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Chlorination

A Visible-Light-Induced α-H Chlorination of Alkylarenes with Inorganic Chloride under NanoAg@AgCl

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Abstract: An efficient, photocatalytic chlorination of alkylarene α-H groups using NaCl/HCl as a chlorine source has been developed, which involves a radical mechanism under visible-light (including sunlight) conditions. A chlorine radical is proposed to be formed by an electron transfer from chloride ion to O_2 in air through the bandgap hole of the semiconductor AgCl. The chlorination protocol is characterized by its use of natural sunlight or other visible light, mild conditions, cheap source of chlorine, green solvent, and high selectivity. The yield of benzylchloride is 95% with a toluene conversion as high as 40%, which rivals traditional chlorination methods.

The direct chlorination of C–H functions is an important industrial reaction used widely in the synthesis of bulk and fine chemicals alike. The selective chlorination of the α–H on an alkylarene is one of most important and fundamental reactions in organic chemistry. Most current chlorination processes are performed by making use of either chlorine gas or expensive *N*-chlorosuccinimide (NCS). Although chlorine gas is cheaper, its production by the chloralkali process involves high energy consumption. NCS is a more selective chlorination reagent; however, it is prepared from chlorine gas, making it more expensive again. It is an important goal, therefore, to invent new chlorination reactions, especially using cheaper, sustainable, and non-toxic chlorination agents. Indeed, inorganic chloride aqueous solution would be an ideal and cheap reagent; however, it is difficult to use directly or to easily convert it to a reactive reagent for chlorination of organic compounds, unless in the presence of strong oxidation agents[1,2]. This paper reports a novel approach to chlorinate α-Hs on alkylarenes directly using inorganic aqueous chloride as a chlorination agent without the use of strong oxidation agents.

Recently, the use of visible-light-mediated photoredox catalysis to generate radical species has become popular.[3–12] Among the inorganic photocatalysts employed to date, semiconductors are common; however, these materials cannot effectively absorb visible light due to a rather large bandgap (> 3.2 eV). Nanoparticles of noble metals, such as Ag, Au, Pt, and Pd exhibit characteristic bands of optical attenuation at visible wavelengths due to localized surface plasmons (LSPs).[13–17] Ag@AgX (X is a halogen) and Ag@AgX/GO as novel plasmonic composite catalysts have been prepared[18] and exhibit good reactivity for degrading organic waste[19] and H_2 production from a mixture of CH_3OH and H_2O;[20] however, there has been no report of Ag@AgX as a visible-light catalyst to carry out chlorination with aqueous inorganic chloride as chlorinating agent. The mechanism of degrading organic compounds involves chloride free-radicals, formed from the AgCl semiconductor as the key oxidation species.[21]

We were interested to not only study the formation of chlorine radicals from chloride ions, but also the substitution characteristics.

Herein, we report that Ag@AgCl acts as an efficient photocatalyst for the selective chlorination of α-Hs on alkylarenes, converting them to the corresponding α-Cl compounds with aqueous NaCl/HCl as the chlorine source.

Ag@AgCl, nano-Ag was loaded onto the surface of AgCl and was firstly prepared by the reaction of AgCl in the presence of methyl orange dye using visible-light irradiation[21] to give an average content of elemental Ag in the Ag@AgCl of 3.2 mol%.[22] Although the photocatalyst exhibited enhanced photocatalytic activity for the degradation of organic contaminants, the catalyst activity was not high enough to efficiently achieve the photocatalytic chlorination of α-H at alkylarene to give the corresponding α-Cl compounds with aqueous NaCl/HCl as the chlorine source, either under sunlight or visible-light conditions in air. The method of preparation of Ag@AgCl was improved. A suspension/solution of AgCl and $AgNO_3$ was irradiated with a 300 W xenon lamp equipped with an ultraviolet cut-off filter to provide visible light with $\lambda \geq 400$ nm in the presence of 0.02 mol sodium formate solution to give considerably improved results; the resulting composite photocatalyst contained 8.7 mol% nano Ag. Energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction of the catalyst are shown in the Supporting Information. SEM analysis of the composite photocatalyst showed that the resulting Ag/AgCl had silver

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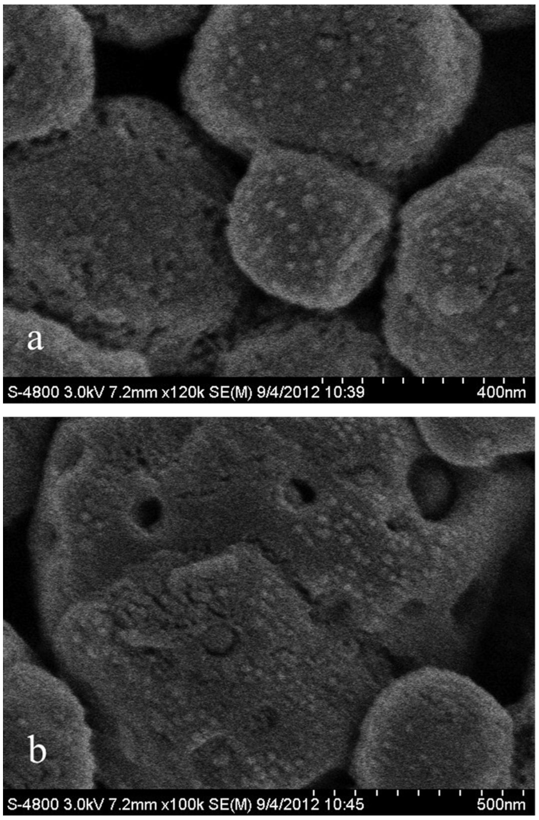
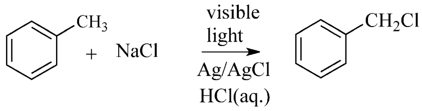


Figure 1. a) SEM of Ag/AgCl; b) SEM of Ag/AgCl after catalytic reaction.

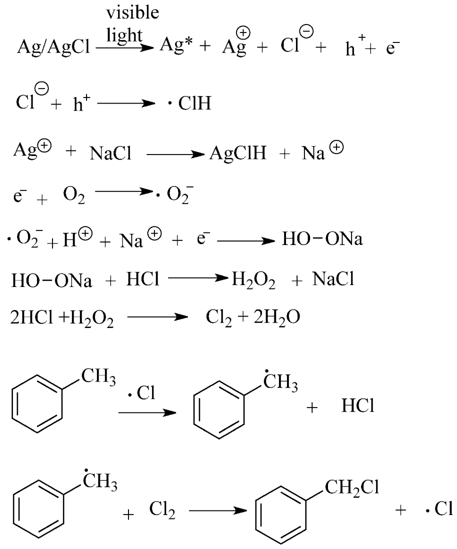
particles with a diameter of 20–50 nm deposited on the 200–500 nm diameter silver chloride surfaces (Figure 1 a).

Under visible-light irradiation, it is expected that the nano Ag/AgCl composite catalyst absorbs photons to produce excited-state valence electrons from the Ag atoms in the Ag@AgCl. Ag atoms with empty orbitals (holes) on the catalyst surface accept an electron from the Cl^- ion on the AgCl, resulting in the formation of Cl^0 atoms, which cause radical chlorination reactions. In a saturated solution of NaCl/HCl, Cl^- ions are transformed continuously into chlorine radicals and drive the chloride substitution reaction. According to this strategy, we realized the α-H chlorination of alkylarenes with NaCl/HCl solution as the chlorinating agent under the irradiation of sunlight or visible light. A mixture of toluene, NaCl/HCl solution, and tetrabutylammonium chloride (TBAC) was reacted in the presence of the Ag/AgCl catalyst under the irradiation of sunlight or visible light in air at room temperature. The reaction was monitored by GC and, after 5–9 h, the conversion was in the range of 19–41 % (see Scheme 1).

The role of the NaCl and HCl was examined first. Either NaCl or HCl act as a chloride source to generate the chlorinating agent for the reaction; however, the synergistic effect was quite clear. As shown in Figure 2 a, NaCl as chloride source reacts with toluene to give a 13 % conversion (**A** in Figure 2 a) using 0.25 g Ag@AgCl with 6.8 mol % of nano-Ag as catalyst over 7 h under the irradiation of visible light. However, aqueous HCl reacts with toluene to give 32 % conversion under the same conditions (**F** in Figure 2 a). In spite of the ionization of both chloride sources to chlorion in the H_2O solution, muriatic acid provides protons to keep the reaction solution pH constant. The effect was confirmed by using a mixture of NaCl and H_2SO_4 for the same reaction, which resulted in an increased reaction conversion as a function of the acid concentration, compared with either **B**, **C**, **E,** or **G**, **H** in Figure 2 a. When saturated NaCl in muriatic acid was used as chloride source for the chlorination of toluene, the conversion increased up to 40 % and exhibited a synergistic effect. The possible reason for this is shown in Scheme 2, that is, the acidic conditions are responsible for producing Cl_2 through the reaction of chlorion with hydrogen peroxide.



Scheme 1. Reaction of toluene with NaCl/HCl by photocatalysis.



Scheme 2. Proposed reaction mechanism.

It is clear that the reaction is a heterogeneous photocatalysis reaction, with the efficient interaction between the phases being a key factor. Hence, good phase-transfer catalysis is required for this purpose, and different catalysts were selected to realize this purpose. Either quaternary ammonium salts or acetic acid were added as phase-transfer catalysts (PTCs) to the reaction mixtures and, in each case, the product benzyl chloride was obtained, with the effects of each of the different PTC on the reaction shown in Figure 2 b. Clearly, TBAC exhibits highest activity with conversion as high as 26 % over 7 h using Ag@AgCl photocatalyst with 3.5 mol % loading of nano-Ag under the irradiation of a 300 W Xe arc lamp.

Catalyst-loading levels and dosing of the nano Ag@AgCl are also important for the conversion of toluene in NaCl/HCl solution to benzylchloride. Figure 2 c shows that the conversion increases with the amount of catalyst used under the irradiation conditions, 26 % conversion being obtained in the presence of

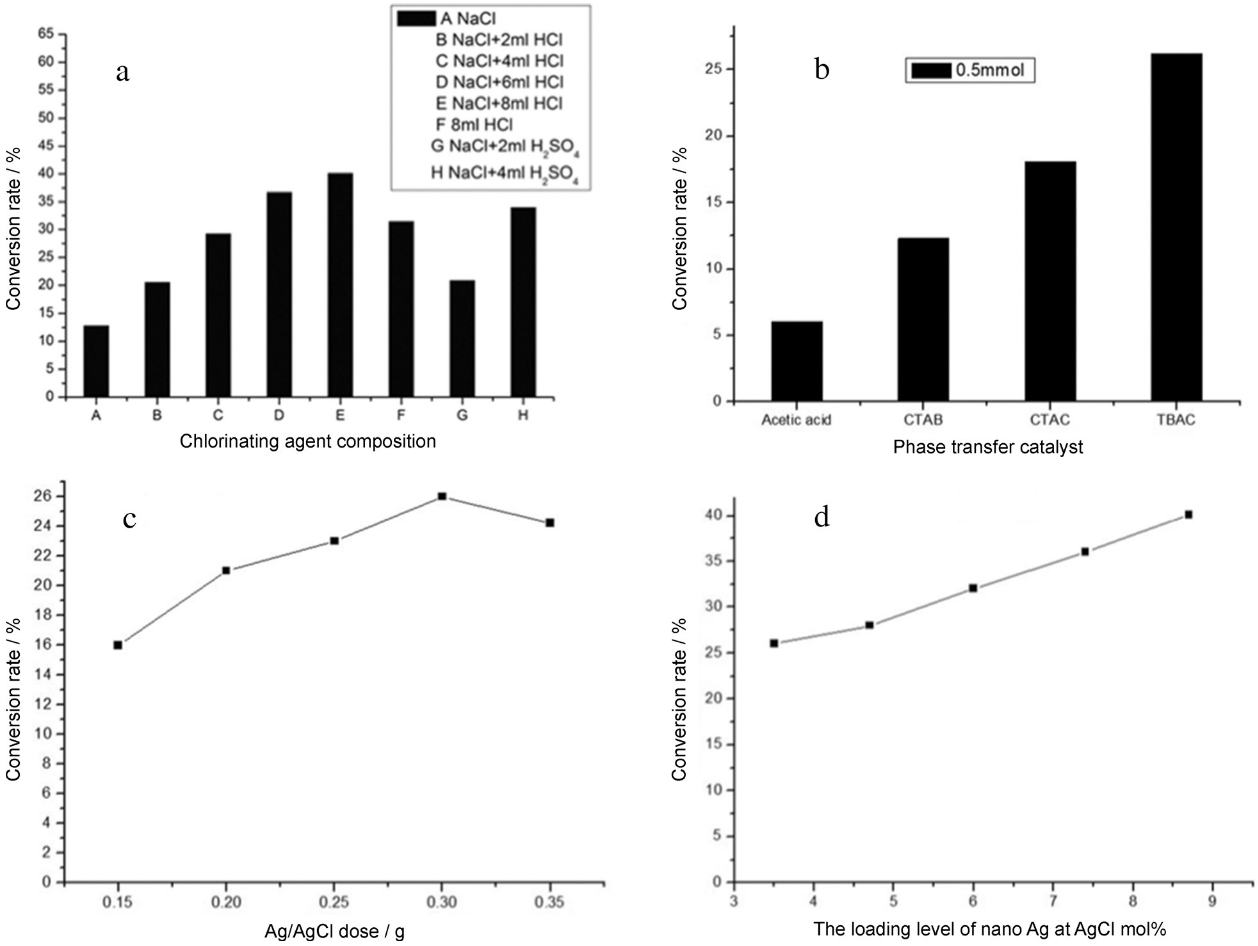


Figure 2. a) Effect of NaCl/HCl ratio on the conversion; b) effect of PTC on the conversion; c) effect of Ag@AgCl dose on the conversation of toluene; d) relationship of the loading level of nano Ag at AgCl with the conversion rates. CTAB = cetyl trimethylammonium bromide, CTAC = cetyl trimethylammonium chloride.

0.3 g of the Ag@AgCl photocatalyst with a 3.5 mol % of loaded nano-Ag. Furthermore, the relationship of the nano-Ag loading level to toluene conversion was examined. As shown in Figure 2 d, the conversion of toluene was just 26 % using 3.5 mol % of loaded nano-Ag. However, when the reaction was repeated using 6 mol % catalyst, this increased to 32 %. Indeed, the highest conversion (40 %, which is near to the traditional method[23]) was obtained using 9 mol % of the nano Ag@AgCl.

Under irradiation using natural sunlight (all other conditions the same), the chlorination of toluene with NaCl/HCl also took place and, importantly, in standard glassware. The photocatalytic chlorination conversion of toluene was as high as 23 % using 0.3 g Ag@AgCl and the 6 mol % nano-Ag as catalyst over 7 h. The average intensity of the sunlight was measured at only 40 mw cm^{-2}, compared with the average visible light intensity of the 300 W xenon lamp at 78.5 mw cm^{-2}. Hence, although the lower light intensity of the sunlight is clearly one of the reasons for the lower conversion, the fact that this reaction proceeded perfectly well under ambient sunlight and normal glassware highlights the potential for this process.

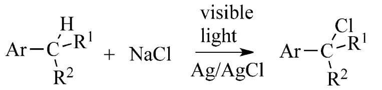
The mechanism of the photocatalytic chlorination reaction is most probably quite complex and, to date, there has been no report of this process. Although the chlorine radical is probably formed during the decomposition of organic contaminants using photocatalysis with Ag/AgCl under visible light, this radical only triggers oxidation reactions.[19] Chlorination needs enough chlorine radical and, in particular, dichlorine to achieve a successful chlorination reaction. In order for the radical to be formed continually, the photocatalytic reaction is carried out in a saturated sodium chloride solution of muriatic acid, resulting in the Ag@AgCl surface being fully saturated by chloride ion.

When visible light irradiates the nano Ag, a photon is absorbed, producing an excited state valence electron from an Ag atom on the Ag@AgCl catalyst. The Ag atom has an empty orbital (hole) on the catalyst surface and accepts an electron from Cl^- ion on the AgCl, resulting in the formation of a Cl^0 atom. The loss of a chloride ion from the catalyst is compensated immediately by chloride from the solution, resulting in the continual production of chlorine radicals under the reaction conditions. The radical production occurs over the whole surface of the catalyst, and is released into the reaction solution to react with toluene with the aid of the PTC. During the process of transfer off the surface, the chlorine radicals can react with each other to form dichlorine. The photogenerated electrons can also be trapped by dissolved O_2 in solution to form superoxide ions (O_2^-) and other oxygen species, such as hydrogen peroxide, which can oxidize Cl^- to Cl_2 to drive the chlorination under strongly acidic conditions. A possible mechanism for the overall process is outlined in Scheme 2.

Although there has been no direct evidence for electron transfer on the Ag@AgCl catalyst surface under visible light, the morphology of the catalyst before and after reaction reveals that the interface of the nano Ag and AgCl undergoes obvious changes. Figure 1 b shows that different circular cavitations appeared on the surface of AgCl after the photocatalytic reaction occurred five times. The formation of these cavitations was caused by the disappearance of AgCl at the interface of the nano Ag, which absorbs the photons leading to the oxidation of chloride ions to chlorine radicals. The photogenerated reducing electrons produced in situ transform silver ions to silver metal. The Ag^0/Ag^I ratio could be demonstrated by X-ray diffraction of the Ag@AgCl after the catalytic reaction was complete. The relative content of Ag^0 increased from 6 to 16 mol% (Supporting Information, Figure 5). It is clear that the AgCl in the catalyst participates in the reaction and the relative content of the Ag@AgCl changes; however, when the catalyst was used repeatedly (4 further times), its catalytic activity remained almost unchanged. The conversion of toluene was still higher than 38% when the Ag@AgCl catalyst was used for a fourth time.

After examining the chlorination reaction of the α-H of toluene with NaCl/HCl in the presence of Ag@AgCl and sunlight or visible light, we then examined the chlorination of other alkylarenes including substituted toluene, ethylbenzene, isopropylbenzene, and methylnaphthalene in order to confirm the scope and utility of the method. As shown in Table 1, the conversion of the different alkylarenes depends on the structure of the starting material. GC analysis of the reaction solution showed that the reaction was highly selective and multiple chlorination products were not detected. Although these conversions were not higher than for toluene, the level of 40% is close to being higher than that reported for the traditional chlorination technology, and this method has considerable advantages (see below). Also, the yield for this level of conversion reaches up to 95% (Table 1, entry 1) for toluene and a p-NO_2-toluene substrate appears to give similar results (Table 1, entry 5). However, the reaction of *iso*-propylbenzene resulted in the formation of 2-phenyl-2-propanol, resulting from hydrolysis of the corresponding chlorination product (Table 1, entry 3).

Table 1. The result of the photocatalytic chlorination of the alkylarene with NaCl/HCl.



Entry	Ar-	R^1	R^2	Conversion [%][a]	Yield [%][b]	Light source[c]
1	Ph	H	H	40	95	lamp
				23	94	sunlight
2	Ph	Me	H	38	92	lamp
				20	85	sunlight
3	Ph	Me	Me	31	42	lamp
				8	38	sunlight
4	*p*-Cl-Ph	H	H	27	87	lamp
5	*p*-NO_2-Ph	H	H	41	93	lamp
				20	90	sunlight
6	*p*-*t*Bu-Ph	H	H	29	88	lamp
				17	85	sunlight

[a] Gas chromatography data using 6 mol% nano Ag@AgCl. [b] Isolated yield. [c] 300 W xenon lamp equipped with an ultraviolet cut-off filter.

We have developed an efficient photocatalytic chlorination of the α-H of alkylarenes using NaCl/HCl as the chlorine source, which occurs through a radical mechanism under either sunlight or visible light conditions. The chlorine radical is formed by electron transfer from chloride ion to O_2 in air through the bandgap hole of the AgCl semiconductor. This chlorination protocol is characterized not only by the use of natural sunlight or visible light, but also by mild conditions, cheap and sustainable chlorine source, green solvent conditions, and high selectivity. The conversion of toluene is the highest of the substrates examined at 40%, which almost equals traditional chlorination methods but has the major advantage of being cheaper, cleaner, more sustainable, and more selective. In addition, the catalyst can be re-used four times with little impact upon reactivity, and the subsequent yield of benzyl chloride is 95%. This novel reaction process possibly provides new insight into understanding the formation of organochlorine-containing compounds in nature. Further work to this heterogeneous catalyst system, especially applied to the halogenation of different substrates, including alkanes and cycloalkanes, will be reported, and the turnover number (TON) of the photocatalyst will be further examined and improved by changing the preparation method and optimizing the components.

Experimental Section

In a typical case, $AgNO_3$ (0.51 g) and polyvinyl pyrrolidone (PVP, K30, 0.625 g) were dissolved in 1.4 M nitric acid solution (50 mL) with stirring at RT. Aqueous KCl solution (50 mL, 0.06 M) was added to the mixture. After 30 min, the mixture was heated at 80 °C for 3 h. The resulting precipitate was collected by centrifugation, dispersed in a solution of deionized water (50 mL) and $AgNO_3$ (0.10 g), and was irradiated with UV irradiation for 20 min in the presence of sodium formate (1 mL, 0.02 M). The resulting product was collected, washed thoroughly with deionized water, then absolute ethanol, and then dried at 70 °C in air for 12 h.

Chlorination procedure of alkylarene with NaCl/HCl under visible light

The phase-transfer catalyst (0.30 g) and the Ag/AgCl (containing 3.5–8.7 mol% nano Ag photocatalyst, 0.90 g) were added, with stirring, to a photocatalytic reaction vessel (PLS-SXE300CUV) charged with alkylarene (0.5 mol). Saturated sodium chloride solution (120 mL) containing conc. hydrochloric acid (6 mL) was added to the solution. The visible light produced by a 300 W xenon lamp equipped with an ultraviolet cut-off filter was used as light source to irradiate the reaction mixture for 5–9 h and the reaction was monitored by GC. The reaction solution was filtered (to reclaim the photocatalyst). The solution was separated and the inorganic phase was collected for future use. The organic phase was dried over anhydrous $MgSO_4$ and the chlorination product was obtained by evaporation.

Chlorination procedure of alkylarene with NaCl/HCl under sunlight

The phase-transfer catalyst (0.20 g) and Ag/AgCl (containing 3.5–8.7 mol% nano Ag photocatalyst, 0.60 g) were added, with stirring, to a three-neck flask charged with alkylarene (0.5 mol). Saturated sodium chloride (120 mL) and conc. hydrochloric acid (6 mL) were added to the solution. At ambient temperature, sunlight irradiation of the reaction mixture was carried out for 5–9 h. The reaction mixture was filtered, separated, and the organic phase was dried and evaporated to give the chloride product.

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Keywords: alkylarenes · NaCl/HCl · nano-Ag · chlorination · photocatalyst

[1] R. C. Larock, *Comprehensive Organic Transformations*, 2nd ed., Wiley-VCH, Weinheim, **1999**, pp. 611 – 617.
[2] F. Radner, *J. Org. Chem.* **1988**, *53*, 3548 – 3553.
[3] M. Neumann, S. Fuldner, B. Konig, K. Zeitler, *Angew. Chem. Int. Ed.* **2011**, *50*, 951 – 954; *Angew. Chem.* **2011**, *123*, 981 – 985.
[4] a) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102 – 113; b) C. Dai, J. M. R. Narayamam, C. R. J. Stephenson, *Nat. Chem.* **2011**, *3*, 140 – 145.
[5] a) S. Fukuzumi, K. Ohkubo, *Chem. Sci.* **2013**, *4*, 561 – 574; b) G. Bottari, G. de la Torre, D. M. Guldi, T. Torres, *Chem. Rev.* **2010**, *110*, 6768 – 6816.
[6] J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* **2012**, *4*, 854 – 859.
[7] D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 77 – 80.
[8] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2009**, *42*, 1890 – 1898.
[9] D. Ravelli, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* **2013**, *42*, 97 – 113.
[10] M. Zhang, Q. Wang, C. Chen, L. Zhang, W. Ma, J. Zhao, *Angew. Chem. Int. Ed.* **2009**, *48*, 6081 – 6084; *Angew. Chem.* **2009**, *121*, 6197 – 6200.
[11] C. Murata, H. Yoshida, J. Kumagai, T. Hattori, *J. Phys. Chem. B* **2003**, *107*, 4364 – 4373.
[12] P. Du, J. A. Moulijn, G. Mul, *J. Catal.* **2006**, *238*, 342 – 352.
[13] S. S. Tan, L. Zou, E. Hu, *Catal. Today* **2006**, *115*, 269 – 273.
[14] F. Zhang, R. L. Jin, J. X. Chen, C. Shao, W. L. Gao, L. Li, N. J. Guan, *J. Catal.* **2005**, *232*, 424 – 431.
[15] a) E. Prodan, C. Radloff, N. J. Halas, P. A. Nordlander, *Science* **2003**, *302*, 419 – 422; b) S. Gao, K. Ueno, H. Misawa, *Acc. Chem. Res.* **2011**, *44*, 251 – 260.
[16] C. Pacholski, A. Kornowski, H. Weller, *Angew. Chem. Int. Ed.* **2004**, *43*, 4774 – 4777; *Angew. Chem.* **2004**, *116*, 4878 – 4881.
[17] a) H. Chen, L. Shao, Q. Li, J. Wang, *Chem. Soc. Rev.* **2013**, *42*, 2679 – 2724;b) A. Tanaka, K. Hashimoto, B. Ohtani, H. Kominami, *Chem. Commun.* **2013**, *49*, 3419 – 3421; c) A. Kubacka, M. Fernández-García, A. Colón, *Chem. Rev.* **2012**, *112*, 1555 – 1614.
[18] a) P. Wang, B. Huang, X. Zhang, X. Qin, Y. Dai, Z. Wang, Z. Lou, *ChemCatChem* **2011**, *3*, 360 – 364; b) M. Zhu, P. Chen, M. Liu, *ACS Nano.* **2011**, *5*, 4529 – 4536; c) M. Zhu, P. Chen, M. Liu, *J. Mater. Chem.* **2011**, *21*, 16413; d) M. Zhu, P. Chen, M. Liu, *Langmuir* **2012**, *28*, 3385 – 3390; e) M. Zhu, P. Chen, M. Liu, *Langmuir* **2013**, *29*, 9259 – 9268.
[19] a) C. Hu, T. Peng, X. Hu, Y. Nie, X. Zhou, J. Qu, H. He, *J. Am. Chem. Soc.* **2010**, *132*, 857 – 862; b) Y. Qu, X. Duan, *Chem. Soc. Rev.* **2013**, *42*, 2568 – 2580; c) X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503 – 6570.
[20] a) Z. Lou, Z. Wang, B. Huang, Y. Dai, *ChemCatChem* **2014**, *6*, 2456 – 2476; b) X. Fu, J. Long, X. Wang, D. Y. C. Leung, Z. Ding, L. Wu, Z. Zhang, Z. Li, X. Fu, *Int. J. Hydrogen Energy* **2008**, *33*, 6484 – 6491.
[21] P. Wang, B. Huang, X. Qin, X. Zhang, Y. Dai, J. Wei, M.-H. Whangbo, *Angew. Chem. Int. Ed.* **2008**, *47*, 7931 – 7933; *Angew. Chem.* **2008**, *120*, 8049 – 8051.
[22] P. Wang, B. Huang, Z. Lou, X. Zhang, X. Qin, Y. Dai, Z. Zheng, X. Wang, *Chem. Eur. J.* **2010**, *16*, 538 – 544.
[23] N. Kakuta, N. Goto, H. Ohkita, T. Mizushima, *J. Phys. Chem. B* **1999**, *103*, 5917 – 5919.

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