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One-step catalytic reduction of 4-nitrophenol through the direct injection of metal salts into oxygen-depleted reactants†

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The injection of aqueous metal salts into a solution containing 4-nitrophenol and borohydride results in the formation of catalytic metal nanoparticles capable of reducing 4-nitrophenol. This single-step procedure when carried out in the absence of dissolved oxygen leads to extraordinary catalytic activity with turnover frequencies as high as 65 000 h⁻¹.

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄ is widely recognized as a trusted model reaction for assessing the catalytic properties of nanostructures.¹ Nowhere has its significance been more consequential than in the demonstration of the exceptional catalytic activity of noble metal nanostructures, providing a precise and rapid evaluation of elemental,² alloyed,³ core-shell,⁴ and Janus⁵ nanostructures of various shapes and sizes⁶ that exist as colloids,⁷ dip catalysts,^{3c,8} or as structures affixed to suspended supports.⁹ The technological relevance of this reaction stems from its use in the preparation of analgesic and antipyretic drugs, corrosion inhibitors, and photographic developers.^{1,10} The catalytic reduction of 4-NP and related nitroaromatics also provides a potential means for addressing a growing concern over these compounds as anthropogenic water pollutants.^{1,10}

Recently, Deraedt *et al.*^{7a} demonstrated an efficient and long-lived Au nanoparticle catalyst formed using an exceedingly simple synthetic procedure where Au³⁺ ions derived from HAuCl₄ are reduced by NaBH₄, the same reducing agent used in the reduction of 4-NP. As part of this study, they also demonstrated the viability of a single-step procedure in which aqueous HAuCl₄ is injected directly into a solution containing 4-NP and NaBH₄, a procedure where it was assumed that Au nanoparticles first form and then act as cata-

lysts for 4-NP reduction. While this methodology gave rise to a competitive apparent reaction rate constant (k_{app}), the Au nanoparticles formed through this direct injection method underperformed those obtained using the conventional two-step approach where nanostructures are first prepared and then injected into the aqueous reactants. Similar conclusions were drawn by Pradhan *et al.*^{7b} for the case of Ag.

Previously, we showed that the dissolved oxygen (DO) content within the starting reactants is the decisive factor in determining the duration of the induction period,¹¹ *i.e.*, the time interval at the onset of the reaction where the 400 nm 4-NP absorbance (A) remains at a near-constant value. *In situ* monitoring of the DO content revealed that the catalytic reduction of 4-NP by metal nanoparticles is accompanied by a precipitous fall in the DO concentration, where the induction period ends when the concentration falls below a critical value that is dependent upon the catalyst used. Here, we demonstrate the catalytic reduction of 4-NP using Au, Pd, Cu, and Ag nanoparticles formed using the single-step direct injection method in both the presence and absence of DO. In all cases, DO is observed to have a detrimental effect upon catalysis that is distinct and separate from that which controls the induction period, demonstrating DO as a significant interferent in this reaction. It is also shown that nanoparticles formed in the presence of high concentrations of 4-NP are far more catalytic, where for the specific case of Ag it is to such an extent that it emerges as what is arguably the most active catalyst ever demonstrated for this reaction.

Aqueous solutions of metal salts of varying concentrations were prepared from HAuCl₄, Pd(NO₃)₂, Cu(NO₃)₂, and AgNO₃. The one-step direct injection method was then validated through the injection of these salts into a cuvette containing 4-NP and NaBH₄ where the concentrations of these reactants at the beginning of the reaction were 100 μM and 10 mM, respectively. Reactions were carried out using deionized water containing either 8.3 mg L⁻¹ of DO (*i.e.*, the ambient value) or values below our detection limit of 0.03 mg L⁻¹. The stringent Ar purging procedures used to obtain and maintain the

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DO concentration at low values are described in our previous study.¹¹ Spectroscopic monitoring revealed that the direct injection of metal salts resulted in the catalytic reduction of 4-NP, where the time evolution of both the 4-NP and 4-AP absorbance peaks (Fig. 1a) and the pseudo-first-order reaction kinetics exhibited in the $\ln(A/A_0)$ vs. time plot (Fig. 1b) show behaviors analogous to those obtained when using the conventional two-step approach.^{1b,9c,12} The spectra obtained at the end of the reaction utilizing 10 μM injections of Au, Cu, and Ag nanoparticles show the signature peak expected for plasmonic nanoparticles (Fig. 1c–e) both in the presence and absence of DO as well as the 4-AP absorbance peak at 300 nm (Fig. 1e). There was no observable plasmon peak for Pd. Transmission electron microscopy (TEM) performed on samples obtained from the reaction product confirm the formation of both nanoparticles and agglomerates (Fig. S3†). Together, these results strongly suggest that the catalysis stemming from the direct injection of metal ions is heterogeneous in nature, a result consistent with the vast majority of the 4-NP literature.¹³

Fig. 2 shows the results of a systematic investigation comparing the values of k_{app} obtained when salts of four different metals of varying concentrations are injected into aqueous reactants in both the presence and absence of DO. It is noted that the large differences in the k_{app} values obtained necessitate the use of a logarithmic scale. Striking is that deaerated reactants, in all cases, give rise to higher values of k_{app} than those obtained when DO is present, a clear indication that the catalytic reduction of 4-NP is compromised by DO. While DO has a relatively small influence on Au and Pd, its impact on Cu and Ag can diminish k_{app} by one and two orders of magnitude, respectively. For the specific case of Ag, the k_{app} values obtained when using deaerated reactants are extraordinary, showing a k_{app} value of $4.1 \times 10^{-2} \text{ s}^{-1}$ after the injection of only 1 μM of AgNO_3 . Such concentrations, representing 1 mol%, are low when compared to those typically used in the 4-NP literature.^{1a} Increasing the concentration to 50 μM leads to a further 30-fold increase in k_{app} , achieving a value of 1 s^{-1} . While Ag outperforms the three other metals, the k_{app}

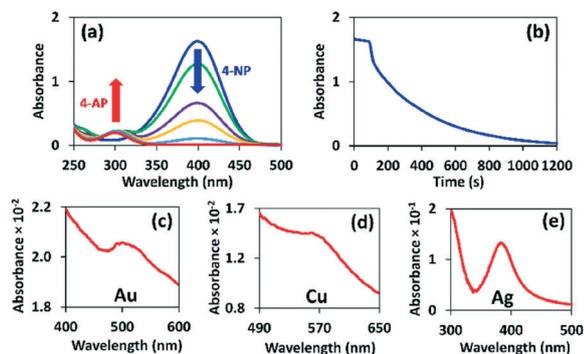


Fig. 1 (a) Absorbance spectra showing a diminishing 4-NP peak and a strengthening 4-AP peak resulting from the injection of 1 μM HAuCl_4 . (b) The time-dependent 400 nm absorbance for the same reaction. Spectra showing the plasmon peak for (c) Au, (d) Cu, and (e) Ag nanoparticles for reactions carried out in the absence of DO.

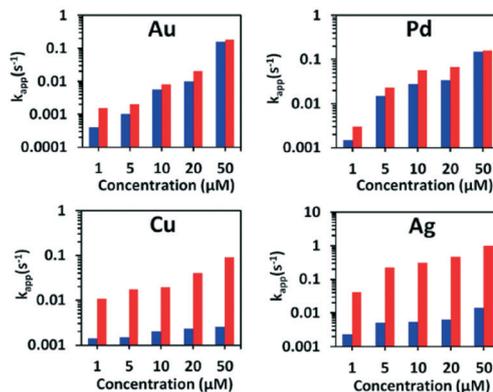


Fig. 2 Dependency of k_{app} on the concentration of metal salt injected into reactants in both the presence (blue) and absence (red) of DO.

values obtained for Au, Pd, and Cu rival and often exceed the values obtained when comparable amounts of catalyst and reactants are used. The induction times for these same reactions are shown in Fig. S4.† Consistent with our previous report¹¹ is the near-elimination of the induction period when the DO content is reduced to values below our detection limits. The small induction periods observed for the deaerated cases (typically $<5 \text{ s}$) may be attributable, not to DO, but to the time required for nanoparticle formation and the attachment of reactants.

The effectiveness of catalysts produced using this direct injection method was further demonstrated using reactions carried out in 500 mL of aqueous reactants with 4-NP and NaBH_4 concentrations of 1 mM and 100 mM, respectively. With only 1 mL of 500 μM salt injected into the reactants, the salt content is only 3 \times greater than that used in the cuvette-based studies, but where more than 1600 \times the number of 4-NP molecules are reduced. With a value of only 0.1 mol%, the reaction is carried out at levels where few 4-NP catalysts have proved viable. Reactions were carried out for each of the four metal salts using the apparatus shown in

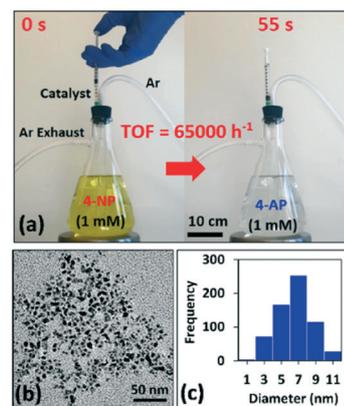


Fig. 3 (a) The catalytic reduction of a 0.5 L deaerated solution of 1 mM 4-NP through the direct injection of 1 mL of 500 μM AgNO_3 . (b) TEM image of the Ag nanoparticles and (c) the associated size distribution where irregularly shaped particles are included using their average diameter.

Fig. 3a. The 4-NP and NaBH_4 aqueous reactants were first purged with Ar for 30 min followed by the injection of the aqueous salt over a 10 s interval where the dispersal of the formed catalysts throughout the large volume is ensured by continuous stirring. Table 1 lists the TOF frequencies achieved for the four metal catalysts studied as well as for other impressive values reported in the literature.^{7a,14} While Au, Pd, and Cu catalysts produced by the direct injection method yield competitive TOF values in these high concentration reactions, Ag catalysts, once again, outperform the three other metals, reducing the 4-NP solution in 55 s (Video S1†) to achieve a turnover frequency (TOF) of 65 000 h^{-1} . We are unaware of any catalyst that has outperformed the Ag catalyst based on this TOF metric. The nanoparticles observed in the reaction product (Fig. 3b and c) have irregular shapes and show less of a tendency to agglomerate than those formed in the low concentration solution.

The direct injection method, despite an obvious lack of synthetic control, leads to the formation of some of the most active nanoparticle catalysts ever demonstrated for 4-NP reduction. The procedure is simple and nanoparticle formation is rapid. The Ag catalyst achieves exceedingly high TOFs at very low concentrations ($108 \mu\text{g L}^{-1}$). Notwithstanding, the procedure is less than satisfactory from the standpoint of obtaining a mechanistic understanding of the nanoparticle formation process and in determining its impact on catalytic properties. In an effort to determine if 4-NP alters the nanoparticle formation process in a manner that influences the resulting catalytic activity, a comparative study was carried out using nanoparticles synthesized in the presence and absence of 4-NP (Fig. 4a and b). For both cases, reactions were carried out using a $1 \mu\text{M}$ salt solution, 1 mM 4-NP, and 100 mM NaBH_4 . Carrying out spectroscopic measurements at such high 4-NP concentrations required the use of a 2 mm path length quartz cuvette (0.7 mL) in order to obtain detectable levels of light throughout the entire reaction. The results demonstrate that the presence of 4-NP in the nanoparticle formation process is crucial in obtaining highly catalytic nanoparticles, achieving 38-, 11.1-, 4.9-, and 1.6-fold enhance-

Table 1 Comparison of TOF values obtained through the direct injection method with those values reported in the literature that exceed 1000 h^{-1}

Catalyst	Amount (mol%)	Reaction time (s)	TOF (h^{-1})
Ag salt	0.1	55	65 000
Pd salt	0.1	505	7100
Cu salt	0.1	980	3600
Au salt	0.1	1130	3180
G0-27 TEG ^{14a}	0.2	80	22 500
AuNPs ^{7a}	0.2	200	9000
AuNPs ^{7a}	0.05	1320	5455
G0-27 TEG ^{14a}	0.02	300	4500
Supported Au (ref. 14b)	5.4	900	4370
Ag/TiO ₂ -0.75 (ref. 14c)	51	175	3078
Pd/CeO ₂ (ref. 14d)	0.56	—	1068
GO/SiO ₂ (ref. 14e)	1.6	—	1028
Supported Ag (ref. 14f)	25.6	10	1024

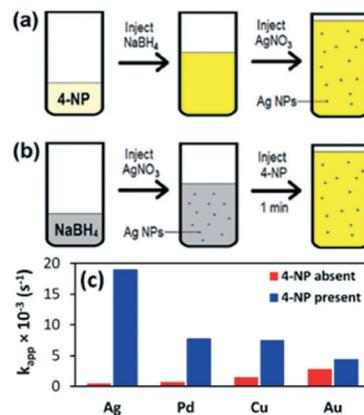


Fig. 4 Schematics showing the (a) single-step injection method in which Ag catalysts are formed in the presence of 4-NP and (b) an alternative method where catalysts are formed in the absence of 4-NP. For the latter case, nanoparticles are first formed in NaBH_4 followed by the addition of 4-NP after 1 min. (c) The k_{app} values derived from the two methods.

ments in k_{app} for Ag, Pd, Cu, and Au, respectively. A comparison of the Ag nanoparticles formed using these two procedures (Fig. S5†) reveals that nanoparticle formation is strongly influenced by 4-NP in that it results in more structures with reduced dimensions, but where the overall increase in surface area is unable to account for the 38-fold enhancement.

Three factors are likely drivers in establishing the high degree of catalytic activity observed using the direct injection method: (i) the generation of ligand-free catalytic surfaces, (ii) catalytically active sites unencumbered by DO, and (iii) a nanoparticle formation process influenced by 4-NP. It is well-known that nanoparticle surface ligands can be detrimental to catalysis.^{2a,15} The ability to form stabilized colloidal nanoparticles using NaBH_4 (ref. 7a and 11) (*i.e.*, a reactant in the catalytic reduction of 4-NP), therefore, removes the possibility of ligand interference in the catalytic processes. Less understood, however, is the detrimental role that DO can have on catalysis. This study, unequivocally demonstrates that large enhancements to k_{app} are obtainable when DO is eliminated. It is revealing that nanostructures formed from readily oxidizable nanostructures, *i.e.*, Ag and Cu, show far greater sensitivity to DO than Au and Pd. It suggests that DO acts as an interferent to 4-NP catalysis, likely competing for active sites on the surface of the nanoparticle. Complete poisoning of the catalyst is, however, unlikely since NaBH_4 , at the concentrations used in these catalysis measurements, is able to remove the oxide layer from both bulk Cu and Ag. If such behavior translates to nanoparticle surfaces then it is more likely that oxygen has a residency time on the nanoparticle surface, temporarily blocking sites that would otherwise be used for 4-NP reduction. It is noted that the influence of DO is distinct from that which is responsible for the induction time and that the greatest impact is felt, not for Au,¹¹ but for readily oxidizable metals. Nanoparticle formation in 4-NP, as opposed to just NaBH_4 , was also demonstrated as crucial in

obtaining highly catalytic nanoparticles. It is conceivable that 4-NP attachment to a growing nanoparticle is at sites conducive to catalysis and that its presence shields such sites from further growth. In such a process, 4-NP acts as a capping agent for active sites, allowing for the emergence of nanostructures with far greater catalytic activity. While we concede that this mechanism is speculative, it is noted that 4-nitriothiophenolate, a related compound that exhibits greater adhesion to metal nanoparticles, has been utilized as a capping agent in the synthesis of intricate Au nanostructures.¹⁶

From a broader perspective the current study brings to light some potential pitfalls in the use of 4-NP reduction as a model reaction for assessing the catalytic activity of metal nanoparticles. Carrying out reactions in the presence of DO can, for example, lead to nanostructures being labelled as poor catalysts, when they are, in fact, highly catalytic. The preceding literature, while recognizing Ag as a catalyst of significance,¹⁰ has not considered Ag to be the leading candidate material for the catalytic reduction of 4-NP even though it is exceedingly catalytic when the confounding effects of DO are removed. The work also forwards the possibility that poor catalysts have been identified as highly catalytic. Such a possibility stems from the fact that exceptionally catalytic nanoparticles are able to quickly form within the reactants used for 4-NP reduction. It is, thus, plausible that the observed catalytic activity, especially from larger nanostructures, stems not from the nanostructure under investigation, but from leached material able to reform as much smaller catalytic nanoparticles. It is noted that Nigra *et al.*^{15d} have already suggested this possibility.

In summary, we have demonstrated that the direct injection of metal salts into a deaerated aqueous solution of 4-NP and NaBH₄ gives rise to the rapid formation of catalytic nanoparticles able to reduce 4-NP at exceedingly high rates. We have also demonstrated the benefit of forming catalysts in the presence of 4-NP and have identified DO as an interferent in the reduction process where its influence is most acute for nanoparticles having a high affinity for oxygen. By identifying these influences as well as presenting potential pitfalls in the use of this model catalytic reaction, the work should lead to more accurate benchmarking of catalytic materials and, when applied beyond this model reaction, could also lead to improved catalytic performance for other reactions carried out in an aqueous environment.

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Notes and references

- (a) P. Zhao, X. Feng, D. Huang, G. Yang and D. Astruc, *Coord. Chem. Rev.*, 2015, 287, 114; (b) P. Hervés, M. Pérez-Lorenzo, L. M. Liz-Marzán, J. Dzubielia, Y. Lu and M. Ballauff, *Chem. Soc. Rev.*, 2012, 41, 5577; (c) T. Aditya, A. Pal and T. Pal, *Chem. Commun.*, 2015, 51, 9140.
- (a) S. Gu, J. Kaiser, G. Marzun, A. Ott, Y. Lu, M. Ballauff, A. Zacccone, S. Barcikowski and P. Wagener, *Catal. Lett.*, 2015, 145, 1105; (b) N. C. Antonels and R. Meijboom, *Langmuir*, 2013, 29, 13433; (c) M. Nemanashi and R. Meijboom, *J. Colloid Interface Sci.*, 2013, 389, 260; (d) Y. Mei, Y. Lu, F. Polzer and M. Ballauff, *Chem. Mater.*, 2007, 19, 1062; (e) R. Fenger, E. Fertitta, H. Kirmse, A. F. Thünemann and K. Rademann, *Phys. Chem. Chem. Phys.*, 2012, 14, 9343; (f) J. Min, F. Wang, Y. Cai, S. Liang, Z. Zhang and X. Jiang, *Chem. Commun.*, 2015, 51, 761.
- (a) S. Thota, S. Chen and J. Zhao, *Chem. Commun.*, 2016, 52, 5593; (b) E. Menumerov, K. D. Gilroy, M. Hajfathalian, C. J. Murphy, E. R. McKenzie, R. A. Hughes and S. Neretina, *Catal. Sci. Technol.*, 2016, 6, 5737; (c) M. Hajfathalian, K. D. Gilroy, A. Yaghoobzade, A. Sundar, T. Tan, R. A. Hughes and S. Neretina, *J. Phys. Chem. C*, 2015, 119, 17308; (d) J. Zhang, G. Chen, D. Guay, M. Chaker and D. Ma, *Nanoscale*, 2014, 6, 2125; (e) R. He, Y.-C. Wang, X. Wang, Z. Wang, G. Liu, W. Zhou, L. Wen, Q. Li, X. Wang, X. Chen, J. Zeng and J. G. Hou, *Nat. Commun.*, 2014, 5, 4327.
- (a) S.-C. Hsu, Y.-C. Chuang, B. T. Sneed, D. A. Cullen and T.-W. Chiu, *Nano Lett.*, 2016, 16, 5514; (b) C.-F. Hsia, M. Madasu and M. H. Huang, *Chem. Mater.*, 2016, 28, 3073; (c) K. K. Haldar, S. Kundu and A. Patra, *ACS Appl. Mater. Interfaces*, 2014, 6, 21946; (d) H.-L. Jiang, T. Akita, T. Ishida, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2011, 133, 1304.
- (a) L. Jia, T. Zhou, J. Xu, X. Li, K. Dong, J. Huang and Z. Xu, *Nanoscale Res. Lett.*, 2016, 11, 72; (b) Y. Zhao, D. Yang, H. Hu, L. Chen, Y. Xu, L. Qi, P. Yang and Q. Zhang, *Surf. Sci.*, 2016, 648, 313; (c) S. Chen, S. V. Jenkins, J. Tao, Y. Zhu and J. Chen, *J. Phys. Chem. C*, 2013, 117, 8924.
- (a) J. Zeng, Q. Zhang, J. Chen and Y. A. Xia, *Nano Lett.*, 2010, 10, 30; (b) S. Gao, Z. Zhang, K. Liu and B. Dong, *Appl. Catal., B*, 2016, 188, 245; (c) H. Ye, Q. Wang, M. Catalano, N. Lu, J. Vermeylen, M. J. Kim, Y. Liu, Y. Sun and X. Xia, *Nano Lett.*, 2016, 16, 2812; (d) X. Li, G. Li, W. Zang, L. Wang and X. Zhang, *Catal. Sci. Technol.*, 2014, 4, 3290; (e) X. Sun and D. Qin, *J. Mater. Chem. C*, 2015, 3, 11833.
- (a) C. Deraedt, L. Salmon, S. Gatard, R. Ciganda, R. Hernandez, J. Ruiz and D. Astruc, *Chem. Commun.*, 2014, 50, 14194; (b) N. Pradhan, A. Pal and T. Pal, *Colloids Surf., A*, 2002, 196, 247–257.
- (a) G. Zheng, L. Polavarapu, L. M. Liz-Marzán, I. Pastoriza-Santos and J. Pérez-Juste, *Chem. Commun.*, 2015, 51, 4572; (b) E. Hariprasad and T. P. Radhakrishnan, *Chem. – Eur. J.*, 2010, 16, 14378.
- (a) J. Lee, J. C. Park and H. Song, *Adv. Mater.*, 2008, 20, 1523; (b) Y. Deng, Y. Cai, Z. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang and D. Zhao, *J. Am. Chem. Soc.*, 2010, 132, 8466; (c) S. Wunder, F. Polzer, Y. Lu, Y. Mei and M. Ballauff, *J. Phys. Chem. C*, 2010, 114, 8814; (d) M. Al-Naji, A. M. Balu, A. Roibu, M. Goepel, W.-D. Einicke, R. Luque and R. Gläser, *Catal. Sci. Technol.*, 2015, 5, 2085; (e) R. Ren, S. Li, J. Li, J.

- Ma, H. Liu and J. Ma, *Catal. Sci. Technol.*, 2015, 5, 2149; (f) M. Li, G. Chen and S. Bhuyain, *Nanoscale*, 2015, 7, 2641.
- 10 X.-Y. Dong, Z.-W. Gao, K.-F. Yang, W.-Q. Zhanga and L.-W. Xu, *Catal. Sci. Technol.*, 2015, 5, 2554.
- 11 E. Menumerov, R. A. Hughes and S. Neretina, *Nano Lett.*, 2017, 16, 7791.
- 12 S. Wunder, Y. Lu, M. Albrecht and M. Ballauff, *ACS Catal.*, 2011, 1, 908.
- 13 (a) S. Gu, S. Wunder, Y. Lu and M. Ballauff, *J. Phys. Chem. C*, 2014, 118, 18618; (b) M. A. Mahmoud, B. Garlyyev and M. A. El-Sayed, *J. Phys. Chem. C*, 2013, 117, 21886.
- 14 (a) C. Deraedt, L. Salmon and D. Astruc, *Adv. Synth. Catal.*, 2014, 356, 2525; (b) W. Guo, Q. Wang, Y. Luan, G. Wang, W. Dong and J. Yu, *Chem. – Asian J.*, 2015, 10, 701; (c) X. Wang, Z. Zhao, D. Ou, B. Tu, D. Cui, X. Wei and M. Cheng, *Appl. Surf. Sci.*, 2016, 385, 445; (d) B. Liu, S. Yun, Q. Wang, W. Hu, P. Jing, Y. Liu, W. Jia, Y. Liu, L. Liu and J. Zhang, *Chem. Commun.*, 2013, 49, 3757; (e) C. Zhu, L. Han, P. Hu and S. Dong, *Nanoscale*, 2012, 4, 1641; (f) W. Zhou, Y. Zhou, Y. Liang, X. Feng and H. Zhou, *RSC Adv.*, 2015, 5, 50505.
- 15 (a) R. Ciganda, N. Li, C. Deraedt, S. Gatard, P. Zhao, L. Salmon, R. Hernández, J. Ruiz and D. Astruc, *Chem. Commun.*, 2014, 50, 10126; (b) S. V. Jenkins, S. Chen and J. Chen, *Tetrahedron Lett.*, 2015, 56, 3368; (c) D. Li, C. Wang, D. Tripkovic, S. Sun, N. M. Markovic and V. R. Stamenkovic, *ACS Catal.*, 2012, 2, 1358; (d) M. M. Nigra, J.-M. Ha and A. Katz, *Catal. Sci. Technol.*, 2013, 3, 2976; (e) Y. Fu, Y. Lu, F. Polzer, M. C. Lux-Steiner and C. H. Fischer, *Adv. Synth. Catal.*, 2016, 358, 1440.
- 16 H.-E. Lee, K. D. Yang, S. M. Yoon, H.-Y. Ahn, Y. Y. Lee, H. Chang, D. H. Jeong, Y.-S. Lee, M. Y. Kim and K. T. Nam, *ACS Nano*, 2015, 9, 8384.