

Electronic Supplementary Information

Facile synthesis of hierarchical core-shell Fe₃O₄@MgAl-LDH@Au as magnetically recyclable catalysts for catalytic oxidation of alcohols

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Experimental Section

1. Preparation of Fe₃O₄@MgAl-LDH

Fe₃O₄ nanospheres with diameter of 450 nm were first pre-synthesized *via* a solvothermal reaction as previously described.¹ Next, 0.104 g Fe₃O₄ nanospheres were dispersed into a 100 ml methanol/water solution ($V_{\text{methanol}}/V_{\text{water}}=1:1$) under ultrasonically agitating for 15 minutes to obtain a uniform suspension. A 100 ml alkaline solution containing 1.280 g Na₂CO₃ and 1.600 g NaOH in methanol/water solution ($V_{\text{methanol}}/V_{\text{water}}=1:1$) was added dropwise into the suspension until the pH=10. Then, another 100 ml methanol/water solution ($V_{\text{methanol}}/V_{\text{water}}=1:1$) containing 2.310 g Mg(NO₃)₂·6H₂O and 1.125 g Al(NO₃)₃·9H₂O was added dropwise into the above suspension under vigorous stirring at constant pH 10 maintained by simultaneous addition of alkaline solution. The obtained slurry was aged at 60°C for 24 h. The resultant was separated using a magnet, washed by deionized water for five times and

then dried at 60 °C for 24 h giving the product Fe₃O₄@MgAl-LDH.

2. Preparation of Fe₃O₄@MgAl-LDH@Au catalyst

The magnetic nanocatalyst was prepared by deposition-precipitation procedure as follows. A 255ml HAuCl₄ aqueous solution (0.0001 M) was first adjusted to pH 8.0 by 0.1 M NaOH and then positioned in 80°C water bath. The 0.5 g Fe₃O₄@MgAl-LDH was added into above solution under stirring at 80°C for 1 h. The resulting slurry was recovered by magnetic separation, followed by washing with deionized water until no Cl⁻ remained and dried at 60°C for 24 h to produce the supported gold nanocatalyst Fe₃O₄@MgAl-LDH@Au.

3. Characterization.

The SEM-EDX measurements were carried out on an Oxford Instruments INCAx-act EDX detector attached to a Zeiss Supra 55 field emission scanning electron microscopy using a 15 kV electron beam and 60 s acquisition time. Transmission electron microscopy (TEM) was carried out on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 100 kV. The HRTEM graphs were recorded on a JEM 2010 transmission electron microscope. Powder X-ray diffraction (XRD) data were taken on a Shimadzu XRD-6000 diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 30 mA). The samples, as unoriented powders, were step-scanned in steps of 0.02° (2 θ) in the range 5-70° using a count time of 4 s per step. The FT-IR spectra were obtained on a Bruker Vector-22 FT-IR spectrophotometer using KBr pellet technique (sample/KBr = 1/100). Specific surface area of the sample was obtained upon the Brunauer-Emmett-Teller (BET) method from the adsorption isotherm measured by using a Quantachrome Autosorb-1C-VP system. The content of actual Au was measured by inductively coupled plasma (ICP) emission spectroscopy using a Shimadzu ICPS-7500 instrument. The magnetization

of the magnetic submicro-sphere particles was tested on a JDM-13 vibrating-sample magnetometer (VSM) at 298 K and ± 15 kOe applied magnetic field.

4. Catalytic reaction

The oxidation of 1-phenylethanol was carried out using a two-necked flask with a reflux condenser. In detail, the as-synthesized magnetic gold nanocatalyst $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}@Au$ was first reduced by H_2 at 200°C for 2 h, and then 0.2 g catalyst (Au: 0.005 mmol) was placed in a reaction vessel, followed by the addition of toluene (5 mL) and 1-phenylethanol (1 mmol), and then the reaction mixture was vigorously stirred at 80°C for 3 h under air flow. After the reaction, the catalyst was separated by an external magnet (4500 G). The reaction products were analyzed by gas chromatograph (Agilent 7890A) which was equipped with a flame ionisation detector and a Agilent J&W HP-5 (5% phenyl polysiloxane, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) capillary column. Biphenyl was used as an internal standard for quantitative GC analysis. After each cycle of catalytic reaction, the catalyst was reclaimed magnetically, washed with toluene for several times and dried at 60°C overnight for reutilization. To confirm whether the oxidation of 1-phenylethanol occurred on the $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}@Au$ nanocatalyst surface, the reaction mixture was magnetic separated by using a magnet after 1 h (conversion 31.7%, selectivity 99%). Further treatment of the solid-free solution did not give any products. It means that oxidation took place only on the surface of the $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}@Au$ nanocatalyst.

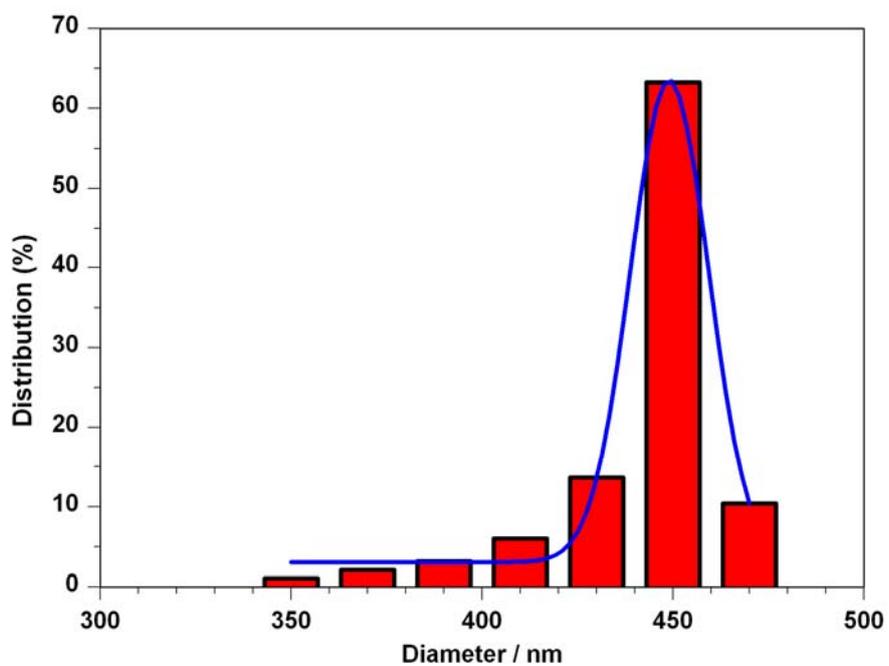


Fig. S1 Particle size distribution of Fe₃O₄.

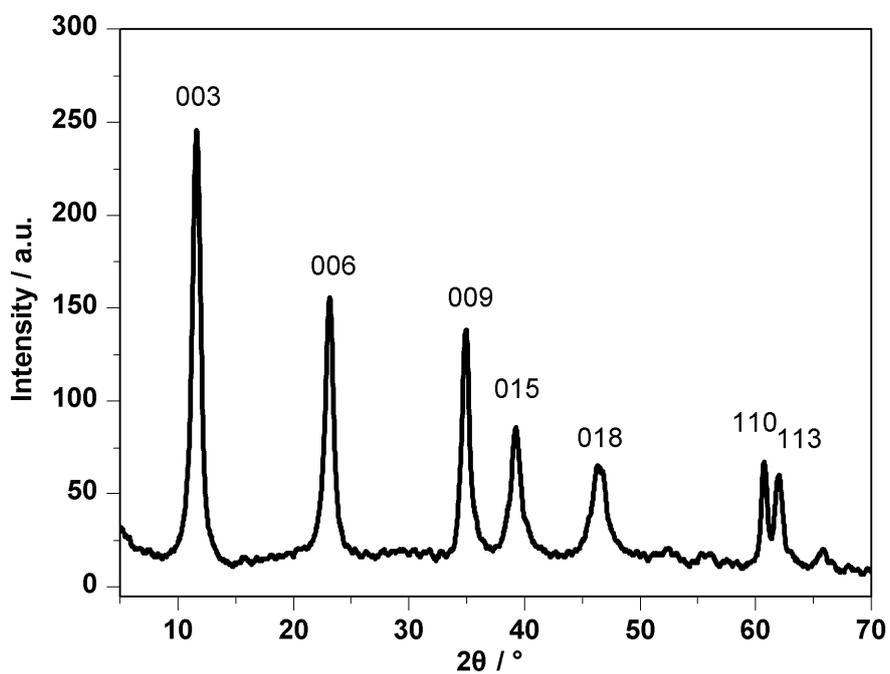


Fig. S2 XRD pattern of carbonate intercalated MgAl-LDH.

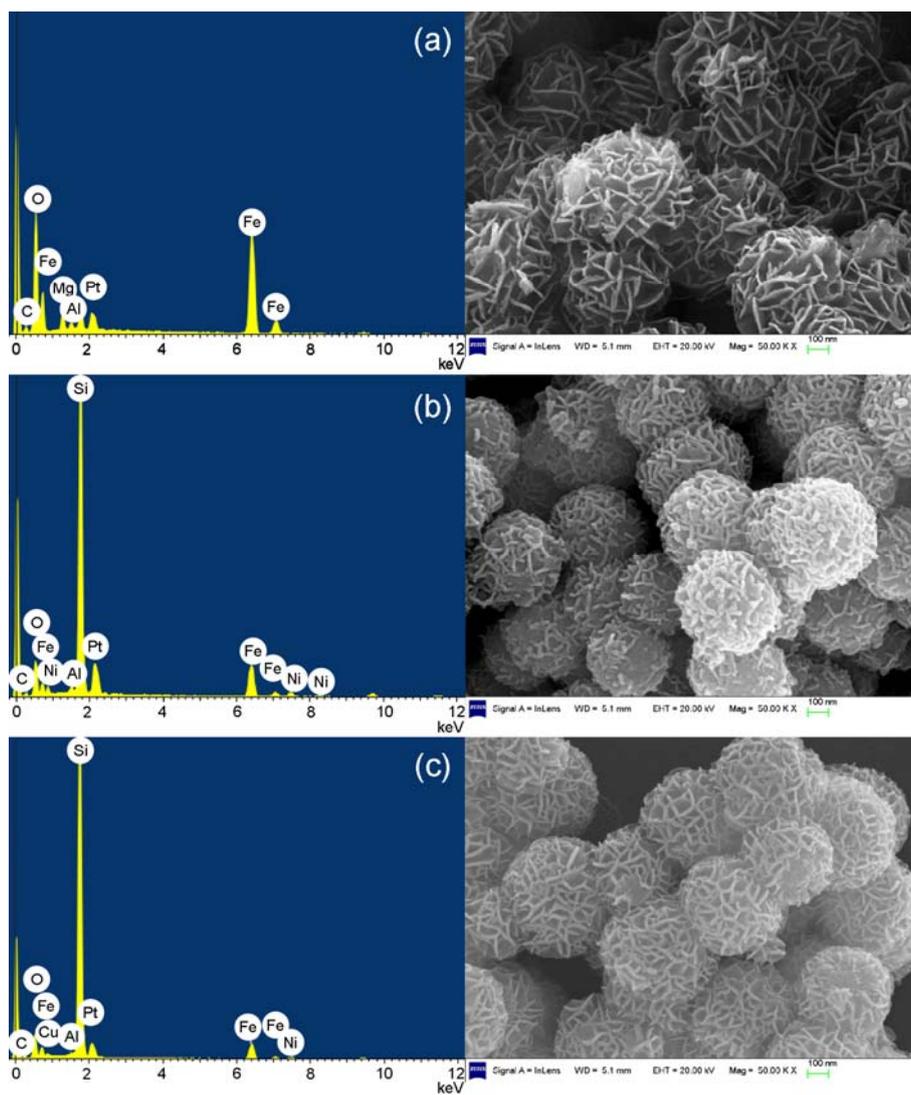


Fig. S3 SEM-EDX results of various core-shell nanospheres (a) $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}$,
(b) $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$, (c) $\text{Fe}_3\text{O}_4@\text{CuNiAl-LDH}$.

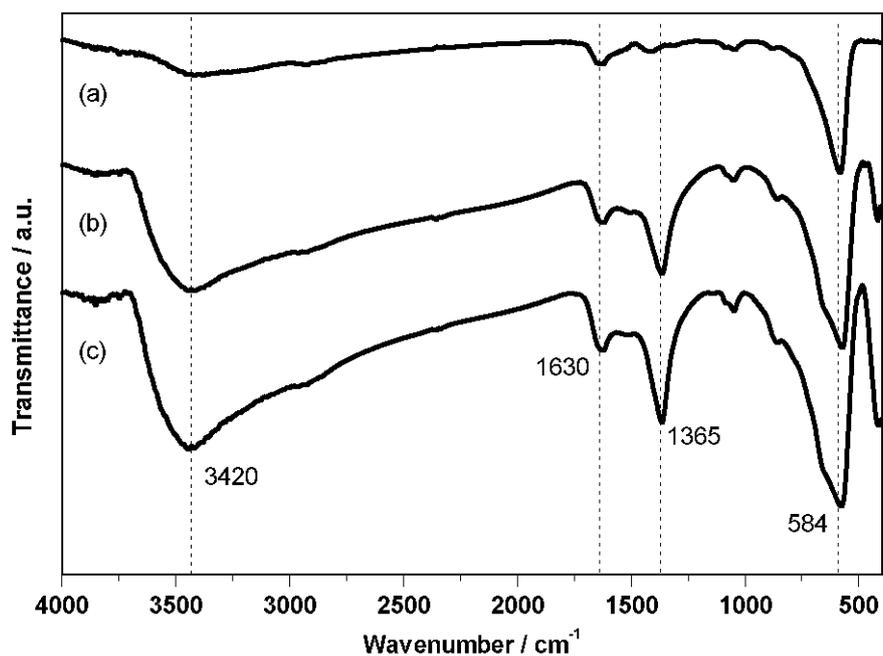


Fig. S4 FTIR spectra of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@MgAl-LDH$ (b) and $\text{Fe}_3\text{O}_4@MgAl-LDH@Au$ (c).

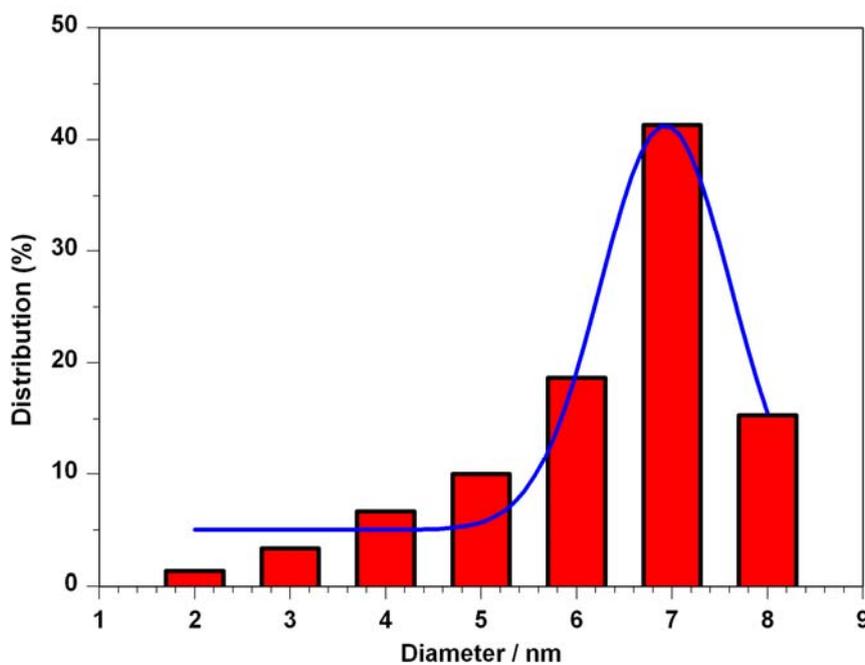


Fig. S5 Particle size distribution of Au nanoparticles of $\text{Fe}_3\text{O}_4@MgAl-LDH@Au$.

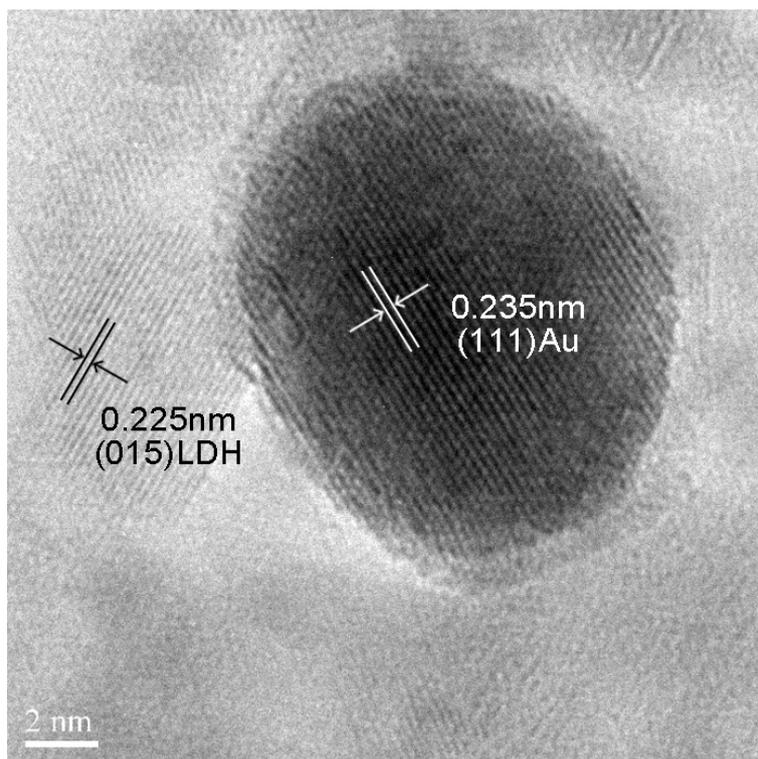


Fig. S6 Enlarged inset in Fig. 1f (HRTEM of $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}@\text{Au}$).

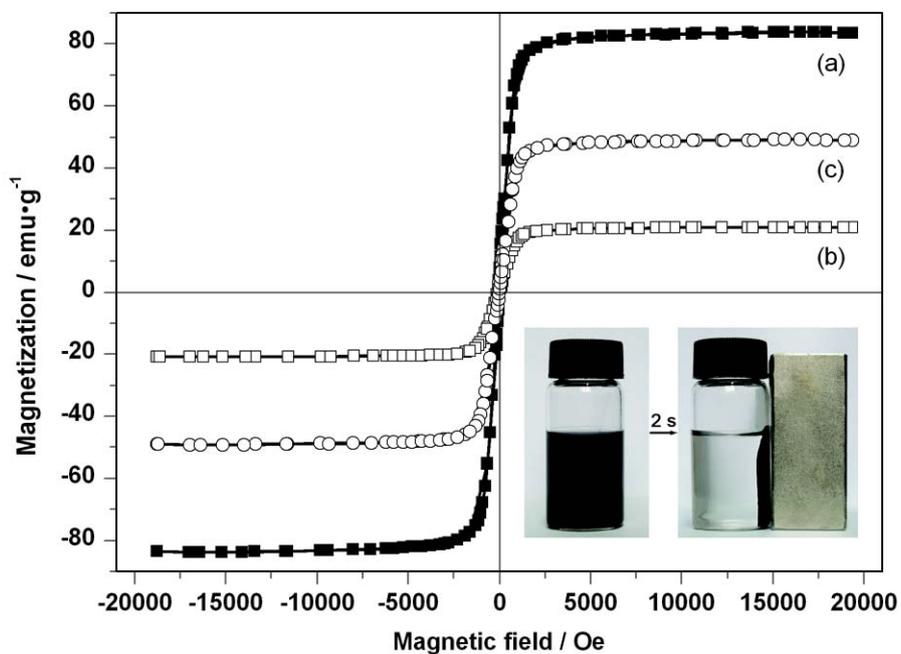


Fig. S7 Magnetization curves of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}$ (b) and $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}@\text{Au}$ (c) at room temperature. The photographs demonstrate the separation of the catalyst by a magnet.

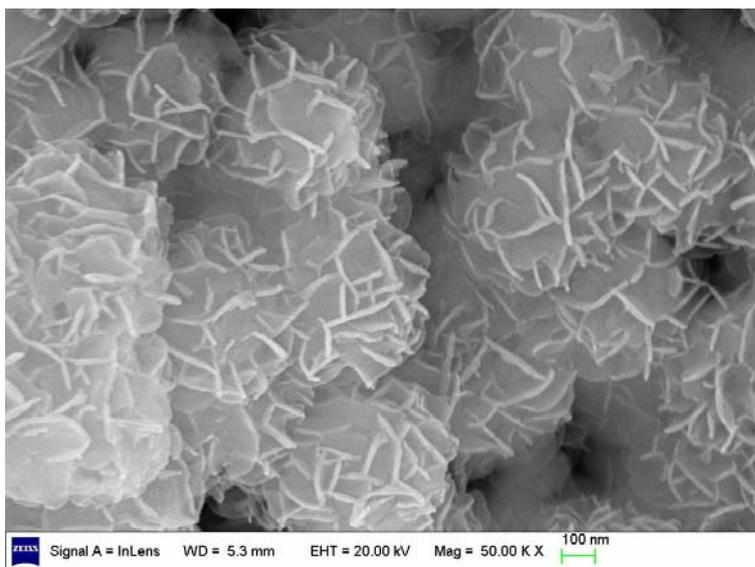


Fig. S8 SEM image of the reclaimed catalyst $\text{Fe}_3\text{O}_4@\text{MgAl-LDH}@\text{Au}$ after 5 cycles of the catalytic reaction

Eqn. S1 Scherrer equation

$D = 0.89\lambda / (\beta \cos\theta)$, where λ is the X-ray wavelength (0.1542 nm), θ the Bragg diffraction angle (deg.), and β the FWHM (rad.) of the XRD lines.

Reference

1. (a) H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen and Y. D. Li, *Angew. Chem., Int. Ed.*, 2005, **44**, 2782; (b) T. Fan, D. K. Pan and H. Zhang, *Ind. Eng. Chem. Res.*, 2011, **50**, 9009.