of Ni: Pd, Ni: Pt, Cu: Pt were determined to be 48.86:51.14, 40.54:59.46, 80.23:19.77.

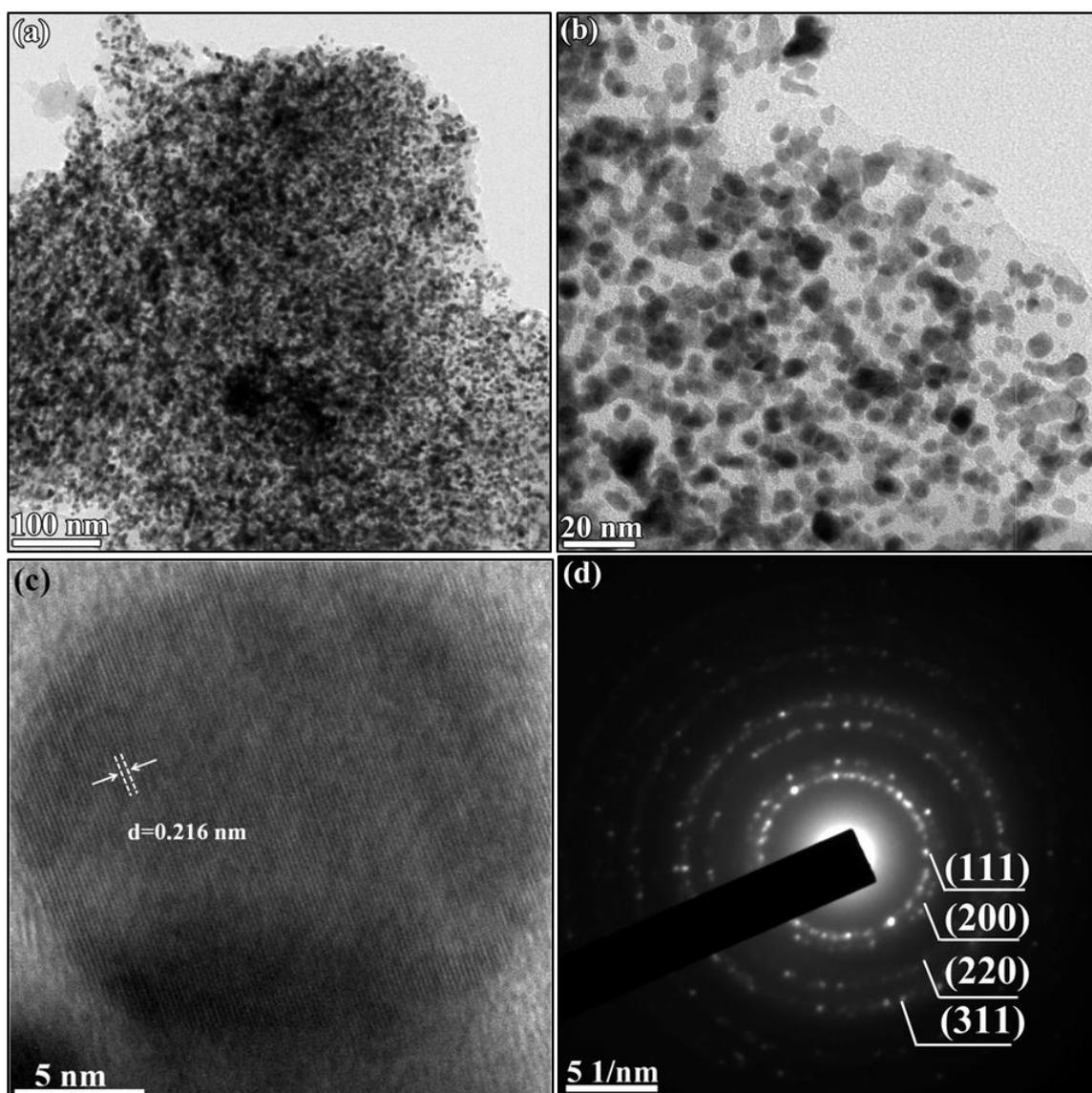


Figure S2. Transmission electron microscope (TEM) images and SAED pattern of Ni-Pt NPS being calcined at 723 K for 3h.

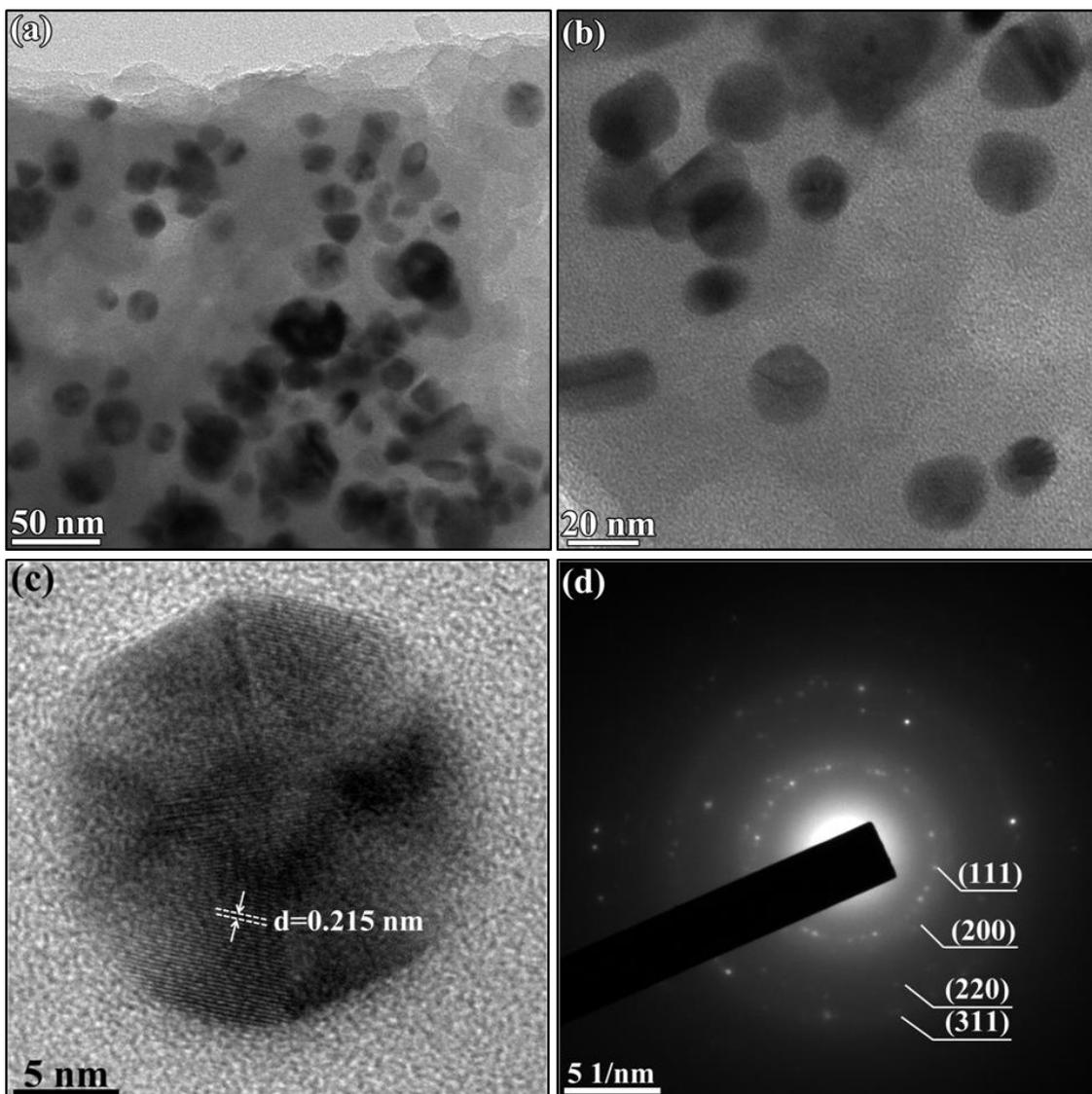


Figure S3. TEM images and selected area electron diffraction (SAED) pattern of Ni-Pd NPS being calcined at 773 K for 3h.

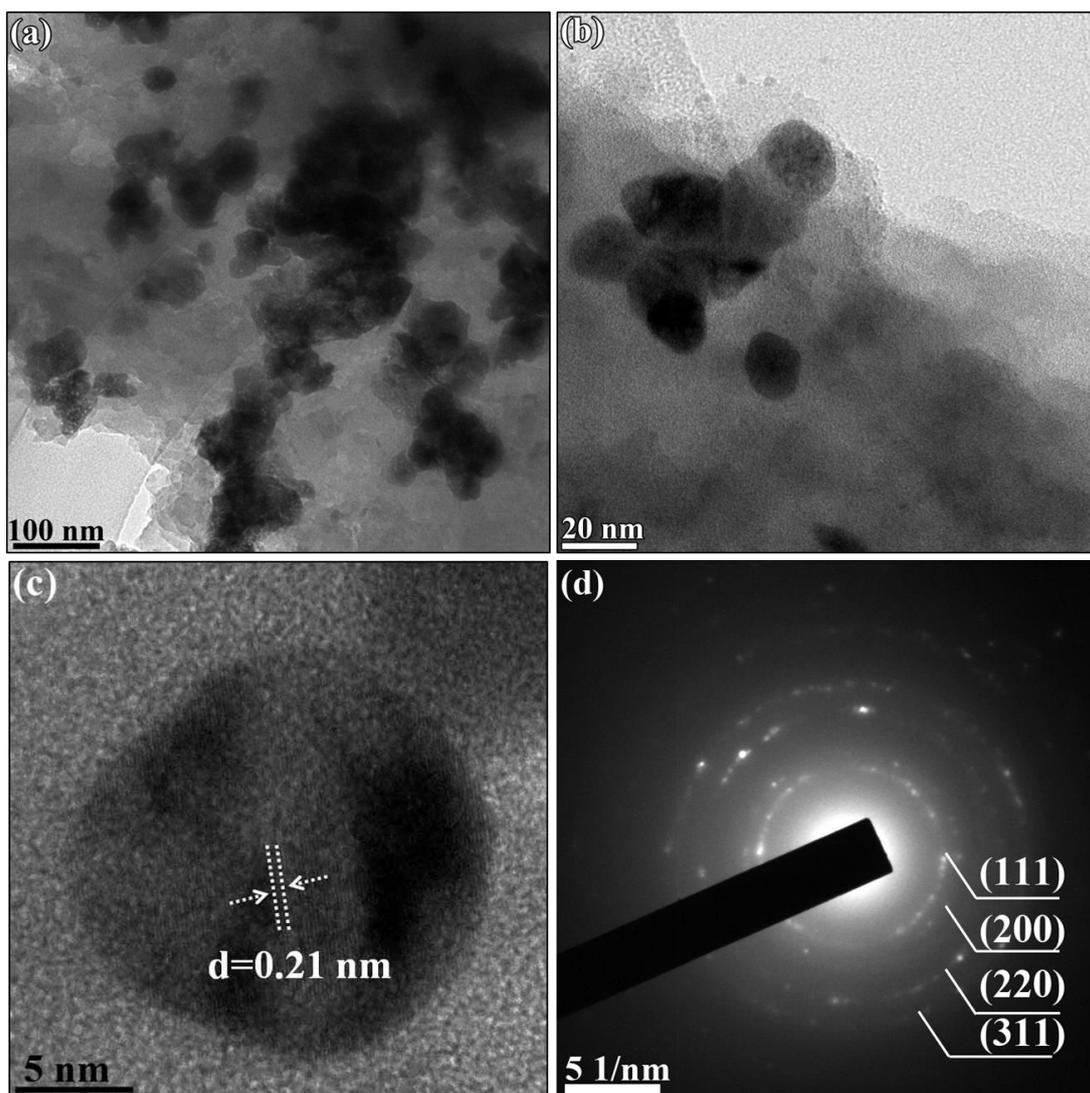


Figure S4. TEM investigation results of Cu-Pt NPS being calcined at 623 K for 3h.

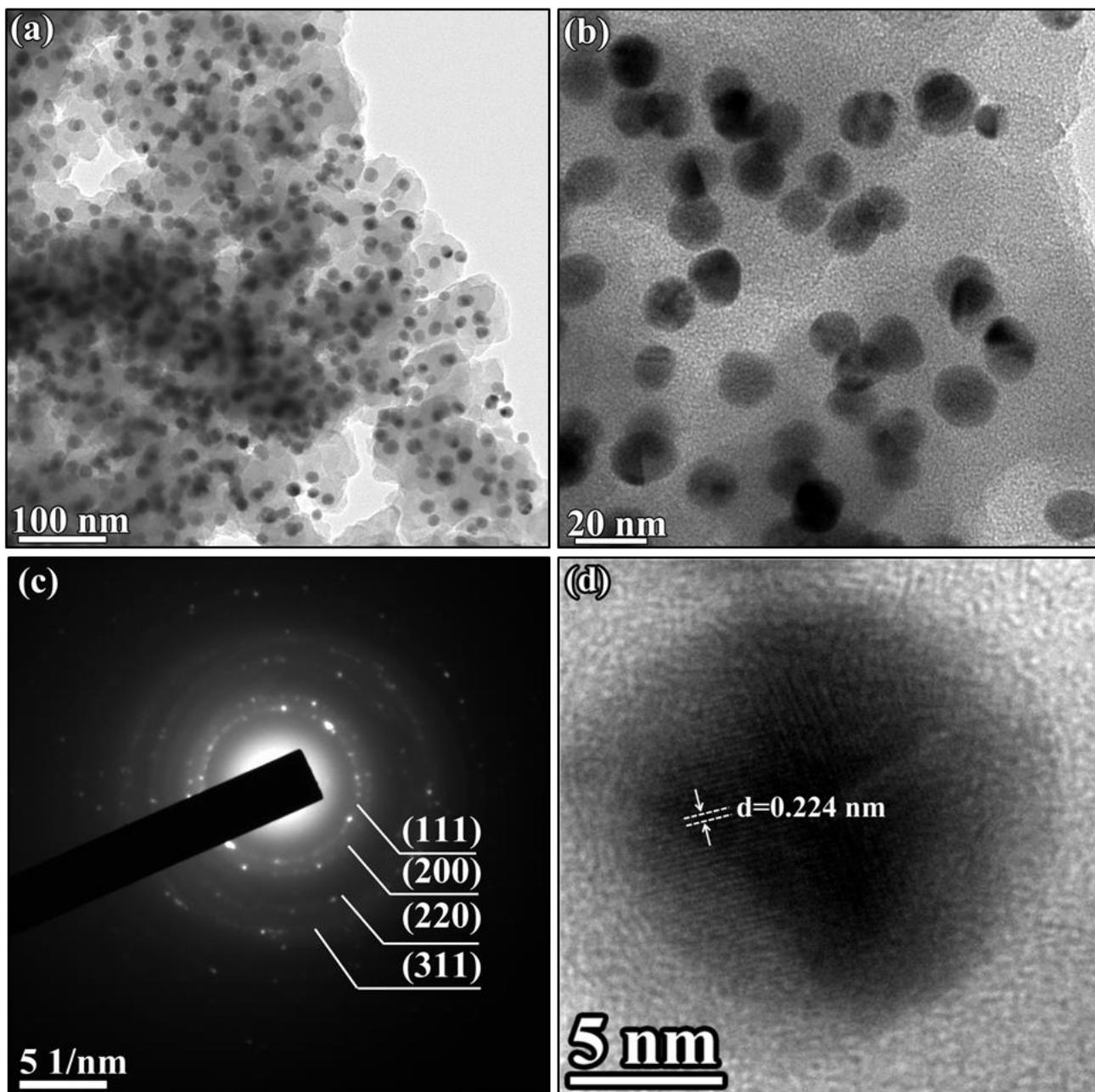


Figure S5 TEM images and SAED pattern of Pd NPS being calcined at 773 K under N<sub>2</sub> protecting atmosphere.

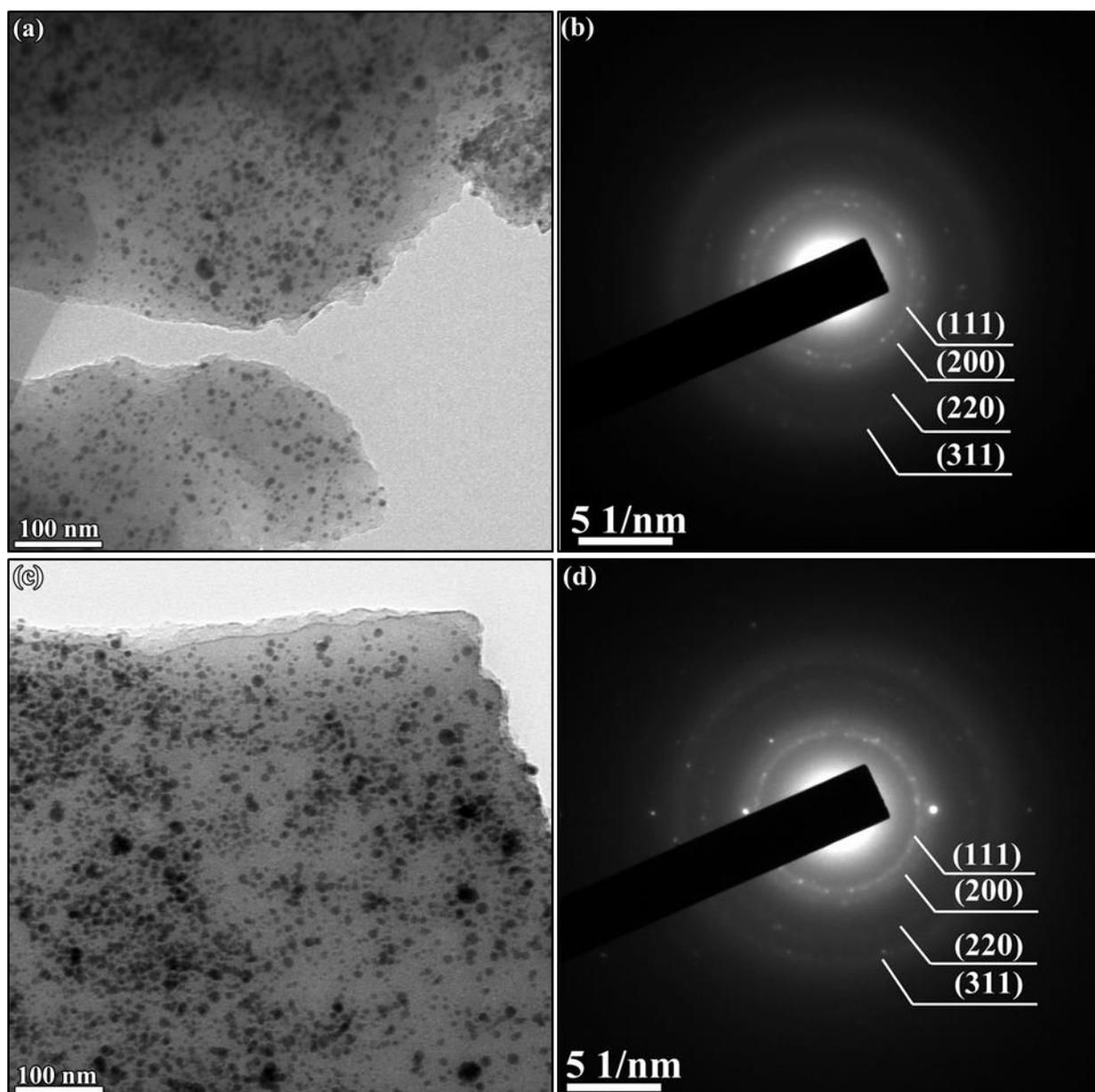


Figure S6. TEM images and SAED analysis results of Ag NPS being calcined at, 673 (a and b), and 773 K (c and d) by using  $\text{AgNO}_3$ , PVP and starch.

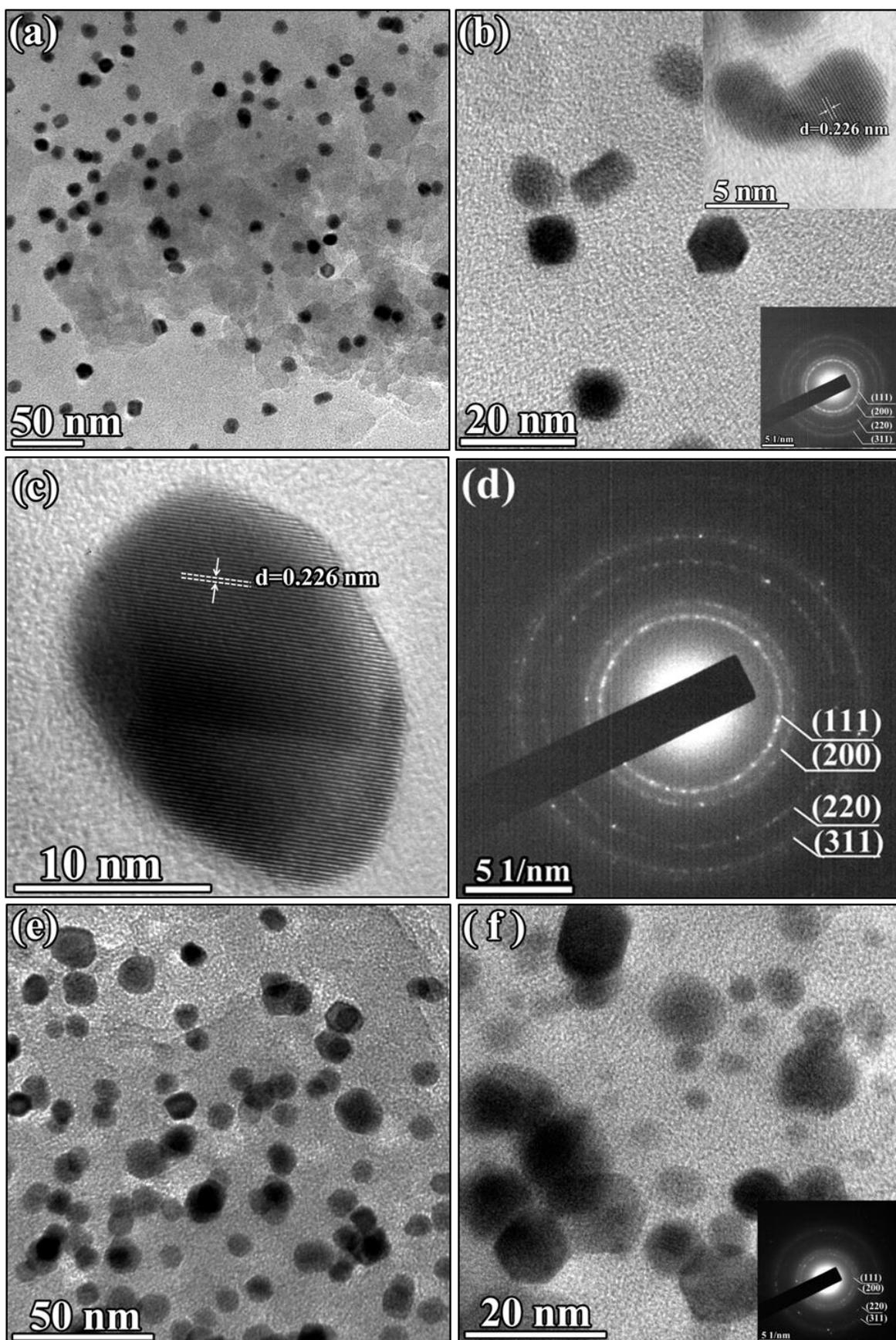


Figure S7. TEM images and SAED analysis results of Pt NPS being calcined at 623 (a, b), 723 (c, d), 823 K (e, f) by using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , starch and tween 80.

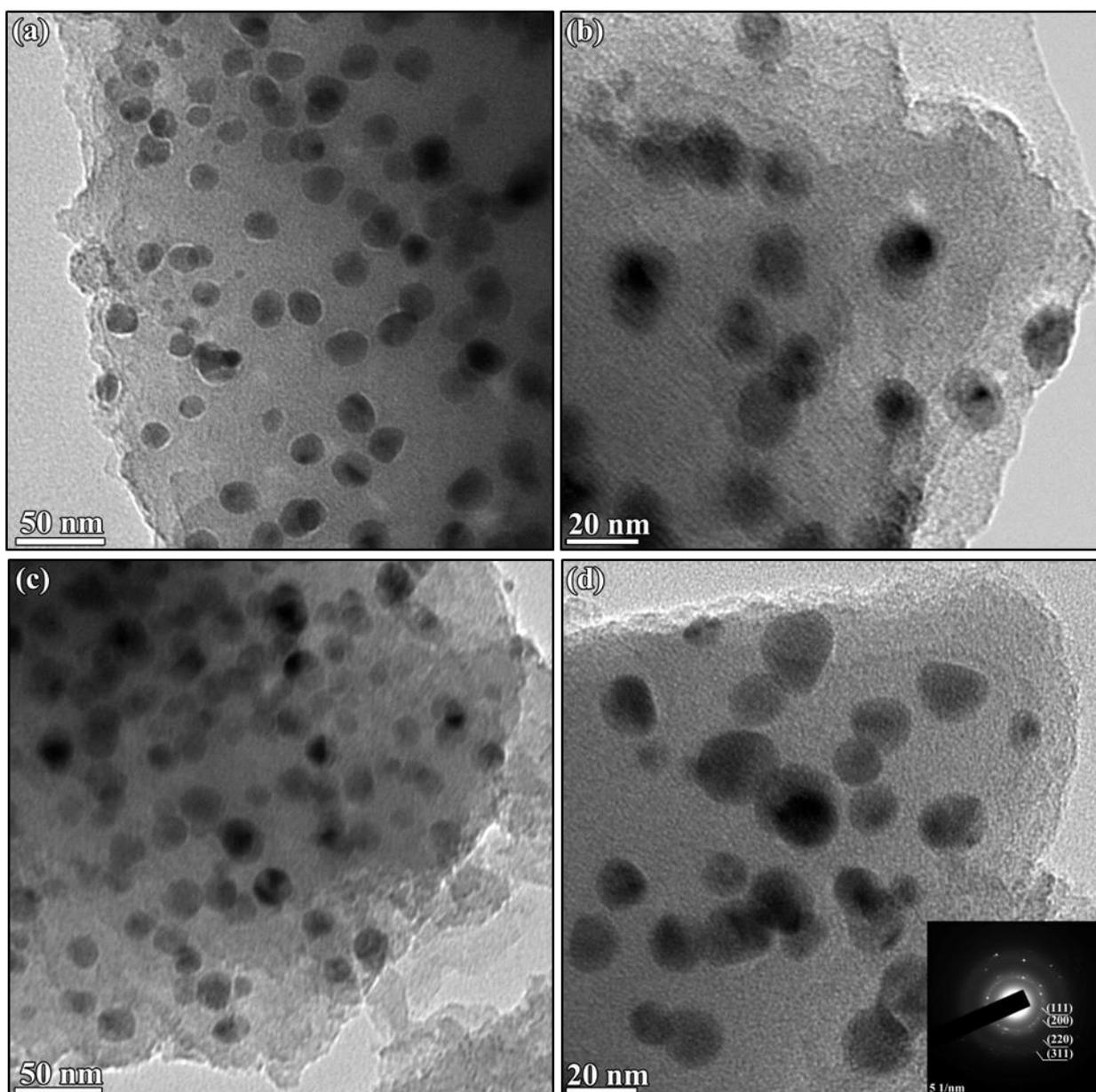


Figure S8. TEM images and SAED analysis results of Cu NPS being calcined at 673 (a,b), and 773 K (c,d) by using  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , starch and PVP.

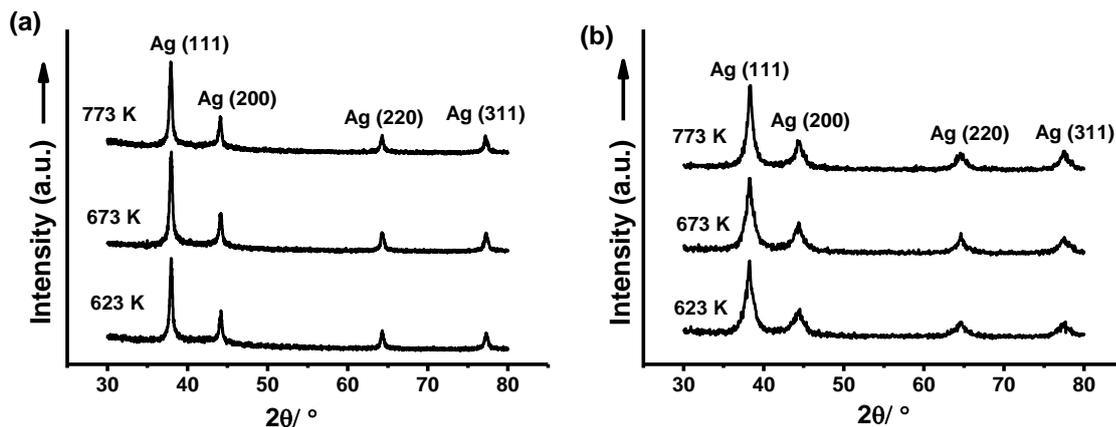


Figure S9. XRD analysis results of Ag NPS prepared by using AgNO<sub>3</sub>, sucrose (a), AgNO<sub>3</sub>, PVP, and CO(NH<sub>2</sub>)<sub>2</sub> (b) as initial chemical agents.

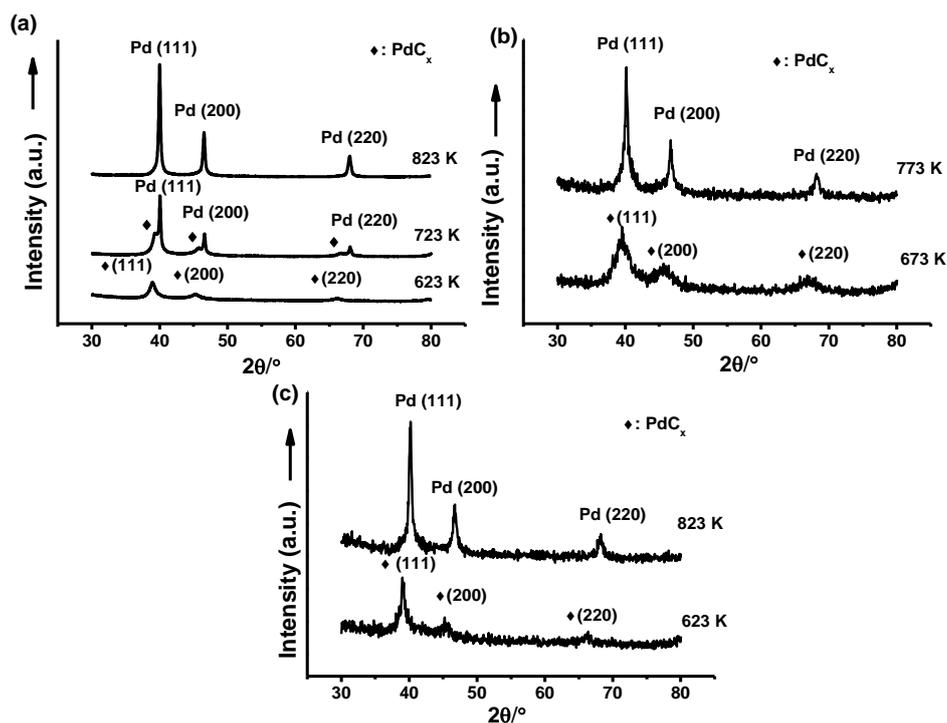


Figure S10. XRD analysis results of Pd NPS prepared by using Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, PVP, and EDTA (a), Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, PVP, and lactic acid (b), Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, PVP, and sucrose (c).

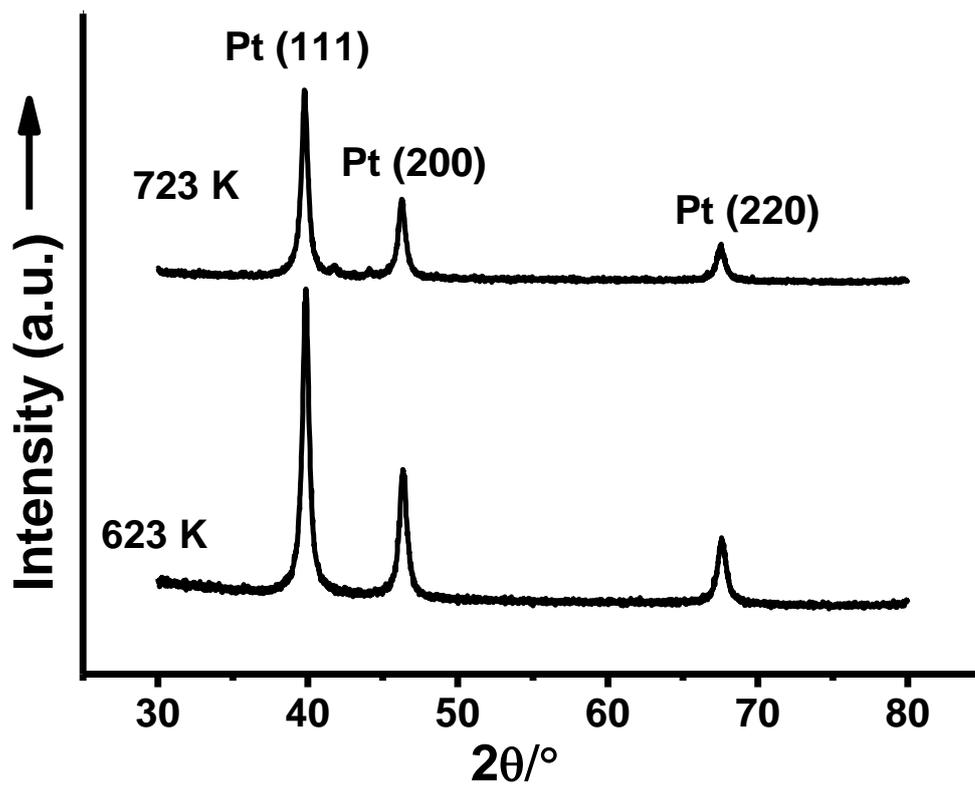


Figure S11. XRD analysis result of Pt NPS prepared by using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , PVP and EDTA.

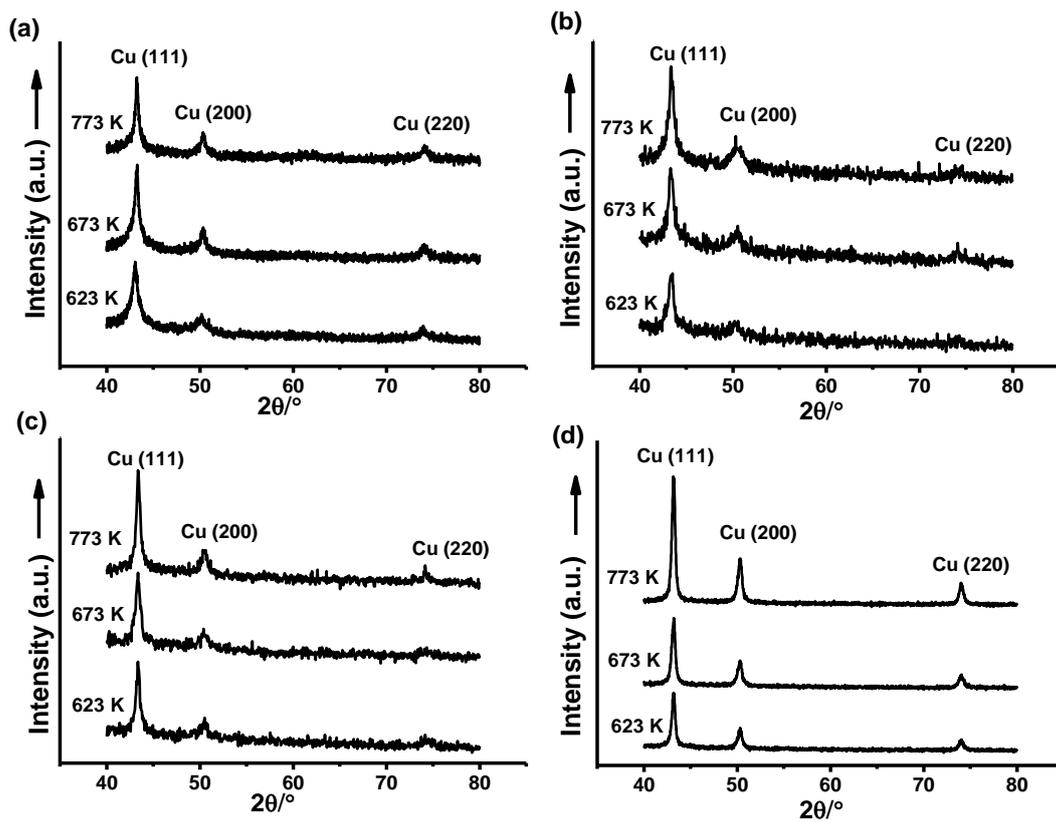


Figure S12. XRD analysis results of Cu NPS prepared by using Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, PVP and EDTA (a), lactose (b), maltose (c), ethylenediamine (d).

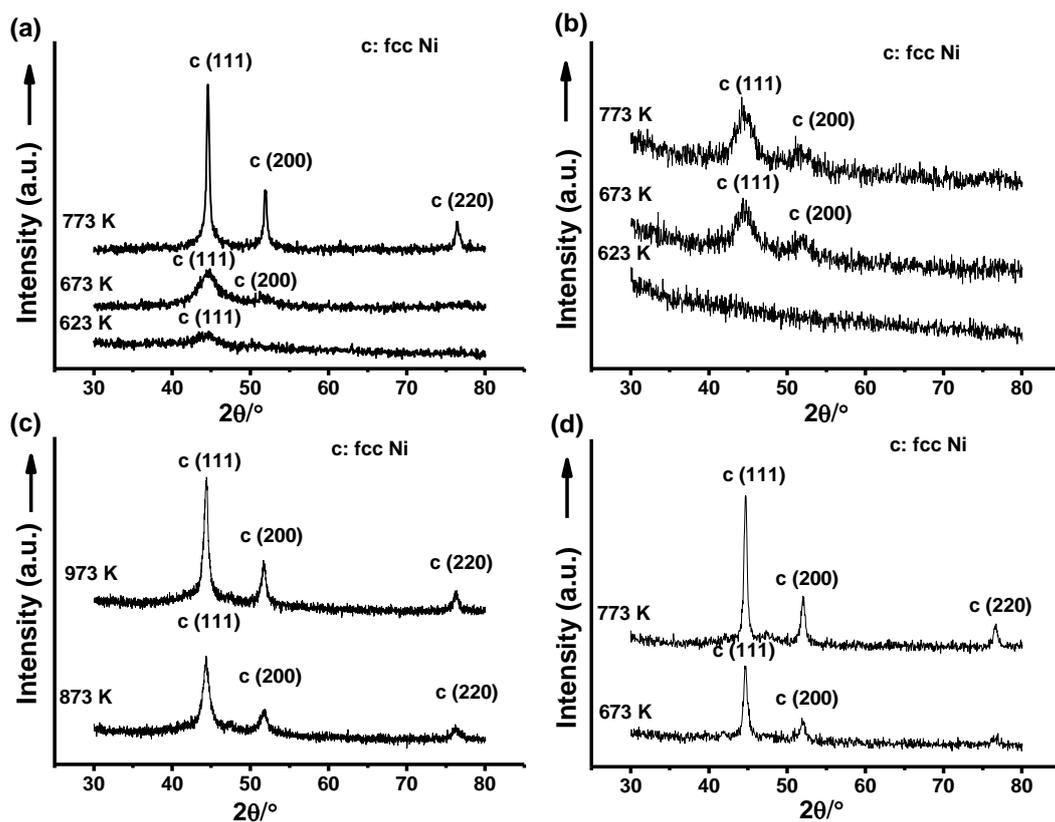


Figure S13. XRD patterns of Ni NPS being calcined at different temperatures using glucose as bonding agent and distilled water as solvent. Using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as metallic source and PVP as surfactant (a and c), using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as metallic source without PVP (b), using  $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$  as metallic source and PVP as surfactant (d).

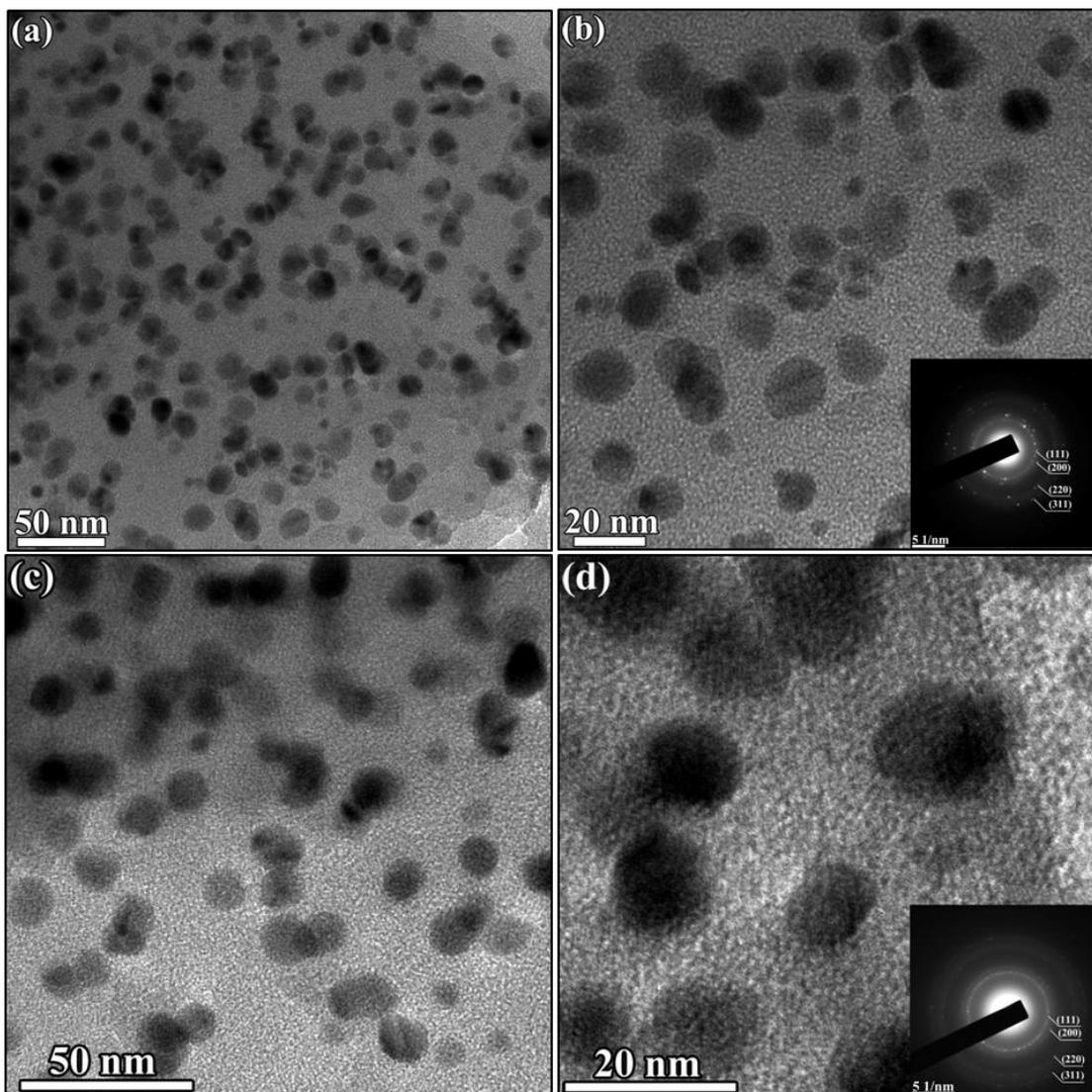


Figure S14. TEM images and SAED analysis results of Ni NPS being calcined at 873 (a and b) and 973 K (c and d) by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP and glucose.

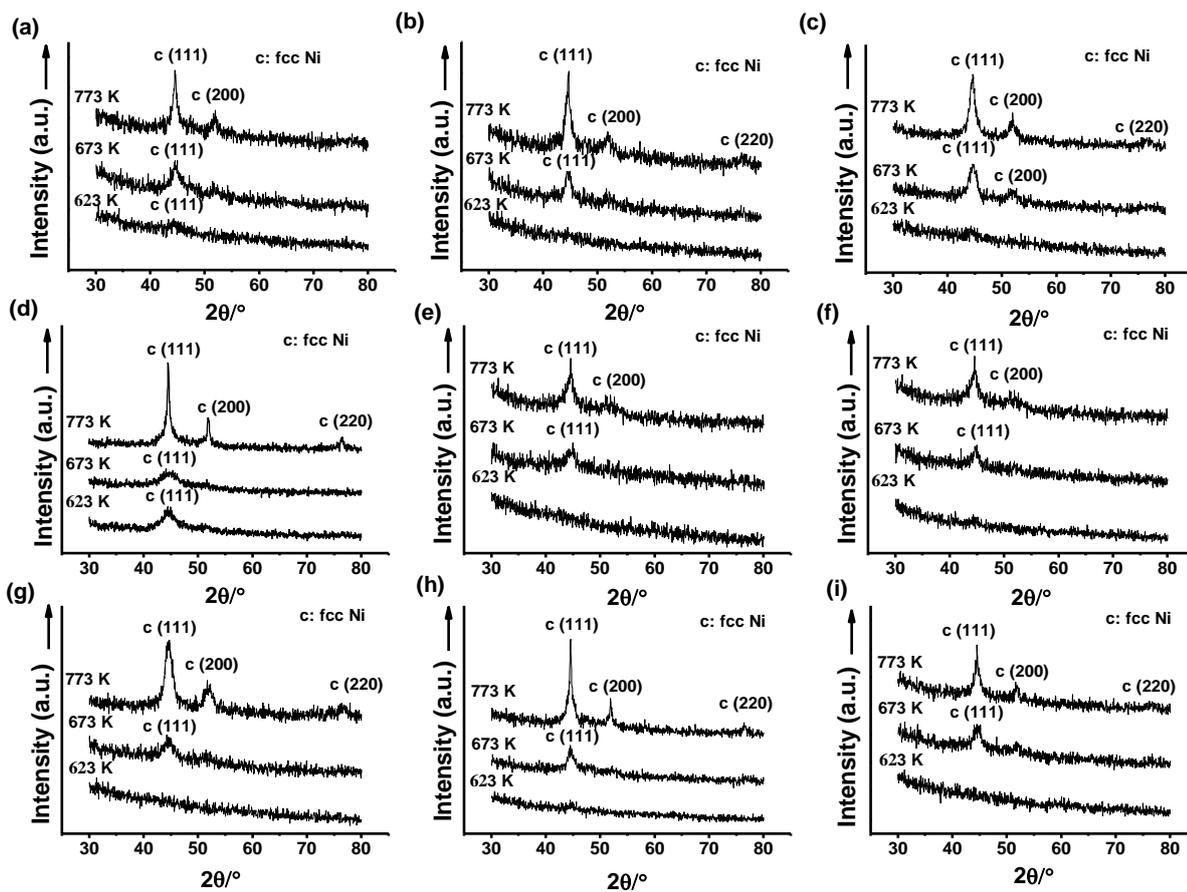


Figure S15. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, ribose (a), mannose (b), trehalose (c), inulin (d), galactose (e), lactose (f), raffinose (g), xylose (h), cyclodextrin (i).

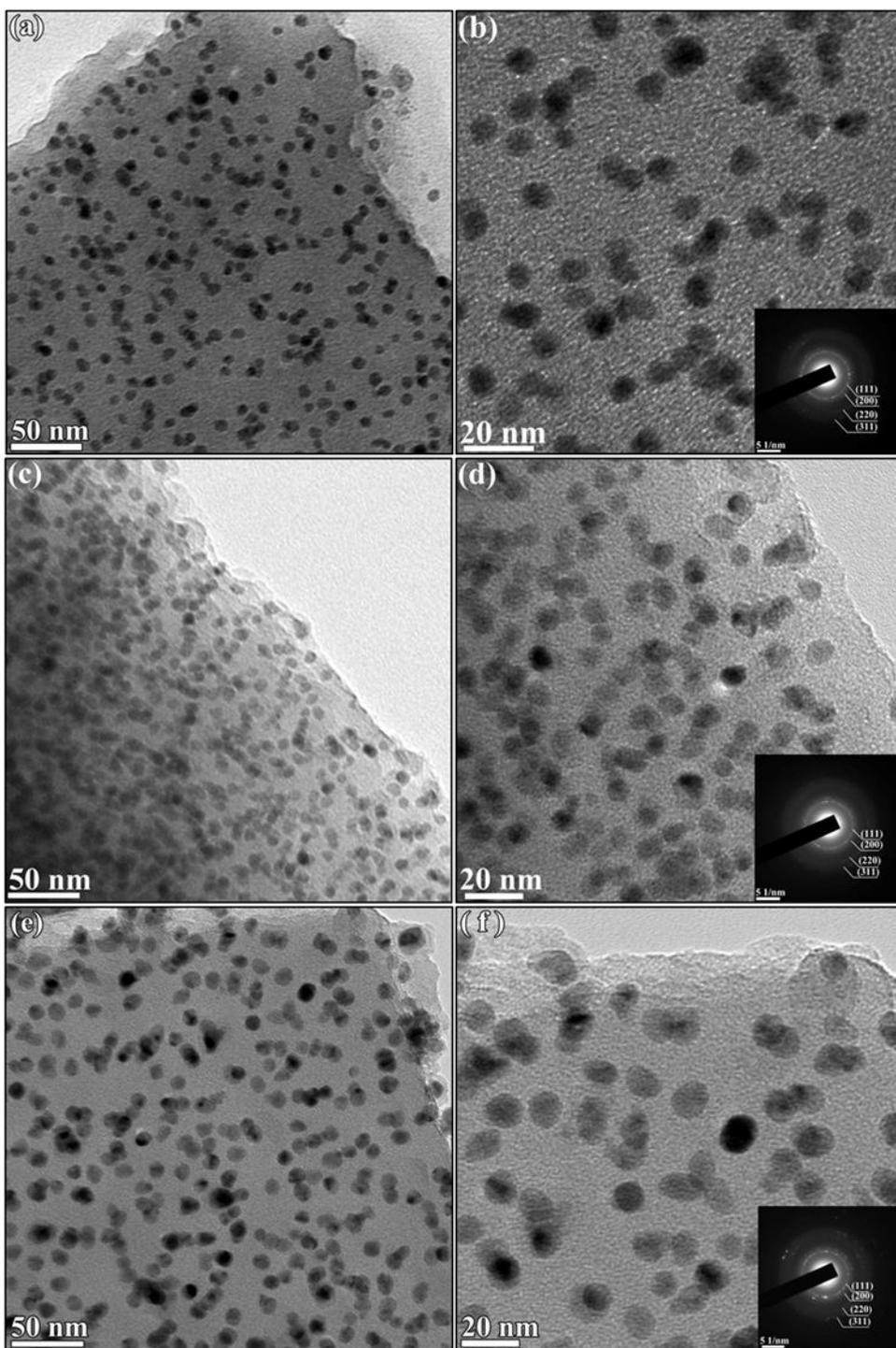


Figure S16. TEM images and SAED analysis results of Ni NPS being calcined at 623 (a, b) and 673 (c, d), and 773 K (e, f) by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP and ribose as initial chemical agents.

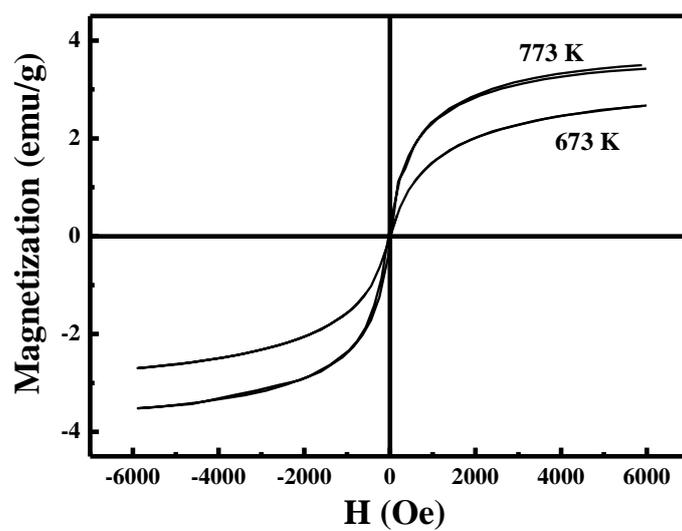


Figure S17. Room temperature vibrating sample magnetometer analysis results of Ni NPS being calcined at 673 and 773 K using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP and ribose as initial agents.

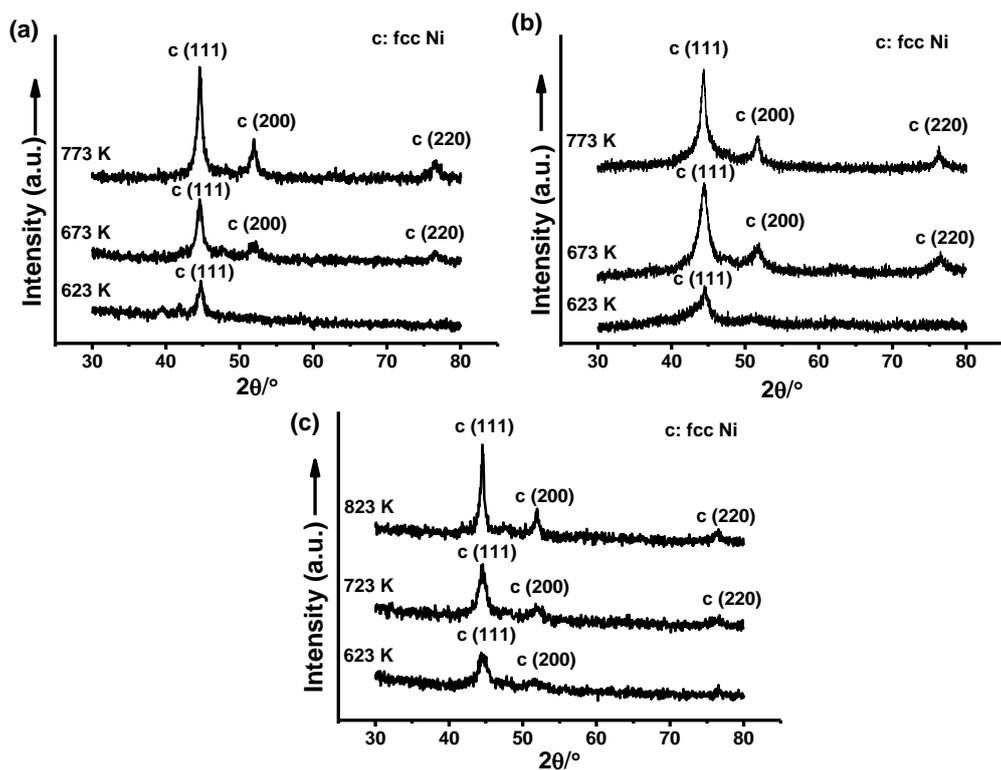


Figure S18. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, EDTA (a),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , pyruvic acid (b),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, and malic acid (c).

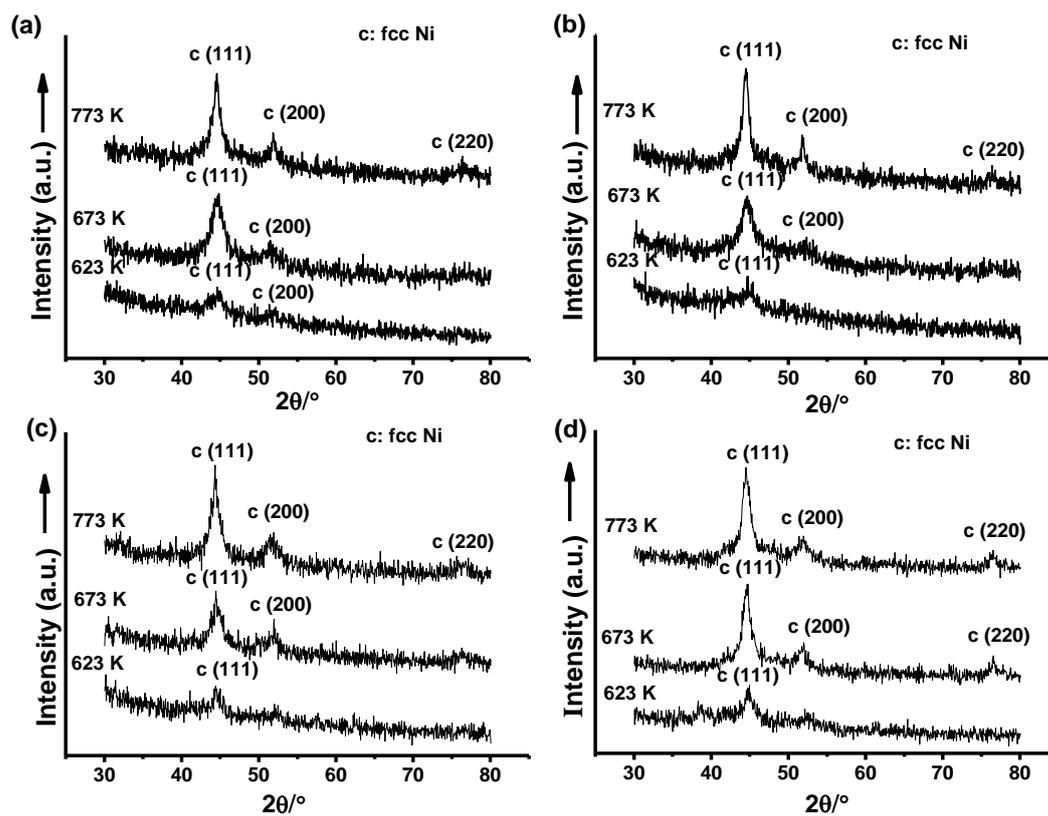


Figure S19. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, gluconic acid (a), ascorbic acid (b), pyrogallol (c), and glyoxylic acid (d) as initial agents.

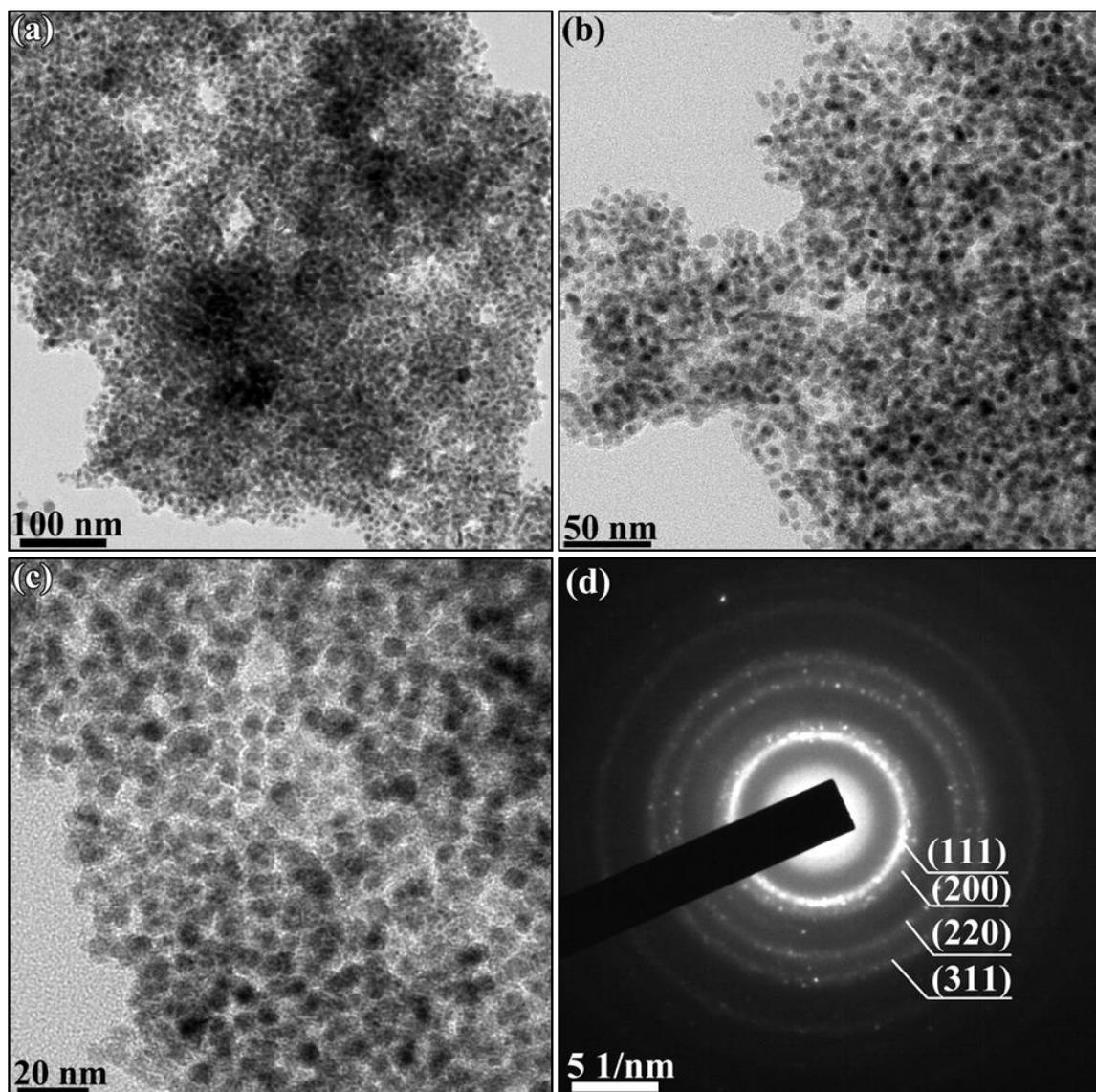


Figure S20. TEM images and SAED analysis results of Ni NPS being calcined at 773 K using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, and pyruvic acid.

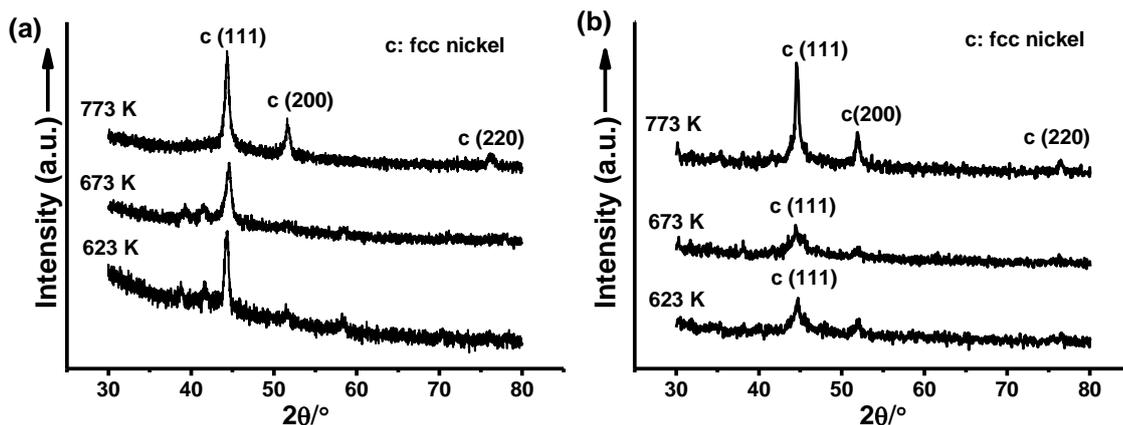


Figure S21. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , gelatin (a), and carboxymethyl cellulose (b) as initial agents.

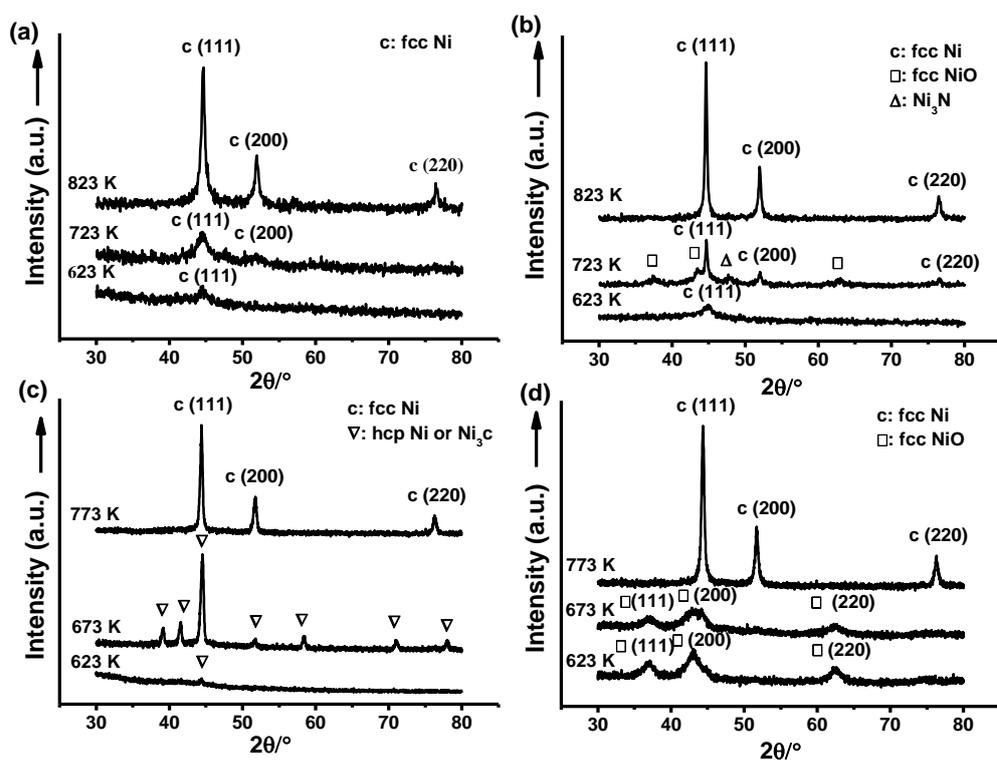


Figure S22. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, ethylenediamine (a), triethanolamine (b), formamide (c), N,N-Dimethylformamide (d).

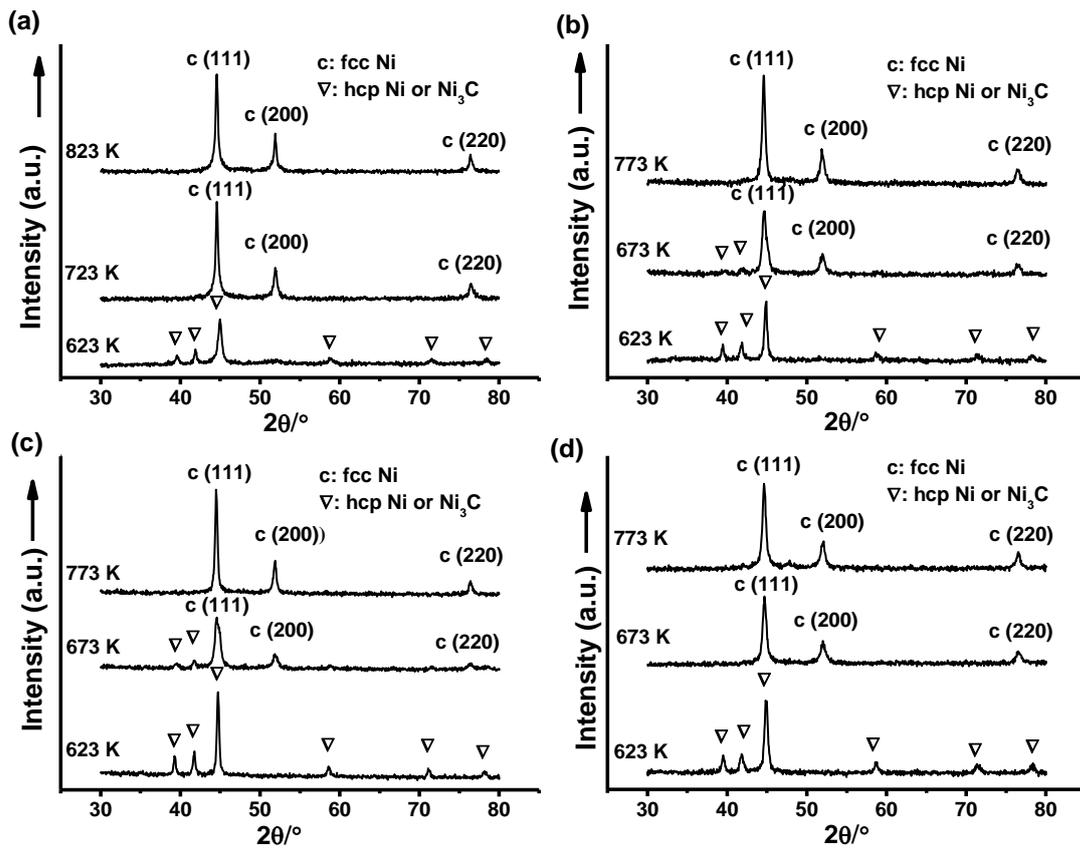


Figure S23. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , ethylene glycol, tween 80 (a),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, glycerol (b),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, diethylene glycol (c),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, 1,2-propanediol (d).

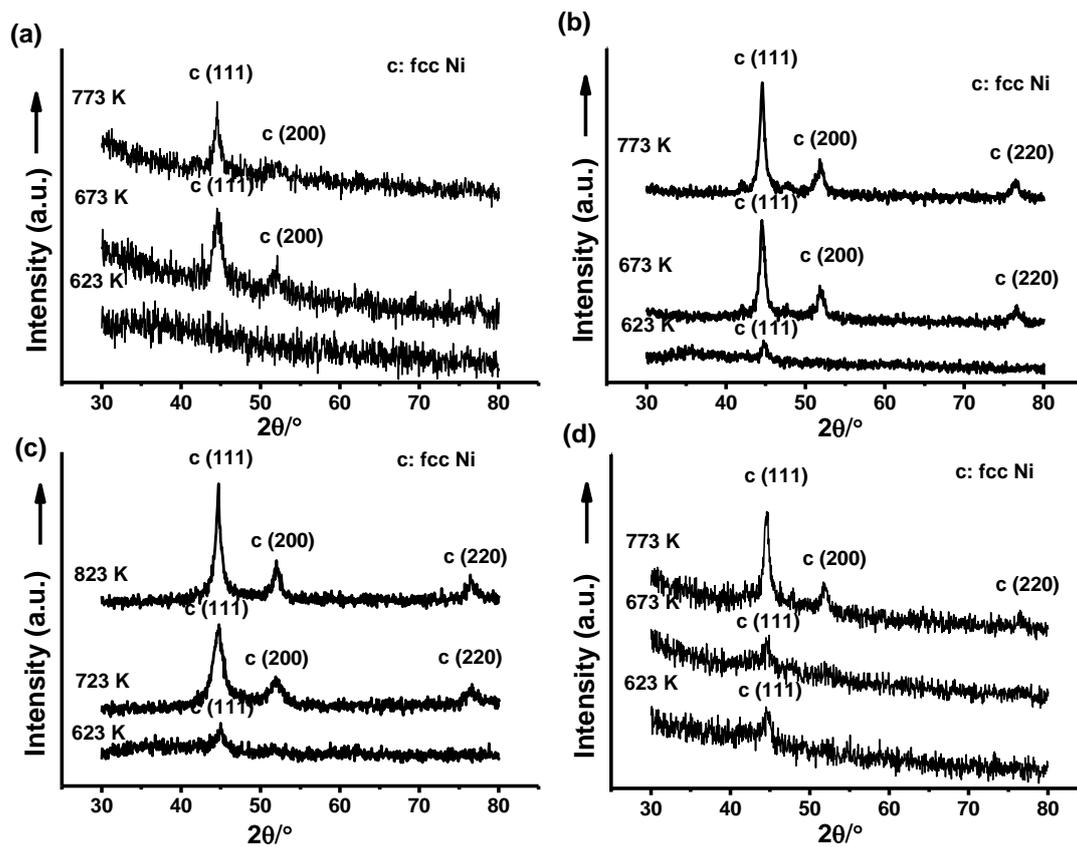


Figure S24. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, maltitol (a),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, xylitol (b),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , tween 80, pentaerythritol (c),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , PVP, inositol (d).

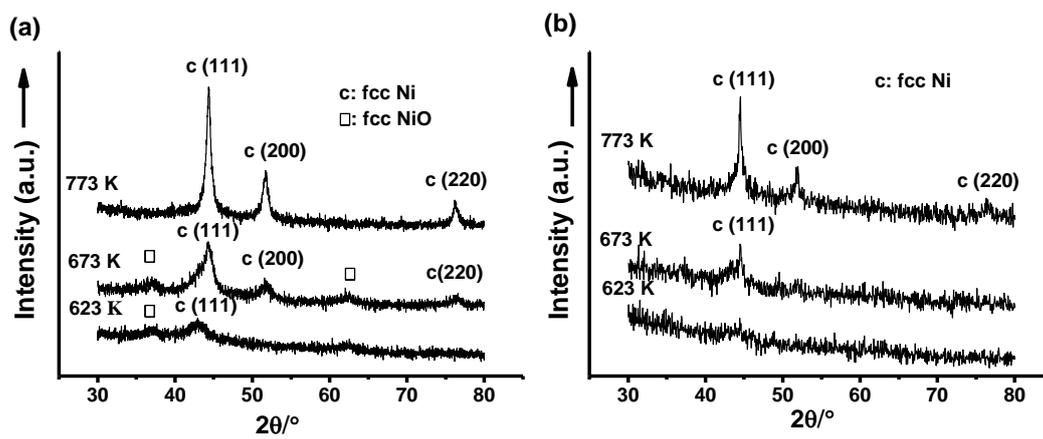


Figure S25. XRD analysis results of Ni NPS prepared by using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , *m*-dihydroxybenzene (a),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , *m*-dihydroxybenzene and PVP (b).

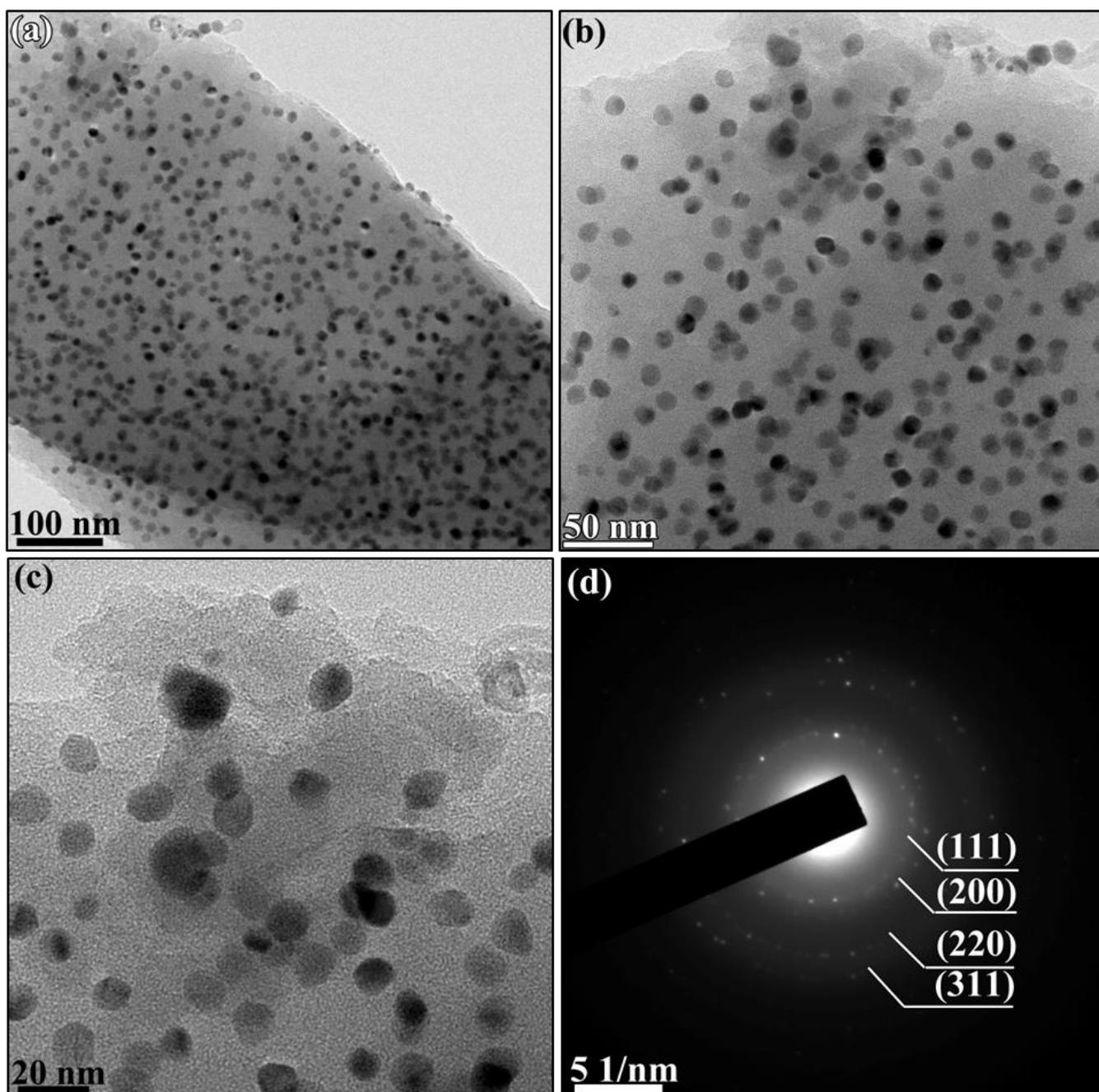


Figure S26. TEM images and SAED analysis results of Ni NPS being calcined at 773 K using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , m-dihydroxybenzene.