A Novel recyclable dual-heterostructured $Fe_3O_4@CeO_2$ /M(M=Pt, Pd and Pt-Pd) catalyst: Synergetic and redox effects for superior catalytic behavior

Supporting Information

Chemicals

Iron chloride hexahydrate (FeCl₃·6H₂O), ethylene glycol ($C_2H_6O_2$), sodium acetate anhydrous ($C_2H_3NaO_2$), cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O), palladium chloride (PdCl₂), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O), sodium borohydride (NaBH₄), PVA (MW=9000-10000), PEG (MW=380-420), ethanol absolute (C_2H_6O), hydrogen peroxide (H₂O₂, 30%), ammonia solution (25%NH₃·H₂O, 25%), nitric acid (HNO₃, 65%), sulfuric acid (H₂SO₄, 98%), methanol (CH₄O), potassium hydroxide (KOH, 99.99%), Nafion[®] perfluorinated resin solution, Pt/C (Pt 10%) catalysts were purchased from Shanghai Aladdin Chemical Reagent Company (Shanghai, China).



Fig.S1 XRD patterns of (a) CeO_2 , (b)Fe₃O₄@CeO₂, (c) Fe₃O₄@CeO₂/Pd, (d) Fe₃O₄@CeO₂/Pt, (e) Fe₃O₄@CeO₂/Pd-Pt and (f) Fe₃O₄ nanocrystals.



Fig.S2 Plots of $C_{\ell}C_0$ and $\ln(C_{\ell}C_0)$ versus reaction time for the reduction of 4-NP over various catalysts.



Fig.S3 The reduction of 4-NP to 4-AP over various catalysts: (a)Fe₃O₄, (b)Fe₃O₄@CeO₂, (c)Fe₃O₄@CeO₂/Ag, (d)Fe₃O₄@CeO₂/Au catalysts.



Fig.S4 (A) CVs of Fe₃O₄@CeO₂/Pt-30wt.%, Fe₃O₄@CeO₂/Pd-30wt.%, Fe₃O₄@CeO₂/Pt-Pd-30wt.% in N₂ saturated 0.5 M KOH and 1.0 M methanol (scan rate: 50 mV s⁻¹); (B) Chronoamperometric (CA) results of methanol oxidation of the Fe₃O₄@CeO₂/Pt-30wt.% catalysts in 0.5 M KOH and 1.0 M methanol at constant voltage of -0.12V for 1 h. CA curves of Fe₃O₄@CeO₂/Pt(30wt.%) and Fe₃O₄@CeO₂/Pt-9d (30wt.%) were recorded at -0.2 V.

Cyclic voltammetry (CV) was used to evaluate the comparative electrochemical properties of these heterostructure nanocatalysts in alkaline solution. The electrochemical activity was evaluated and normalized to the real surface area per mass Pt. Fig.S4(A) shows the CV curves of Fe₃O₄@CeO₂/Pt (30wt.%), Fe₃O₄@CeO₂/Pd (30 wt.%) and Fe₃O₄@CeO₂/Pt-Pd (30 wt.%) catalysts for methanol electro-oxidation in 0.5 M KOH and 1.0 M methanol at the scan rate of 50 mV s⁻¹. It reveals that the methanol current density of Fe₃O₄@CeO₂/Pt (30 wt.%) catalyst (17.4 mA cm⁻²) is higher than that of Fe₃O₄@CeO₂/Pd (30 wt.%) (0.40 mA cm⁻²) and Fe₃O₄@CeO₂/Pt (30 wt.%) is obviously higher than that of other catalysts. The higher methanol oxidation current density over Fe₃O₄@CeO₂/Pt (30wt.%) nanocrystals is further confirmed by the chronoamperometric (CA) measurements performed in 0.5 M KOH and 1.0 M methanol at -0.12 V for 1 hour. We can observe from Fig.S4(B) that the current intensity decay of the Fe₃O₄@CeO₂/Pt (30 wt.%) is much lower than those of the Fe₃O₄@CeO₂/Pd (30 wt.%) and Fe₃O₄@CeO₂/Pt (30 wt.%) and Fe₃O₄@CeO₂/Pt (30 wt.%) is much lower time range.



Fig.S5 HAADF-STEM images of the: (a) $Fe_3O_4@CeO_2/Pt$ (10 wt.%), (b) $Fe_3O_4@CeO_2/Pt$ (20 wt.%), (c) $Fe_3O_4@CeO_2/Pt$ (30 wt.%), and mapping results of the Pt elements: (d), (e) and (f) corresponding to (a), (b) and (c).



Fig.S6 Experimental and fixed XPS spectra of the Fe₃O₄@CeO₂/Pt (20-30wt.%) catalysts.

Table S1 Actual Pd and Pt contents loaded in various catalysts and their corresponding values of specific surface area(S_{BET}), saturation magnetization (*Ms*) and the reaction rate constant catalyzed reduction of 4-nitrophenol.

Samples	S_{BET} (m ² ·g ⁻¹)	<i>Ms</i> (emu∙g ⁻¹)	Actual content of noble metals (wt.%)	Reaction rate constant (min ⁻¹)
CeO ₂	171.7	_	_	0
Fe ₃ O ₄	35.3	74.7	_	0.02
Fe ₃ O ₄ @CeO ₂	121.7	31.3	_	0.03
Fe ₃ O ₄ @CeO ₂ /Pd	96.1	34.2	1.62 %	1.29
Fe ₃ O ₄ @CeO ₂ /Pt	81.6	40.5	1.36 %	1.07
Fe ₃ O ₄ @CeO ₂ /Pd-Pt	84.7	37.8	Pd-0.72 %, Pt-1.47 %	0.62