

Supporting Information for

**Facile synthesis of Pd-Ir bimetallic octapods and nanocages through galvanic replacement and co-reduction, and their use for hydrazine decomposition<sup>‡</sup>**

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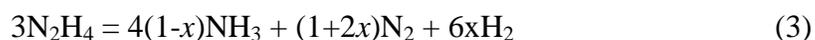
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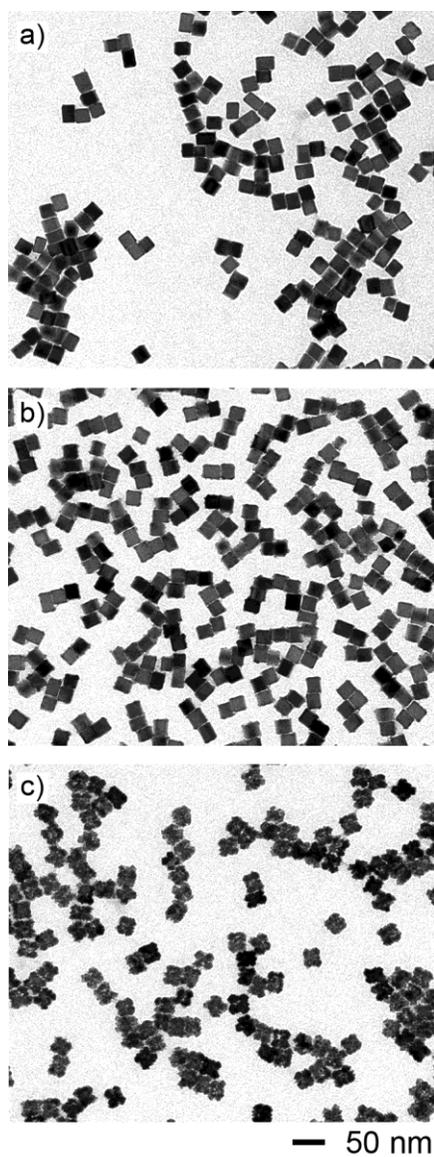
## The H<sub>2</sub> selectivity of a catalyst

Generally, hydrazine can be decomposed to generate a mixture of N<sub>2</sub> and H<sub>2</sub> (Eq. 1) or a mixture of NH<sub>3</sub> and N<sub>2</sub> (Eq. 2). The overall reaction is expressed as Eq. (3). Since the reaction according to Eq. (2) does not generate H<sub>2</sub>, the H<sub>2</sub> selectivity,  $x$ , of a catalyst can be defined as the percentage of decomposition according to Eq. (1). When NH<sub>3</sub> is removed from the gas mixture, the H<sub>2</sub> selectivity can be calculated from the amounts of N<sub>2</sub> and H<sub>2</sub> based on Eqs. (4) and (5).

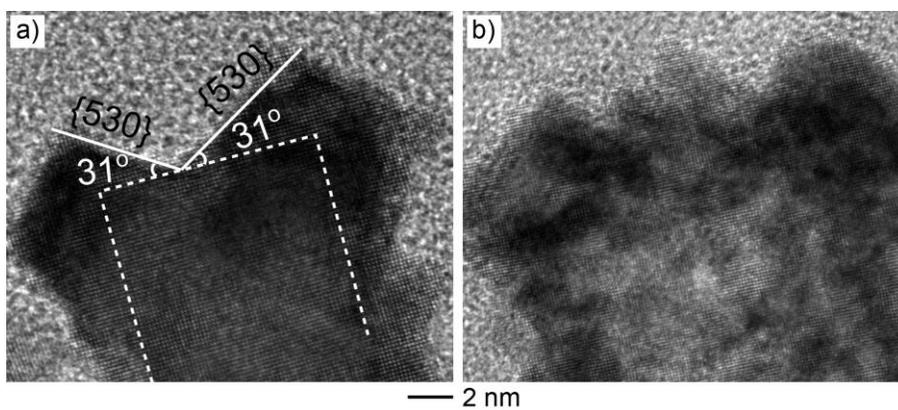


$$n(\text{N}_2+\text{H}_2)/n(\text{N}_2\text{H}_4)=[(1+2x) + 6x]/3 \quad (4)$$

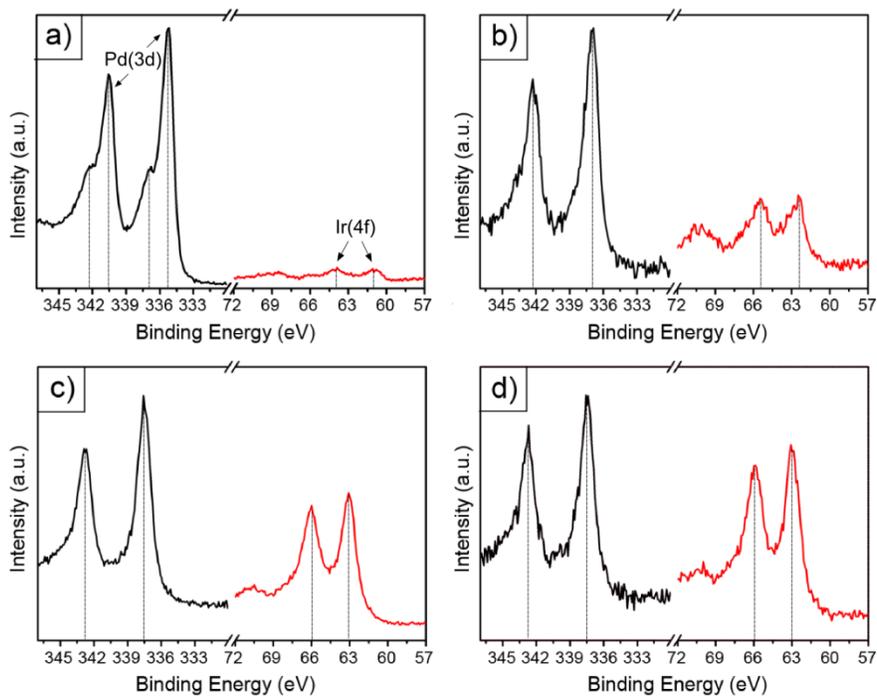
$$x = [3n(\text{N}_2+\text{H}_2)/n(\text{N}_2\text{H}_4)-1]/8 \times 100\% \quad (5)$$



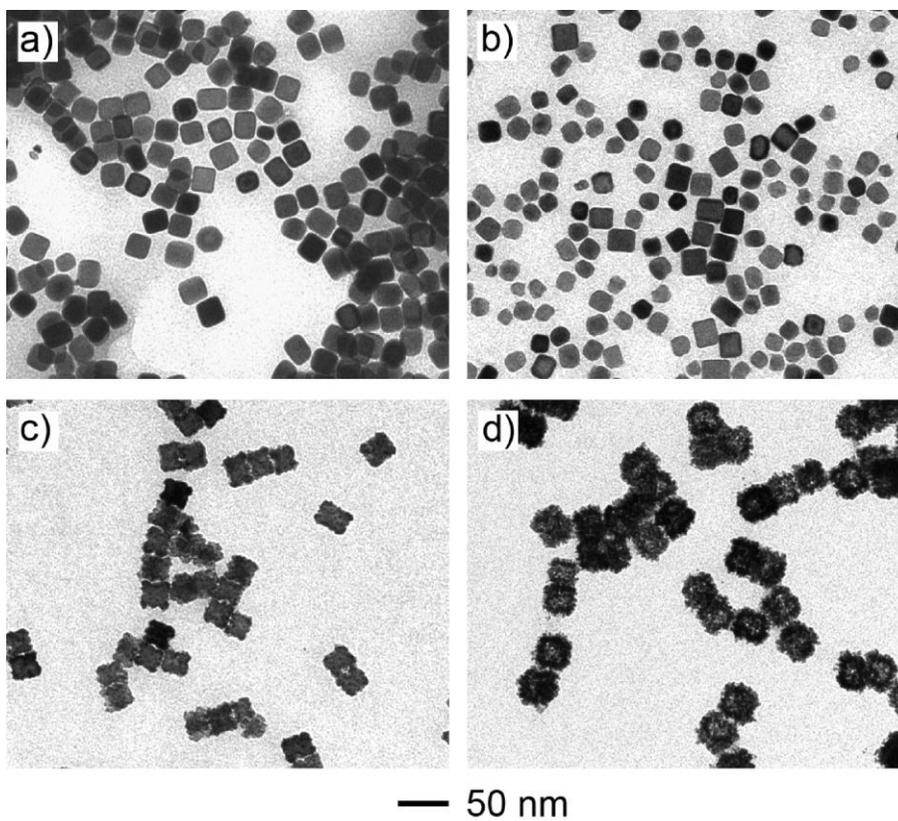
**Fig. S1** TEM images of Pd-Ir bimetallic nanostructures obtained at different stages of a standard synthesis: a) 0.5 h, b) 1 h, and c) 9 h. The scale bar applies to all images.



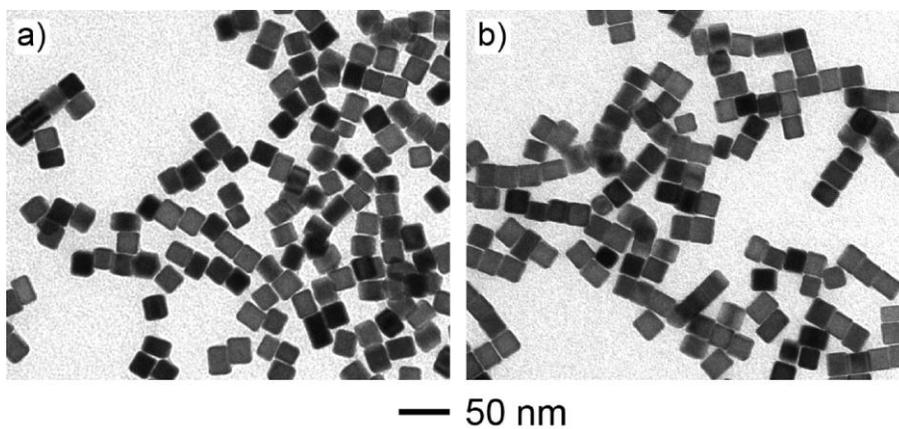
**Fig. S2** High-resolution TEM images of the octapod and cage shown in Fig.2, c and d.



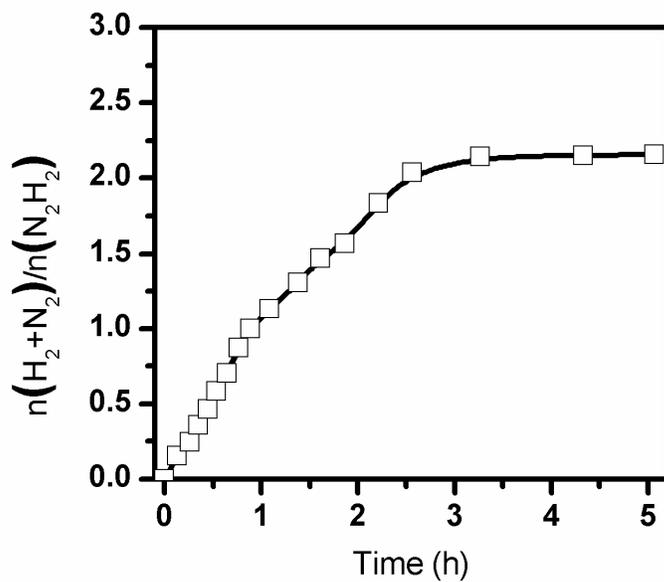
**Fig. S3** X-ray photoelectron spectra (XPS) of Pd-Ir bimetallic nanostructures obtained at different stages of a standard synthesis: a) 1 h, b) 2 h, c) 9 h, and d) 24 h. Black and red curves correspond to elemental Pd and Ir, respectively.



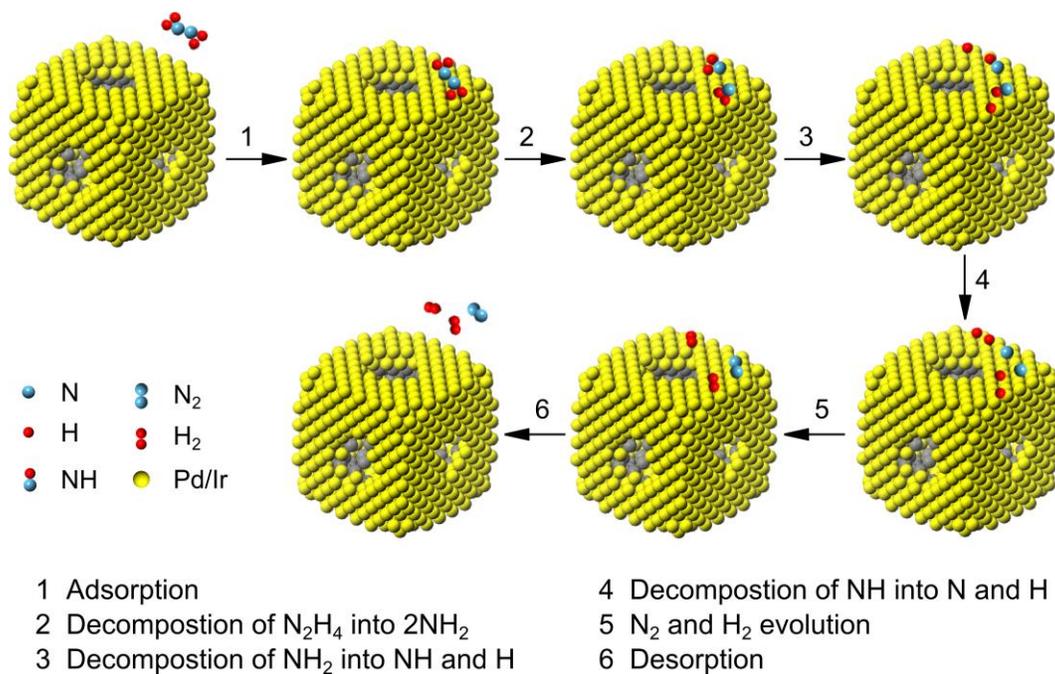
**Fig. S4** TEM images of Pd-Ir bimetallic nanostructures obtained using the standard procedure, except that the reaction temperature was set to a, b) 100 °C and c, d) 160 °C, respectively. The products were obtained at different stages of the syntheses: a, c) 2 h and b, d) 24 h.



**Fig. S5** TEM images of Pd nanostructures obtained from a standard synthesis, in which no Ir precursor was added. The samples were obtained at different stages of the same synthesis: a) 2 h and b) 24 h, respectively.



**Fig. S6** Catalytic decomposition of hydrazine monohydrate to generate  $\text{H}_2$  in the presence of 14-nm Pd-Ir nanocages as a catalyst.



**Fig. S7** A plausible mechanism involved in the decomposition of N<sub>2</sub>H<sub>4</sub> over a Pd-Ir alloyed nanocage.