## **Electronic Supplementary Information**

for

## Catalytic application of shape-controlled Cu<sub>2</sub>O particles protected by Co<sub>3</sub>O<sub>4</sub> nanoparticles for hydrogen evolution from ammonia borane

Yusuke Yamada,\*<sup>a</sup> Kentaro Yano<sup>a</sup> and Shunichi Fukuzumi\*<sup>a,b</sup>

<sup>a</sup> Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan. Fax: +81-6-6879-7370; Tel: +81-6-6879-7368; E-mail: fukuzumi@chem.eng.osaka-u.ac.jp <sup>b</sup> Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea.



**Fig. S1** Powder X-ray diffraction pattern of  $Cu_2O$  before and after ammonia borane hydrolysis. (a) after reaction and (b) before reaction. Numbers in parenthesis indicates the (*hkl*) index. After reaction,  $Cu_2O$  is reduced to Cu metal.



**Fig. S2** XPS spectra of  $Cu_2O@SiO_2$ . (a) Si 2p region and (b) Cu 2p region. The atomic ratio of Si vs Cu calculated from peak intensities was 94 vs 6. The ratio has not changed before and after reaction.



Fig. S3 SEM images of Cu<sub>2</sub>O (50 facets)-Co<sub>3</sub>O<sub>4</sub>(plate) composites.



**Fig. S4** Time course of hydrogen evolution by ammonia borane hydrolysis with shape-controlled Cu<sub>2</sub>O particles decorated with Co<sub>3</sub>O<sub>4</sub> rods (black open circle, 50-facet; red closed square, cube; blue closed triangle, octahedron; green closed diamonds, RCO). [NH<sub>3</sub>BH<sub>3</sub> = 0.5 mmol, Cu<sub>2</sub>O-Co<sub>3</sub>O<sub>4</sub> [1/5 (w/w)] = 12 mg, water = 20 mL, 293 K].



**Fig. S5** Time course of hydrogen evolution by AB hydrolysis with Cu<sub>2</sub>O particles (50-facets) partially covered with shape-controlled  $Co_3O_4$  (black, sphere; red, nanoplate; blue, rod) at room temperature (NH<sub>3</sub>BH<sub>3</sub>, 0.5 mmol; catalyst, 12 mg; water, 20 mL). The ratios of Cu<sub>2</sub>O/Co<sub>3</sub>O<sub>4</sub> (w/w) were 1/1.