# Electronic Supplementary Information

## Simple Synthesis of Pd-$Fe_3O_4$ Heterodimer Nanocrystals and their Applications to Magnetically Recyclable Catalyst for Suzuki Cross-Coupling Reactions

Youngjin Jang,‡[a] Jooyoung Chung,‡[b] Seyoung Kim,[b] Samuel Woojoo Jun,[a] Byung Hyo Kim, [a] Dong Won Lee,[a] B. Moon Kim*[b] and Taeghwan Hyeon*[a]

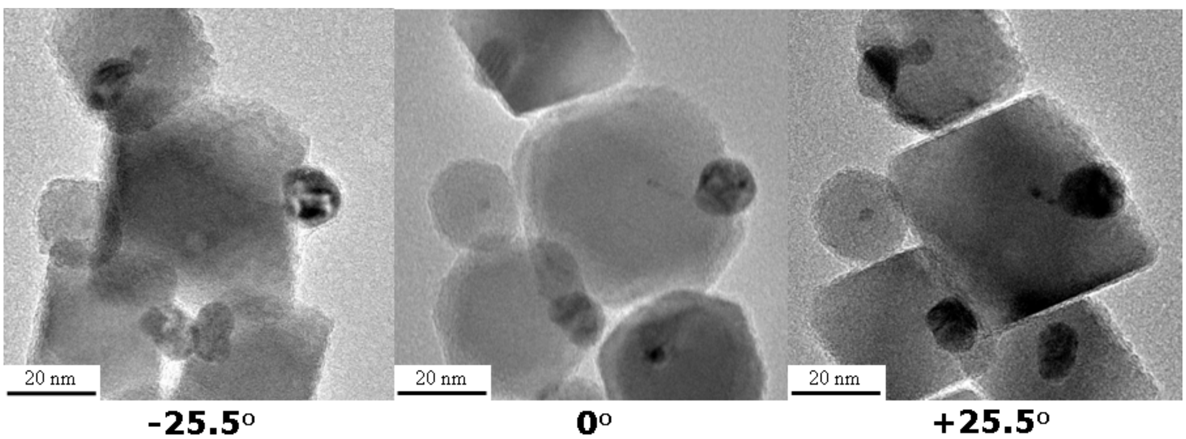



**Fig. S1** TEM images of Pd-$Fe_3O_4$ heterodimer nanocrystals at various tilted X° angles.

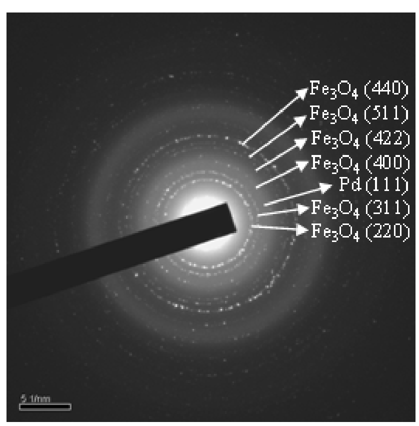



**Fig. S2** ED pattern of Pd-$Fe_3O_4$ heterodimer nanocrystals.

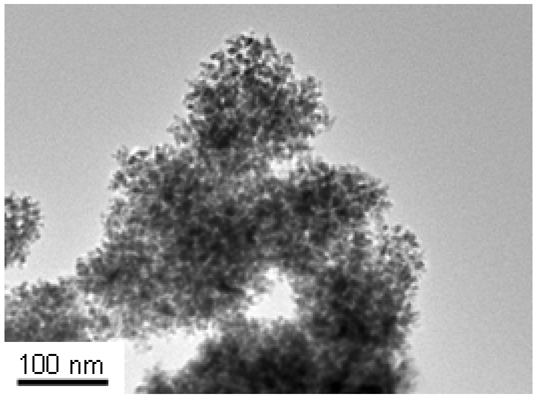



**Fig. S3** TEM image of Pd particles when only $Pd(acac)_2$ was added under the same synthesis conditions.

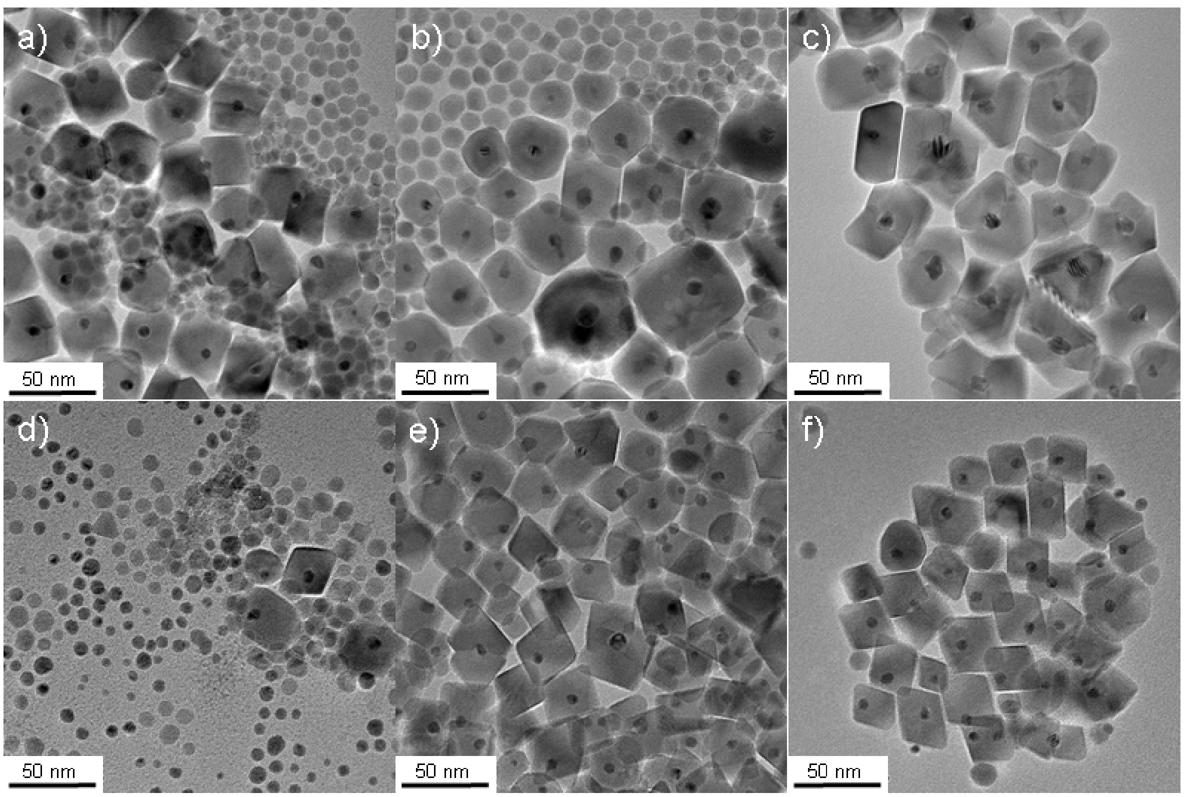



**Fig. S4** TEM images of the products synthesized at different aging temperatures of a) 180 $^{o}$C, b) 200 $^{o}$C, and c) 220 $^{o}$C, and at different heating rates of d) 4 $^{o}$C/min, e) 2 $^{o}$C/min, and f) 1 $^{o}$C/min.

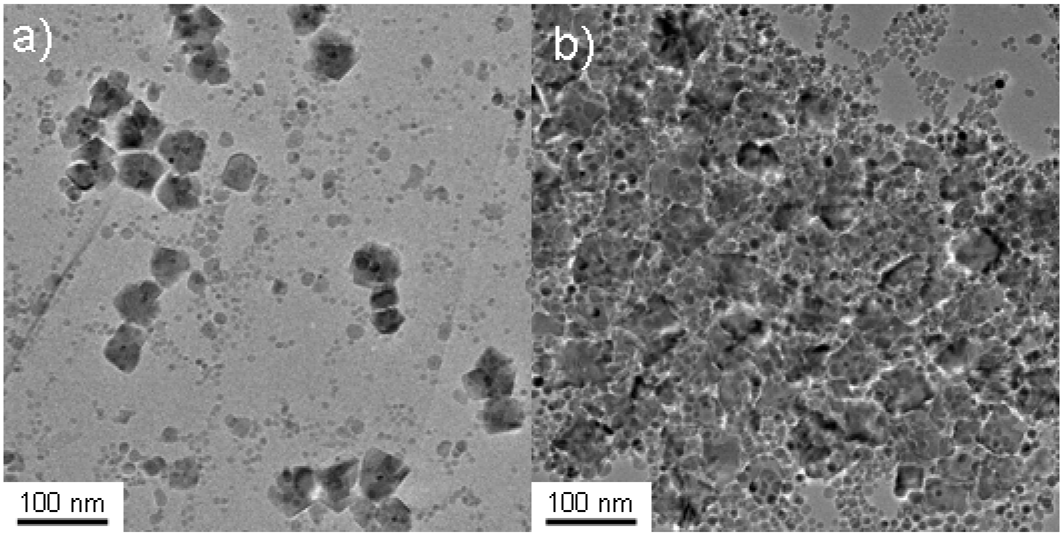



**Fig. S5** TEM images of products prepared under reaction condition of a) no aging, b) 1h aging at 220 $^{o}$C.

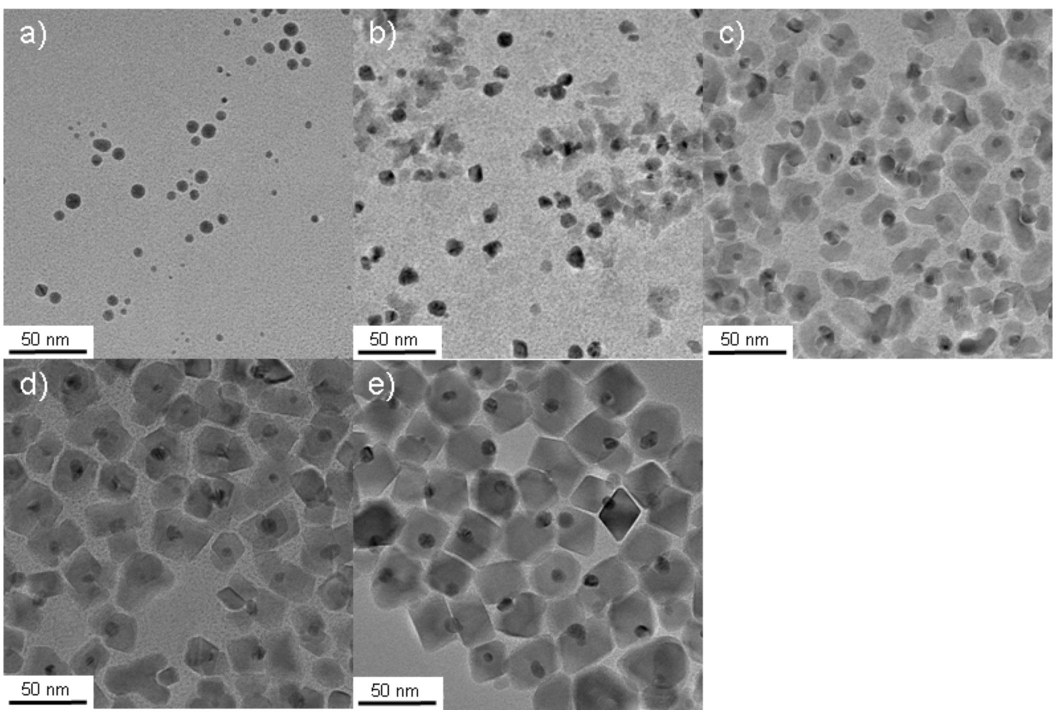



**Fig. S6** TEM images of the samples taken at a) 200 $^{o}$C, b) 220 $^{o}$C, c) 250 $^{o}$C, d) 270 $^{o}$C, and e) 300 $^{o}$C showing growth process.

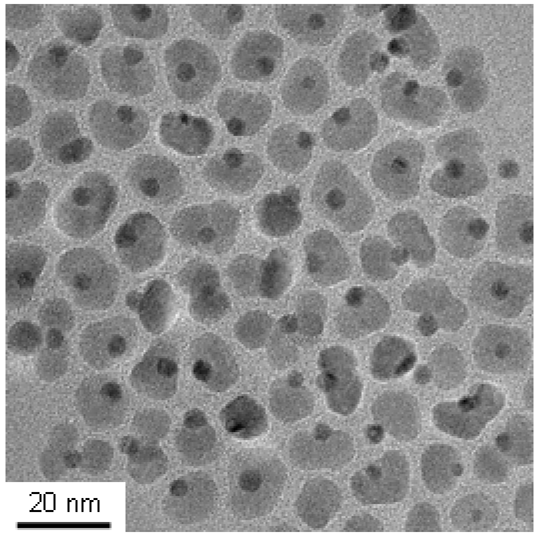



**Fig. S7** TEM image of the products obtained by using as-synthesized Pd nanoparticles as seeds in two pot synthesis.

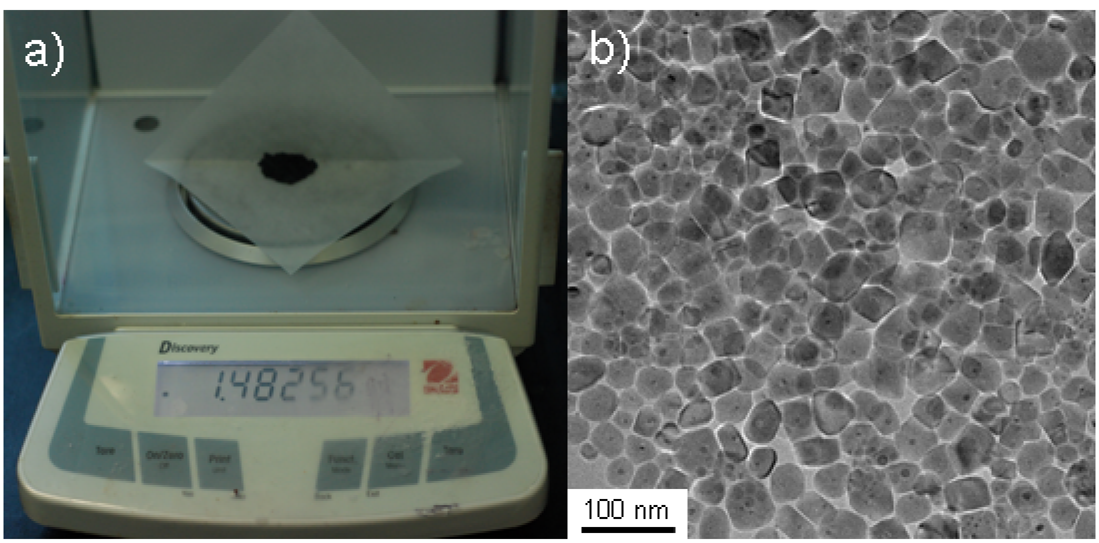



**Fig. S8** a) A photograph showing 1.48 g of Pd-$Fe_3O_4$ heterodimer nanocrystals in one batch, b) TEM image of Pd-$Fe_3O_4$ heterodimer nanocrystals in large-scale synthesis.

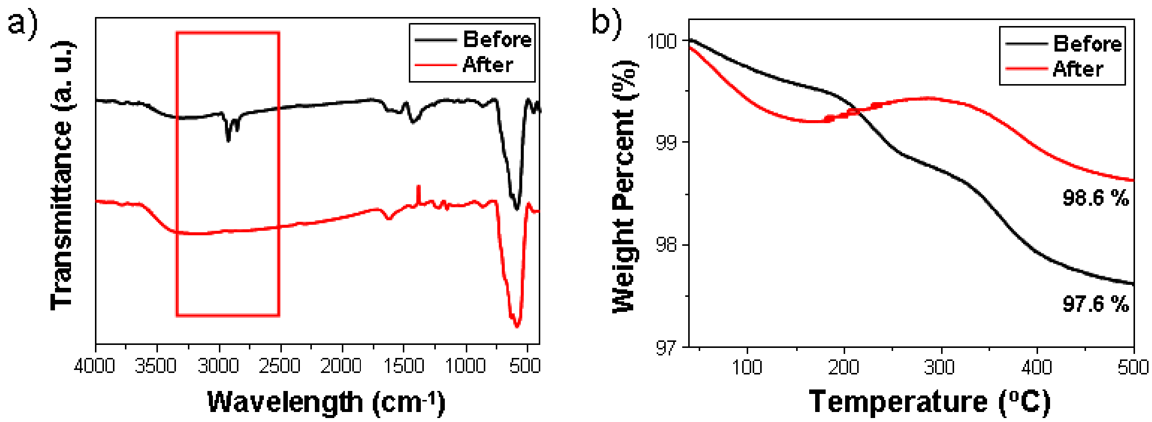



**Fig. S9** a) FT-IR spectra and b) TGA curves of Pd-$Fe_3O_4$ heterodimer nanocrystals after one cycle of catalytic reaction.

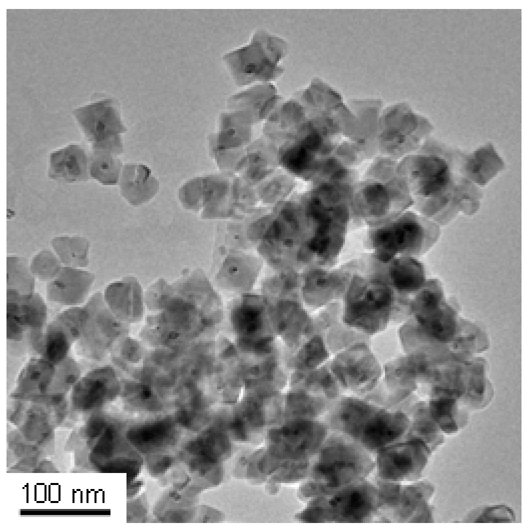



**Fig. S10** TEM image of Pd-$Fe_3O_4$ heterodimer nanocrystals after 10 cycles of the catalytic reaction.

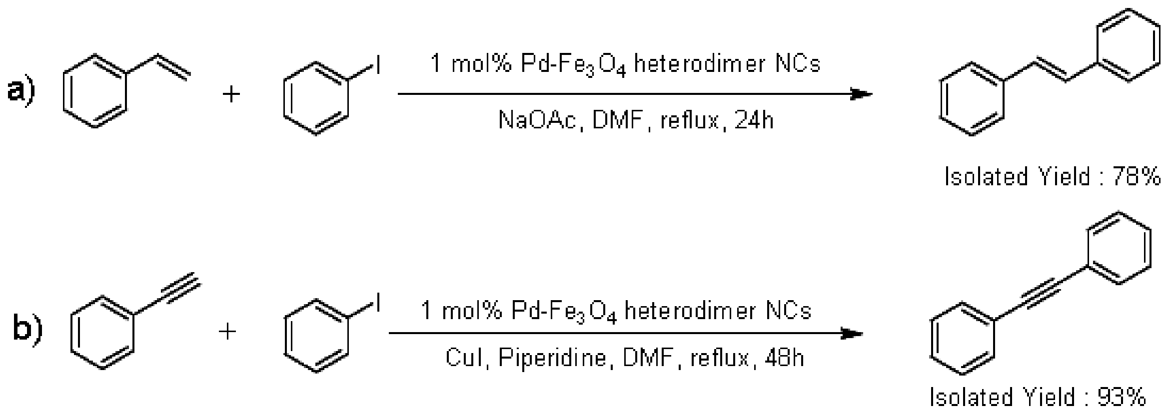
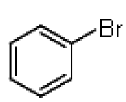
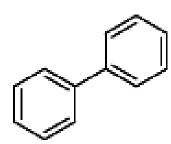



**Fig. S11** Preliminary results on utilizing Pd-$Fe_3O_4$ heterodimer nanocrystals for a) Heck and b) Sonogashira coupling reactions.

**Table S1** Optimization of reaction conditions for the Suzuki coupling reaction of phenylboronic acid with bromobenzene

| Entry | Substrate | Product | Solvent | Base | Yield(%) |
|---|---|---|---|---|---|
| 1 | | | DME : $H_2O$ =3:1 | $Na_2CO_3$ | 70 |
| 2 | | | Isobutanol | $Na_2CO_3$ | trace |
| 3 | | | Isobutanol | $K_3PO_4$ | trace |
| 4 |  |  | 2-methoxyethanol | $Na_2CO_3$ | 32 |
| 5 | | | 2-methoxyethanol | $K_3PO_4$ | 26 |
| 6 | | | DMF | $Na_2CO_3$ | 35 |
| 7 | | | 1,4-dioxane | $Na_2CO_3$ | 65 |

* All the reactions were performed using 1 mol% of catalyst and 1.2 eq. $PhB(OH)_2$, 1.3 eq. base at reflux temperature for 24 h under a nitrogen atmosphere (based on isolated yield).

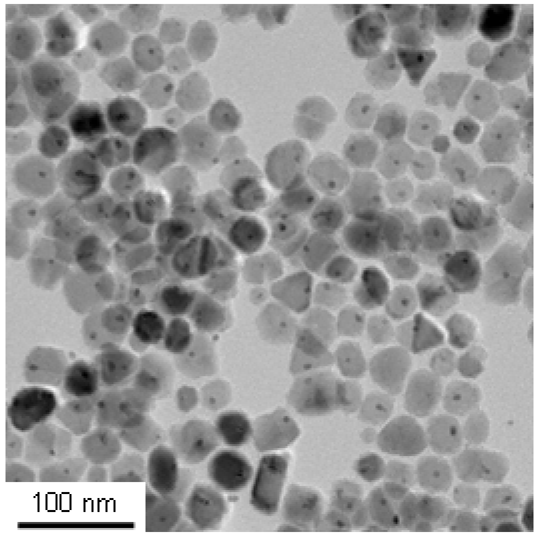



**Fig. S12** TEM image of Pt-$Fe_3O_4$ heterodimer nanocrystals.