SUPPLEMENTARY INFORMATION

Redox Synthesis and high catalytic efficiency of transition-metal nanoparticle-graphene oxide nanocomposites

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1. The synthesis and characterizations of the nanocatalysts

Synthesis of GO: The synthesis of GO was followed the literature (ref. 34 in the main text). 1 g graphite powder was sonicated and stirred in an ice bath in 46 mL H₂SO₄ with 1 g of NaNO₃ for 30 minutes. 6 g KMnO₄ was then added slowly with continuous sonication. After 30 minutes, the flask was removed and the mixture was allowed to stir slowly overnight at 30°C. Then, 50 mL H₂O was added slowly under the nitrogen sparging followed by 1 hour of stirring. Finally, 300 mL 3% H₂O₂ was added into the flask yielding a yellowish-brown GO suspension. The GO suspension was washed several times thoroughly with diluted HCl (3%) and deionized water *via* centrifugation, until the pH was neutral. After centrifugation it was then sonicated and thereafter dried *in vacuo* at 60 °C overnight to obtain a GO powder.



Figure S1. TEM image of the as-synthesized graphene oxide by modified Hummers' method.



Figure S2. Scheme of the operation procedure for the synthesis of the nanocatalyst RhNPs/GO.



Figure S3. Reduction of RhCl₃ by GO in water at 0 °C (water/ice) in air monitored by UV-vis. spectroscopy. The absorptions at 379 and 480 nm correspond to the *d-d* transitions of Rh³⁺. After reduction to Rh(0)NP/GO, these two absorption bands disappeared.



Figure S4. Reduction of RhCl₃ by GO in water at 45 °C monitored by UV-vis. spectroscopy. The absorption at 379 and 480 nm correspond to the *d*-*d* transitions of Rh³⁺. After 1 min string, these two absorption bands disappeared, suggesting fast reduction of Rh³⁺ by GO at 45 °C.



Figure S5. The colors of the as-synthesized RhNPs/GO nanocatalysts at different temperatures.



Figure S6. TEM and size distribution of the RhNPs/GO-0°C (3.6±0.4 nm).



Figure S7. TEM and size distribution of the RhNPs/GO-20°C (2.6±0.3 nm).



Figure S8 Size distribution of the RhNPs/GO-45°C (1.8±0.3 nm).



Figure S9. TEM-dark field image of the RhNPs/GO-45°C at different magnifications.



Figure S10. XPS spectrum of Rh 3*d* over the nanocatalyst RhNPs/GO-45 °C.



Figure S11. Raman spectra of the nanocatalyst RhNPs/GO-45°C showing no significant change compared to pure GO.





Figure S12. Size distribution of the nanocatalyst RhNPs/GO-70°C (4.5±0.4 nm).



Figure S13. TEM images and size distribution of the RhNPs/GO-90°C (5.2±0.5 nm).

2. <u>Reduction of 4-NP by NaBH₄ (at 20 °C)</u>



Scheme S1. Catalytic reduction of 4-NP by NaBH₄.

The standard reaction mechanism of catalytic reduction of 4-NP by NaBH₄ is shown below:





Figure S14. UV-vis. spectra of the 4-NP reduction by NaBH₄ catalyzed by 10 ppm of RhNPs/GO-0 °C (top); consumption rate of 4-NP -ln(C_t/C_0) vs. reaction time (bottom, R² = 0.9872).



Figure S15. UV-vis. spectra of the 4-NP reduction by NaBH₄ catalyzed by 1 ppm of RhNPs/GO-0 °C (top); consumption rate of 4-NP $-\ln(C_t/C_0)$ vs. reaction time (bottom, R² = 0.9913).



Figure S16. UV-vis. spectra of the 4-NP reduction by NaBH₄ catalyzed by 10 ppm of RhNPs/GO-20 °C (top); consumption rate of 4-NP $-\ln(C_t/C_0)$ vs. reaction time (bottom, R² = 0.9827).



Figure S17. UV-vis. spectra of the 4-NP reduction by NaBH₄ catalyzed by 10 ppm of RhNPs/GO-45 °C (top); consumption rate of 4-NP $-\ln(C_t/C_0)$ vs. reaction time (bottom, R² = 0.9931).



Figure S18. UV-vis. spectra of the 4-NP reduction by NaBH₄ catalyzed by 1 ppm of RhNPs/GO-45 °C (top); consumption rate of 4-NP $-\ln(C_t/C_0)$ vs. reaction time (bottom, R² = 0.9941).



Figure S19. UV-vis. spectra of the 4-NP reduction by NaBH₄ catalyzed by 10 ppm of RhNPs/GO-70 °C (top); consumption rate of 4-NP $-\ln(C_t/C_0)$ vs. reaction time (bottom, R² = 0.9923).



Figure S20. UV-vis. spectra of the 4-NP reduction by NaBH₄ catalyzed by 10 ppm of RhNPs/GO-90 °C (top); consumption rate of 4-NP $-\ln(C_t/C_0)$ vs. reaction time (bottom, R² = 0.9968).

Catalysts	MNPs size	Catalyst (mg)	Catalyst	NaBH ₄	k _{app}	Ref
	(nm)	/Metal loading	(mol%)	(equiv.)	$(\times 10^{-3} s^{-1})$	
		(wt%)				
		/concentration				
RhNPs/GO-45 °C	1.8±0.3	2.5×10 ⁻⁶ mg	1×10-6	81	4.29	This
						work
Au/G	14.6	2.26 wt%		71	3.17	1
Au/TWEEN/GO	6-15		62	23	4.23	2
GO-NIPAAm-Au	10	37.1 wt%		100	4.6	3
GO@NH ₂ -Au	14.0±1		4.5	80	35.6	4
Au-silane-GO	10	0.02 mg		40	2.7	5
Au/PDIL-GS	4.7	0.03 mg		100	6.72	6
G/PDA–Au	16	5.6 wt%		1320	3.75	7
Au/SRG	17			80	8.3	8
Py-W/GO/AuNPs	4-11	1.69wt%		28.6	1.76	9
AuAg/PRGO	6	0.03 mg		107.1	3.0	10
Ag:Au=0.82						
Au-Ag-GO	Au=50	1 mg		53.3		11
Au:Ag=1:2, wt%	Ag=5					
Au-Pd/GO	3-7	30 mg		214.6	27.1	12
Au:Ag= 1:1, mol%						
Ag@Pd/G	2.4 nm	0.1 mg		50	8.67	13
Au–Ag/GO	20	AuAg=14.3wt%		114.3	50	14
Au–Ag/GO	5		0.47 mol%	114.3	142.7	15
G-Au@Pt	20	0.825 mg		100	9.44	16
Au@Fe ₃ O ₄ –G	5	0.05 mg		250	16.15	17
GOAFe ₃ O ₄ /Au	3-7	0.02mg/22.05wt%		66.7	32.2	18
Au/Fe ₂ O ₃ GO	8		5mol%	50	4.2 (35℃)	19
Fe ₃ O ₄ -G-Au	50	10 mg/1%		352.9	8.3	20
Ag/rGO(PM)	5-20	$3-4 \times 10^9 \text{ ml}^{-1}$		300	26.5	21
GO-Ag(SDBS)	14±6	$1-2 \times 10^{10} \text{ ml}^{-1}$		600	1.7±0.1	22
RGO/Ag/CeO ₂	10	14.6wt%		150	4.5	23
Pt ₁ /Ni ₂₅ -G	15.4	4μg		150		24
rGO/Pt-Ni (25:75)	4.2	3mg/37.85wt%	Pt: Ni=1.22	300	1.12	25
PdNCs/SnO ₂ -GNS	3.4		0.28mol%	300	20.3	26
Fe ₃ O ₄ /graphene/PtPd	3	0.1mg		324.3	36.8	27
Pd–CoFe ₂ O ₄ -G	2-10	0.04mg		110.8	11	28
Pd@rGO	3-14	0.05mg		200	25	29

Table S1. Selected examples of 4-NP reduction catalyzed by MNPs/graphene basednanocatalysts.^a

Pd-rGO-CNT	4	5mg/1.12 wt%.	100	20	30
Pd-CNT-GH	2-3	2.98 wt %.	100	7.17	31
Pd/rGO	2.8-3.9	2.4 wt%	333	4.5	32

^{*a*} The Table is arranged by catalyst type.

3. Dehydrogenation of H₃N-BH₃ by RhNPs/GO nanocatalyst



Figure S21. Time plots of the catalytic dehydrogenation of AB by the nanocatalyst RhNPs/GO-45°C with various catalyst loading.



Figure S22. Time plots of the catalytic dehydrogenation of AB by the nanocatalyst RhNPs/GO-45°C with various amount of AB.



Figure S23. Time plots of the catalytic dehydrogenation of AB by RhNPs/GO-45°C nanocatalysts at various temperatures.

The activation energy (E_a) was calculated through the Arrhenius equation (Eq.(S1)).

$$\ln k = \ln A - \frac{E_a}{RT} \tag{S1}$$

Where: k is the reaction rate, A is the pre-exponential factor, R is gas constant and T is temperature.

The apparent activation energy of hydrolysis of AB was determined to be approximately 21.4 kJ/mol.



Figure S24. ¹H NMR spectrum of NH₃BH₃. ¹H NMR (400 MHz, DMSO) δ_{ppm} : 0.85-1.51 (q, 3H), 4.41 (s, 3H).

Synthesis of NH₃BD₃³³

In a dried Schlenk tube, sodium borodeuteride (NaBD₄, 0.02 mol) and ammonium carbonate ((NH₄)₂CO₃, 0.02 mol) were mixed, dry THF (150 mL) was then added and the mixture was allowed to stir at 40 °C under an argon flow until the hydrogen evolution ceased. The solvent was then removed by rotary evaporation. The crude product was then dissolved in dry diethyl ether and filtered to remove any insoluble materials (repeated 3 times). The solvent was then removed, and the product was then dried at room temperature to obtain the small needle-like white solids (yield: 70%). The purity of the product was assessed by means of ¹H NMR spectroscopy.

Caution: Hydrogen is generated during the synthesis of NH_3 -BD₃, which is a potential fire hazard. Thus it is recommended that the reaction should be carried out in a well-ventilated hood with an argon flow, and that the reaction vessel outlet be led directly into the hood exhaust.



Figure S25. ¹H NMR (400 MHz, DMSO) spectrum of NH₃BD₃. δ_{ppm} : 4.38 (s, 3H).



Figure S26. ¹H NMR (400 MHz, DMSO) spectrum of ND₃BH₃. δ_{ppm} : 0.92-1.37 (q, 3H).

Catalyst amount	Maximum H ₂ /AB	Completion time	TOF
	ratio	(min)	$(mol_{H2} / mol_{catalyst} \cdot$
			min
0.15 mol%	3	7.75 min	258.1
0.10 mol%	3	9.5 min	315.8
0.05 mol%	3	24 min	250.0
0.02 mol%	3	112 min	133.9

Table S2. Performances of the catalyst RhNPs/GO-45°C for the hydrolysis of AB with various catalytic amounts.

Catalyst	Metal/AB	Maximum H ₂ /AB	TOF	Activation energy	Ref
	ratio	ratio	$(mol_{H2} \cdot molcat^{-1} \cdot$	E_a	
	(mol %)	(mol/mol)	min ⁻¹)	(KJ/mol)	
Rh/CeO2	0.08	3.0	2010	42.6	33
Rh/CNTs	0.25	3.0	706	32 ± 1	34
Pd-Rh@PVP NPs	0.3	3.0	1333.0	46.1 ± 2	35
Pt@MiL-101	0.29	3.0	414	40.7	36
RhNPs/GO-45 °C	0.1	3.0	315.8	21.4	This work
Pt25@TiO2	0.16	3.0	311		37
Ru-Pd@PVP		3.0	308.0	54.5 ± 2	38
Ru-Pt@PVP	0.3	3.0	308.0	56.3 ± 2	39
Rh@TiO ₂	0.116	3.0	260	65.5±2.	40
Pd/SiO ₂ -CoFe ₂ O ₄	0.19	3.0	254	52	41
Ru@Ni/C	0.4	3.0	250	37.9	42
Pt/x-Al ₂ O ₃	1.8	3.0	222		41
Ag/SiO ₂ -CoFe ₂ O ₄	0.28	3.0	204	32 ± 1	43
Pt/CeO ₂	1.8	3.0	182		44
Pt@SiO ₂	0.24	3.0	158.6	53.9	45
Rh@PAB	0.05	3.0	130		46
Rh/γ-Al ₂ O ₃	1.8	3.0	128.2	21	47
Pd-Pt@PVP	0.3	3.0	125.0	51.7	48
Zeolite-Rh(0)	0.2	3.0	92.0	66.9 ± 1.3	49
Pt ₇₀ Ru ₃₀	0.1	3.0	59.6	38.9	50
40 wt % Pt/C	1.8	3.0	55.56	21-23	51
Co ₃₅ Pd ₆₅ /C	2.4	3.0	22.7	27.5	52
PtO ₂	1.8	3.0	20.83		53
Pt black	1.8	3.0	13.89		53
Au@Co	2	3.0	13.7		54
NXC/AuCo	2	3.0	42.1	50.15	55
PSSA-co-MA-Pd	5	3.0	5	44	56
Ag/CeO ₂ -SBA-15	0.0074	3.0	0.4		57
Ag-SBA-15	9.3	3.0	0.2		58

Table S3. Recent literature studies of H_2 generation from aqueous AB catalyzed by noble metal nanoparticle based catalysts.

4. <u>Characterizations and click, Sonogashira Reactions</u>



Figure S27. TEM and size distribution of the nanocatalyst AuNPs/GO (3.3 ± 0.5 nm).



Figure S28. 4NP reduction catalyzed by AuNPs/GO nnaocatalyst: Consumption rate of 4-NP: $-\ln(C_l/C_0)$ vs. reaction time.

<u>Click reaction between benzyl azide and phenylacetylene by CuNPs/GO</u> <u>nanocatalyst</u>

Procedure for the azide-alkyne cycloaddition reactions

A glass vessel equipped with a magnetic stir bar was charged with 0.1 mmol of benzyl azide and 0.105 mmol of phenylacetylene under Ar. The catalyst was added into the vessel under Ar, and water was added in order to obtain a given volume of aqueous solution (1 mL). The reaction mixture was then stirred for 24 h at 35 °C under Ar. After the reaction, 5 mL water was added and the final product was extracted from

water with CH_2Cl_2 (3 \times 5 mL). The organic layer was dried over Na_2SO_4 and filtered,

and the solvent was removed *in vacuo* to give the **1-benzyl-4-phenyl-1H-[1,2,3]triazole**. Crude product was checked by 1H NMR to calculate the conversion. In parallel, the reaction was checked using TLC. The product was then purified by silica chromatography.

Characterizations of CuNPs/GO sample





Figure S29. TEM images and Size distribution of the CuNPs/GO (3.0 ± 0.4 nm).



Figure S30. X-ray photoelectron spectroscopy of Cu 2p.

In sample Cu/GO both species are almost in the same proportion (51.9% in Cu^{2+} and 48.1% in Cu^{0}).

Bond	Binding energy (eV)	Cu/GO
C-C	284.6	73.2 %
C-0	286.3	19.1 %
C=O	288.3	7.7 %

The percentage composition of interest elements is resumed in the table:

	Cu/GO
Cu	2.1 %
С	45.1 %
0	52.8 %



Figure S31. The C 1s XP spectra (left) and O 1s XP spectra (right) of Cu/GO sample.



Figure S32. ¹H NMR spectrum of **1-benzyl-4-phenyl-1H-[1,2,3]triazole**. ¹H NMR (300 MHz, CDCl₃) δ_{ppm}: 7.84-7.79 (m, 2H), 7.67 (s, 1H), 7.41-7.67 (m, 7H), 5.59 (s, 2H).

Procedure for the Sonogashira Reaction

A dry Schlenk flask equipped with a magnetic stir bar was charged with alkyne (0.6 mmol), iodobenzene (0.5 mmol), and triethylamine (1.5 mmol) under Ar. Catalyst (0.05 mol%) was then added under Ar, and water was then added in order to obtain a given volume of aqueous solution (2 mL). The mixture was allowed to stir for 24 h at room temperature. After the reaction, 3 mL water was added and the aqueous phase was extracted three times with 5 mL Et₂O. The organic phase was dried over Na₂SO₄, and the solvent was removed in vacuo. In parallel, the reaction was checked using TLC with petroleum ether as the eluent and ¹H NMR spectroscopy. Purification by flash chromatography was conducted with silica gel as the stationary phase and petroleum ether as the mobile phase. No yield difference when water/EtOH mixture (1:1, 2 mL) solvent was used.



Figure S33. TEM images and size distribution of the PdNPs/GO (2.8±0.5 nm).



Figure S34. TEM images and size distribution of the PdCuNPs/GO (3.5 ± 0.4 nm).

XPS of the PdCu/GO nanocatalyst



Figure S35. X-ray photoelectron spectroscopy of Cu 2p.



Figure S36. X-ray photoelectron spectroscopy of Pd 2p.

The percentage composition of elements of interest is summarized in the following table:

	CuPd/GO
Cu	2.7 %
С	38.8 %
0	56.5 %
Pd	2 %

Explanations of Pd XPS:

The CuPd NPs surface showed both the surface Cu(0) and the Cu²⁺ oxidation states of Cu (Figure S36), however the Pd XPS peak at 335.9 eV seemed to be associated with the peak $3d_{5/2}$ of palladium oxide or Pd²⁺. Previously it has been suggested that, for the PdCu nanoalloys, the binding energies of Pd $3d_{5/2}$ region shifted to higher binding energy with increasing Cu content, as compared with 335.1 eV for pure Pd. For instance the binding energies of Pd $3d_{5/2}$ region for Pd₇₅Cu₂₅, Pd₅₀Cu₅₀ and Pd₃₀Cu₇₀ are located at 335.4, 335.6 and 336.0 eV, respectively.^[S59] In our case, as suggested by XPS, the Pd: Cu molar ratio is 1:1.35, which is located at the range between Pd₅₀Cu₅₀ and Pd₃₀Cu₇₀ in that case. Thus the presence of the binding energy for Pd $3d_{5/2}$ at 335.9 eV is reasonably ascribed to the present Pd $3d_{5/2}$ binding energy to Pd(0).



Figure S37. The C 1s XP spectra (left) and O 1s XP spectra (right) of CuPd/GO sample.

Bond	Binding energy	CuPd/GO
	(eV)	
C-C	284.6	86.6 %
C-0	286.3	9.55 %
C=0	288.3	3.85 %



Figure S38. ¹H NMR spectrum of diphenylacetylene (CDCl₃ 400 MHz) δ_{ppm} : 7.34-7.40 (m, 6H), 7.54-7.57 (m, 4H).

5. <u>Reusability tests of thenanocatalyst RhNPs/GO-45°C for the hydrolysis of AB</u>



Figure S39. TEM and size distribution of the nanocatalyst RhNPs/GO-45°C after the reusability test.

6. References

S1 J. Li, C. Y. Liu, Y. Liu, J. Mater. Chem. 2012, 22, 8426-8430.

S2 W. Lu, R. Ning, X. Qin, Y. Zhang, G. Chang, S. Liu, Y. Luo, X. Sun, *J. Hazard. Mater.* **2011**, *197*, 320-326.

S3 A. Chen, J. Qi, Q. Zhao, Y. Li, G. Zhang, F. Zhang, X. Fan, *RSC Adv.* 2013, *3*, 8973-8977.

S4 Y. Ju, X. Li, J. Feng, Y. Ma, J. Hu, X. Chen, Appl. Surf. Sci. 2014, 316, 132-140.

S5 H. Yao, T. C. Huang, H. J. Sue, RSC Adv. 2014, 4, 61823-61830.

S6 S. Li, S. Guo, H. Yang, G. Gou, R. Ren, J. Li, Z. Dong, J. Jin, J. Ma, *J. Hazard. Mater.* **2014**, *270*, 11–17.

S7 J. Luo, N. Zhang, R. Liu, X. Liu, RSC Adv. 2014, 4, 64816–64824.

S8 W. Liu, D. Sun, J. Fu, R. Yuan, Z. Li, RSC Adv. 2014, 4, 11003–11011.

S9 J. Nanda, A. Biswas, B. Adhikari, A. Banerjee, *Angew. Chem. Int. Ed.* **2013**, *52*, 5041-5045.

S10 H. Chen, X. Fan, J. Ma, G. Zhang, F. Zhang, Y. Li, *Ind. Eng. Chem. Res.* 2014, 53, 17976–17980.

S11 B. Neppolian, C. Wang, M. Ashokkumar, Ultrason. Sonochem. 2014, 21, 1948-1953.

S12 M. Tang, T. Wu, H. Na, S. Zhang, X. Li, X. Pang, *Mater. Res. Bull.* 2015, 63, 248–252.

S13 C. H. Liu, X. Q. Chen, Y. F. Hu, T. K. Sham, Q. J. Sun, J. B. Chang, X. Gao, X.
H. Sun, S. D. Wang, ACS Appl. Mater. Interfaces 2013, 5, 5072–5079.

S14 T. Wu, J. Ma, X. Wang, Y. Liu, H. Xu, J. Gao, W. Wang, Y. Liu, J. Yan, *Nanotechnology* **2013**, *24*, 125301.

S15 T. Wu, L. Zhang, J. Gao, Y. Liu, C. Gao, J. Yan, J. Mater. Chem. A, 2013, 1, 7384-7390.

S16 J. Qi, W. Lv, G. Zhang, Y. Li, G. Zhang, F. Zhang, X. Fan, *Nanoscale* **2013**, *5*, 6275–6279.

S17 B. Lu, Z. Zhang, J. Hao, J. Tang, RSC Adv. 2014, 4, 21909–21917.

S18 J. Hu, Y. L. Dong, X. J. Chen, H. J. Zhang, J. M. Zheng, Q. Wang, X. G. Chen, *Chem. Eng. J.* **2014**, *236*, 1-8.

S19 H. Woo, J. W. Kim, M. Kim, S. Park, K. H. Park, RSC Adv. 2015, 5, 7554–7558.

S20 F. Chen, Y. Wang, Q. Chen, L. Han, Z. Chen, S. Fang, *Mater. Res. Express* 2014, 1, 045049.

S21 M. J. Fernández-Merino, S. Villar-Rodil, J. I. Paredes, P. Solís-Fernández, L. Guardia, R. García, A. Martínez-Alons, J. M. D. Tascón, *Carbon* **2013**, *63*, 30–44.

S22 M. Ayán-Varela, M. J. Fernández-Merino, J. I. Paredes, S. Villar-Rodil, C. Fernández-Sánchez, L. Guardia, A. Martínez-Alonso, J. M. D. Tascón, *J. Mater. Chem. A*, **2014**, *2*, 7295–7305.

S23 Z. Ji, X. Shen, J. Yang, G. Zhu, K. Chen, *Appl. Catal. B: Environ.* 2014, 144, 454–461.

S24 R. Liu, Q. Zhao, Y. Li, G. Zhang, F. Zhang, X. Fan, J. Nanomater. 2013, 2013, 1-7.

S25 P. K. Sahoo, B. Panigrahy, D. F. Bahadur, RSC Adv. 2014, 4, 48563-48571

S26 H. Li, S. Gan, D. Han, W. Ma, B. Cai, W. Zhang, Q. Zhang, L. Niu, J. Mater. Chem. A 2014, 2, 3461–3467.

S27 X. Li, X. Wang, S. Song, D. Liu, H. Zhang, Chem. Eur. J. 2012, 18, 7601-7607.

S28 X. Lu, L. Yang, X. Bian, D. Chao, C. Wang, Part. Part. Syst. Charact. 2014, 31, 245–251.

S29 B. K. Barman, K. K. Nanda, Appl. Catal. A: Gen. 2015, 491, 45-51.

S30 T. Sun, Z. Zhang, J. Xiao, C. Chen, F. Xiao, S. Wang, Y. Liu, *Sci. Rep.* 2013, *3*, 2527–2532.

S31 Z. Zhang, T. Sun, C. Chen, F. Xiao, Z. Gong, S. Wang, *ACS Appl. Mater*. *Interfaces* **2014**, *6*, 21035–21040.

S32 K. Bramhaiah, N. S. John, RSC Adv. 2013, 3, 7765–7773.

S33 S. Akbayraka, Y. Tonbula, S. Özkar, Appl. Catal. B: En. 2016, 198, 162–170.

S34 Q. Yao, Z. -H. Lu, Y. Jia, X. Chen, X. Liu, Int. J. Hydrogen Energy. 2015, 40, 2207-2215.

S35 M. Rakap, Appl. Catal. B: Environ. 2015, 163, 129-134.

S36 A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama, Q. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 13926–13929.

S37 M. A. Khalily, H. Eren, S. Akbayrak, H. H. Susapto, N. Biyikli, S. Özkar, M. O. Guler, *Angew. Chem. Int. Ed.* **2016**, *55*, 12257-12261.

S38 M. Rakap, Int. J. Green. Energy.

http://dx.doi.org/10.1080/15435075.2014.895737.

S39 M. Rakap, Appl. Catal. A: Gen. 2014, 478, 15-20.

S40 S. Akbayrak, S. Gençtürk, İ. Morkan, S. Özkar, RSC Adv. 2014, 4, 13742-13748.

S41 S. Akbayrak, M. Kaya, M. Volkan, S. Özkar, *Appl. Catal. B: Environ.* **2014**, *147*, 387-393.

S42 N. Cao, J. Su, X. Hong, W. Luo, G. Cheng, Chem. -Asian J. 2014, 9, 562-571.

S43 J. Chen, Z. –H. Lu, Y. Wang, X. Chen, L. Zhang, *Int. J. Hydrogen Energy*. 2015, 40, 4777 -4785.

S44 X. Wang, D. P. Liu, S. Y. Song, H. J. Zhang, *Chem. Commun.* **2012**, *48*, 10207-10209.

S45 Y. Hu, Y. Wang, Z. -H. Lu, X. Chen, L. Xiong, *Appl. Surf. Sci.* 2015, 341, 185-189.

S46 S. Karahan, M. Zahmakıran, S. Özkar, Chem. Commun. 2012, 48, 1180-1182.

S47 M. Chandra, Q. Xu, J. Power Sources 2007, 168, 135-142.

S48 M. Rakap, J. Power Sources. 2015, 276, 320-327.

S52 M. Zahmakıran, S. Özkar, Appl. Catal. B: Environ. 2009, 89, 104-110.

S50 Q. Zhou, C. Xu, Chem. Asian J. 2016, 11, 705-712.

S51 Q. Xu, M. Chandra, J. Alloys Compd. 2007, 446, 729-732.

S52 D. Sun, V. Mazumder, O. Metin, S. Sun, ACS Nano, 2011, 5, 6458-6464.

S53 Q. Xu, M. Chandra, J. Alloys Compd. 2007, 446, 729-732.

S54 J. Yan, X. Zhang, T. Akita, M. Haruta, Q. Xu, J. Am. Chem. Soc. 2010, 132,

5326-5327.

- S55 L. Guo, X. Gu, K. Kang, Y. Wu, J. Cheng, P. Liu, T. Wang, H. Su, J. Mater. Chem. A. 2015, 3, 22807-22815.
- S56 O. Metin, S. Sahin, S. Ozkar, Int. J. Hydrogen Energy 2009, 34, 6304-6313.
- S57 X. Qian, Y. Kuwahara, K. Mori, H. Yamashita, Chem. Eur. J. 2014, 20, 1-8.
- S58 K. Fuku, R. Hayashi, S. Takakura, T. Kamegawa, K. Mori, H. Yamashita, *Angew Chem. Int. Ed.* **2013**, *52*, 7446-7450.
- S59 C. Xu, Y. Liu, J. Wang, H. Geng, H. Qiu, J. Power Sources, 2012, 199, 124-131.