

## ELECTRONIC SUPPORTING INFORMATION

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### **Low Cost Nano Materials Crystallize in the NiAs Structure Type as Alternative to the Noble Metals in the Hydrogenation Process\*\***

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## **Experimental Details**

**Chemicals:** SbCl<sub>3</sub> (anhydrous, 99%, Alfa Aesar), NiCl<sub>2</sub> (anhydrous, 99%, Alfa Aesar), CoCl<sub>2</sub>.6H<sub>2</sub>O (99%, SDFCL), NaBH<sub>4</sub> (98%, Sigma Aldrich), tetra ethylene glycol (TEG) (99%, Alfa Aesar), Ethanol (absolute 99.9%), as purchased without further purification.

**Synthesis of 10 nm NiSb and CoSb by polyol condition:** In this method NiCl<sub>2</sub> (1 mmol), CoCl<sub>2</sub>.6H<sub>2</sub>O (1 mmol) and SbCl<sub>3</sub> (1 mmol) were dissolved in 25 ml of TEG taken in a schlenk line apparatus. The temperature of the solution slowly increased to 50 °C under constant N<sub>2</sub> purging. Stiochiometric amount of freshly prepared NaBH<sub>4</sub>-TEG solution was slowly injected in to the reaction flask under vigorous magnetic stirring. Upon reduction, the solution was heated to 180 °C and maintained at this temperature for two hours. The resulted product was collected by centrifuging at 3000 rpm and washed several times with water and ethanol, dried under vacuum and stored in ambient conditions.

**Synthesis of 50 nm NiSb by solvothermal condition:** In the conventional solvothermal method, 1 mmol of NiCl<sub>2</sub> and 1 mmol of SbCl<sub>3</sub> were dissolved in 40 ml (80% volume) of TEG under constant stirring and transferred to a teflon lined stainless steel autoclave. Five mmol of NaBH<sub>4</sub> was added as the reducing agent and black colored particles were formed with the evolution of hydrogen gas. The autoclaves were immediately sealed after the completion of the reduction reaction, placed in an oven, heated to 240 °C for 72 hrs. Particles were isolated and washed several times with water and ethanol. Samples were dried under vacuum and stored in ambient condition.

**Characterization:** Powder X-ray diffraction (XRD) data were collected on a Bruker Discover D8 X-ray diffractometer using Cu K $\alpha$  radiation. The crystallite size was calculated using Scherrer equation on the powder XRD data. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns, were collected using a JEOL JEM-2010 TEM. Samples for TEM measurement were prepared by sonicating the nanocrystalline intermetallic powders in ethanol and dropping a small volume onto a carbon-coated nickel grid. Scanning electron microscopy (SEM) images and electron dispersive energy spectrum (EDS) were performed with a scanning Leica 220i electron microscope equipped with Bruker 129 eV energy dispersive X-ray analyser. Samples for SEM and EDS were prepared by sonicating the powder in ethanol and drop-casting a small volume onto a clean Si wafer. UV-Vis characterization was carried out in the Perkin lambda 900 instrument.

**Catalytic reaction:** In a typical catalytic reaction, 1 mL ( $1.0 \times 10^{-4}$  M) aqueous solution of *p*-NP and 1 mL (100 mg/L) aqueous NiSb intermetallic colloidal suspensions were mixed together in a 1 cm quartz cuvette. Freshly prepared 1 mL ( $6 \times 10^{-2}$  M) aqueous NaBH<sub>4</sub> solution was added to the reaction mixture and time-dependent absorption spectra were recorded in the UV-Vis spectrophotometer at 25 °C.

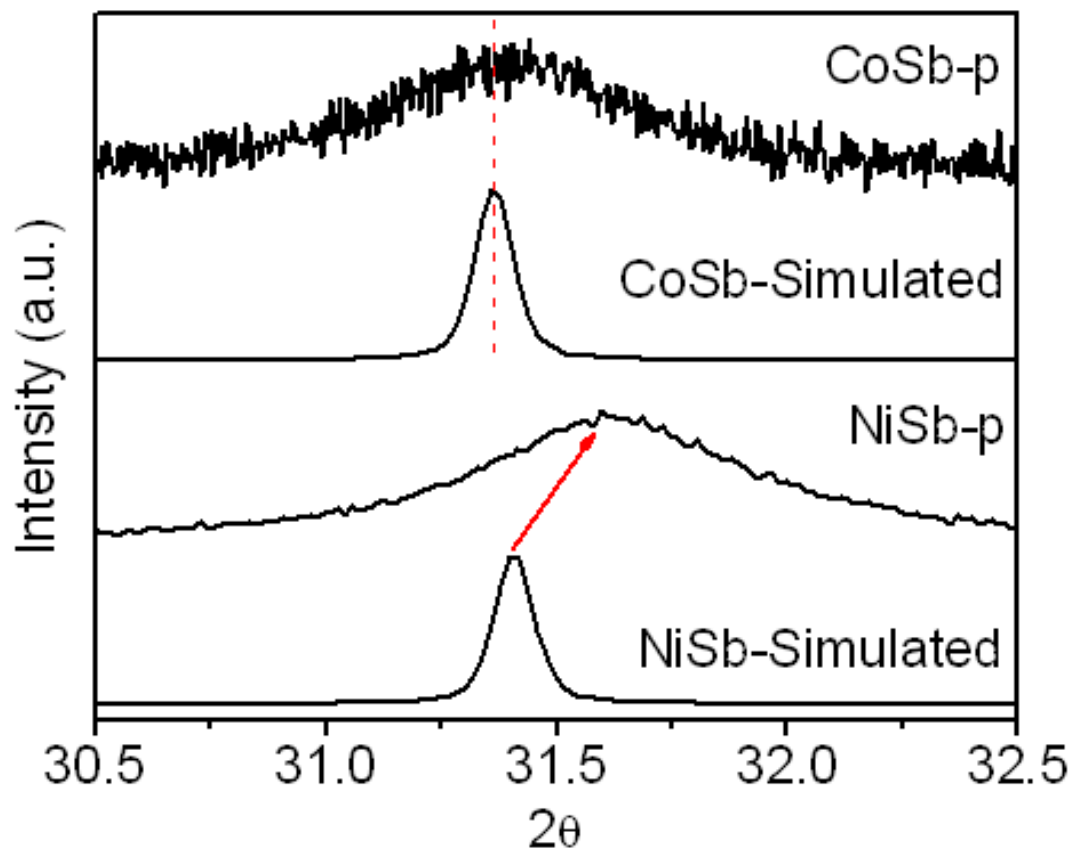
**Reusability:** After the complete conversion of *p*-NP to *p*-AP, 1 ml of *p*-NP solution was introduced to the cuvette with the above mentioned parameters and the recyclability test was evaluated. As the excess amount of reducing agent present in the solution, addition of extra reducing agent was not required for the reusability reaction. Similar reduction time was observed from the recyclability reaction compared with the initial run

**Table S1.** Rate constants obtained for the reduction of p-Np to p-Ap by as synthesized catalyst nanoparticles. Catalyst loading is 0.1 mg/mL. \* Second cycle of catalysis.

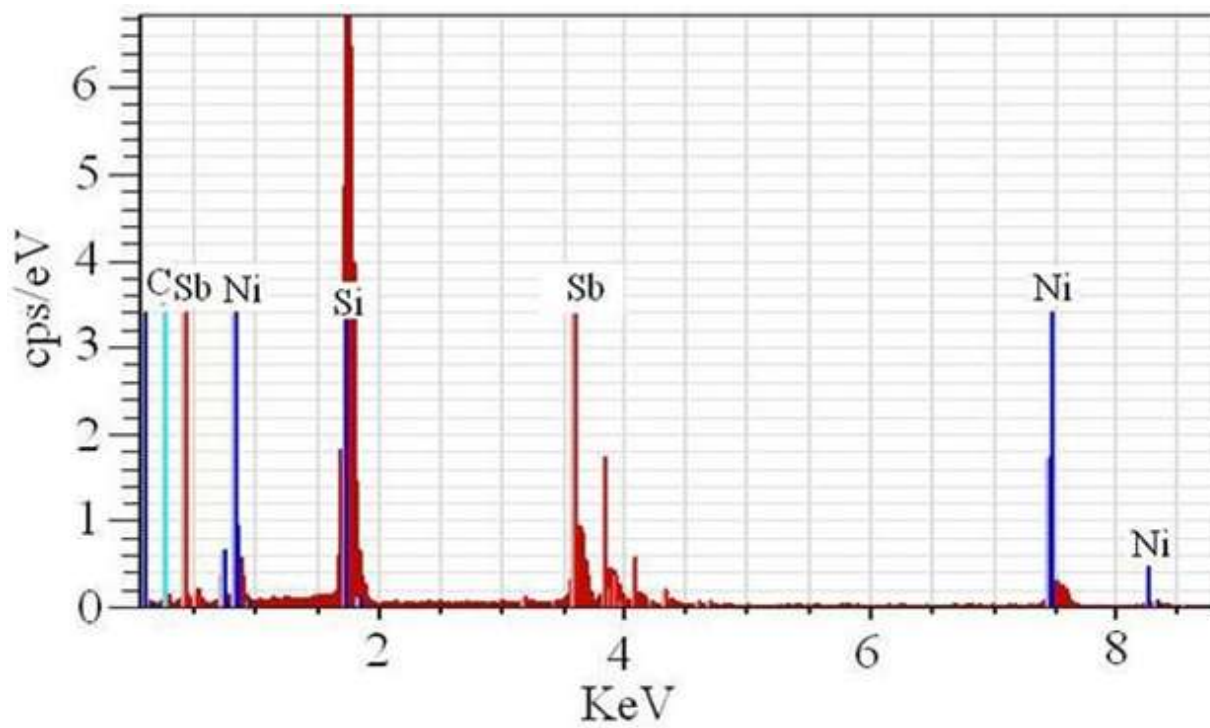
<b>Compositio n</b>	<b>Rate constant <i>k</i> (s<sup>-1</sup>)</b>
NiSb-p	3.60 x 10 <sup>-3</sup>
NiSb-p*	1.93 x 10 <sup>-3</sup>
NiSb-s	1.53 x 10 <sup>-3</sup>
NiSb-s*	1.51 x 10 <sup>-3</sup>
CoSb-p	1.80 x 10 <sup>-3</sup>
CoSb-p*	1.51 x 10 <sup>-3</sup>

**Table S1:** Comparison of rate constants obtained for the reduction of p-nitrophenol to p-aminophenol using various metal and alloy nanoparticles as catalysts

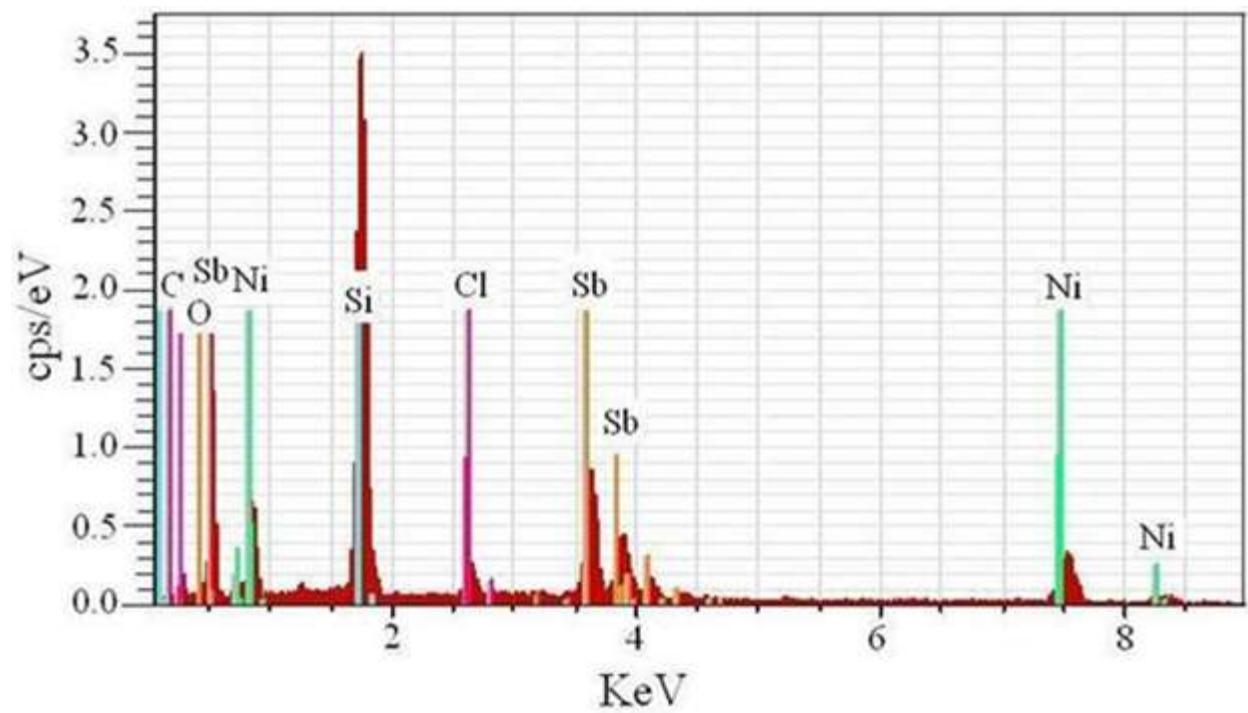
<b>Composition</b>	<b>Metal loading (mg/mL)</b>	<b>Rate constant (s<sup>-1</sup>)</b>	<b>Reference</b>
<b>Au</b>	0.18	1.98 x 10 <sup>-3</sup>	[1]
<b>Pt thin film</b>	0.28	1.98 x 10 <sup>-3</sup>	[2]
<b>Ni<sub>33.8</sub>Co<sub>66.2</sub></b>	0.1	1.22 x 10 <sup>-3</sup>	[3]
<b>Pt Pure</b>	4 (μg)	0.125 x 10 <sup>-3</sup>	[4]
<b>Fe<sub>33.5</sub>Ni<sub>66.5</sub></b>	0.1	0.95 × 10 <sup>-3</sup>	[5]
<b>RANEY Ni</b>	4 (μg)	0.14 x 10 <sup>-3</sup>	[4]
<b>Ni-Pt nanoparticles</b>	4 (μg)	1.939 x 10 <sup>-3</sup>	[4]



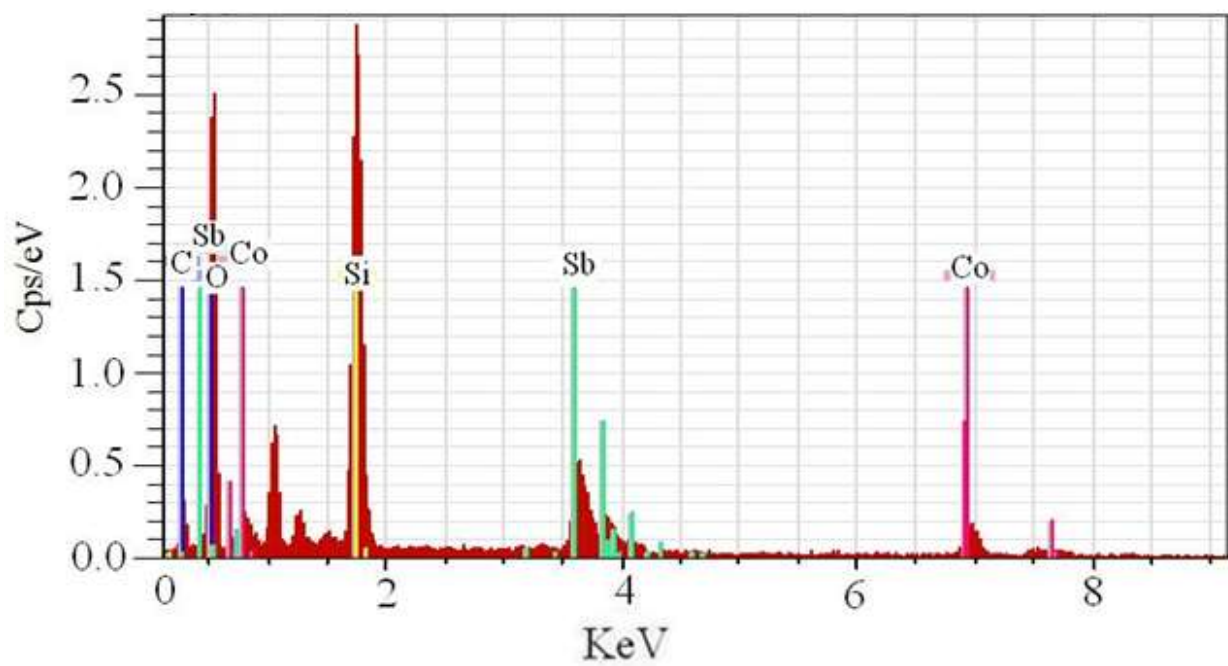
**Figure S1:** Powder X-ray diffraction comparison of the main peak corresponding to 101 plane of CoSb and NiSb samples with the corresponding reported bulk material.



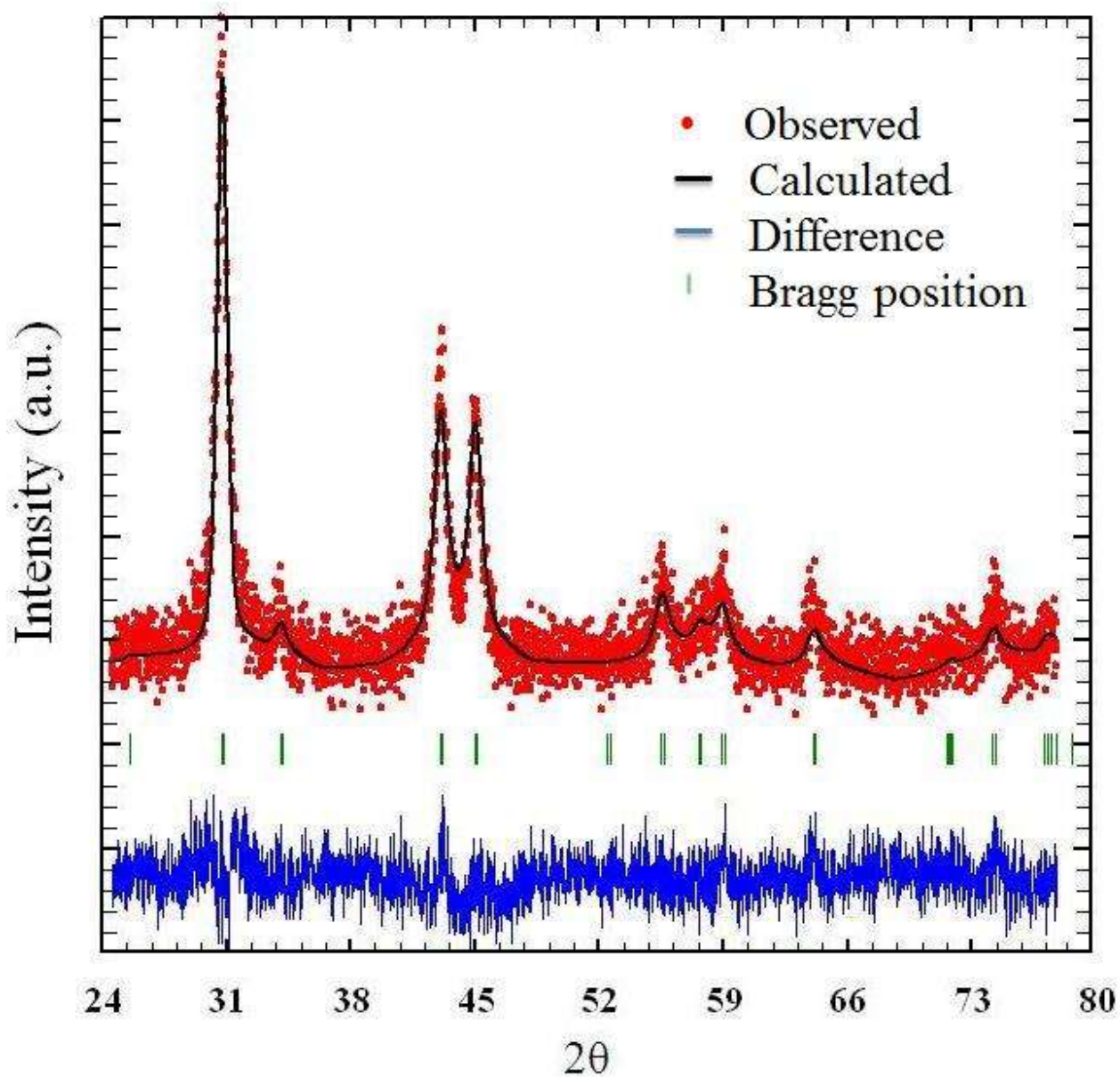
**Figure S2:** EDAX spectrum of NiSb-s nanoparticle.



**Figure S3:** EDAX spectrum of NiSb-p nanoparticle.



**Figure S4:** EDAX spectrum of CoSb-p nanoparticle.



**Figure S5:** Powder X-ray diffraction pattern of NiSb synthesized by the polyol method. The solid line through the experimental points is the Rietveld refinement pattern. The difference between the observed and the experimental pattern and short vertical bars indicate the Bragg position.



## References

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