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PII:	S0040-4039(15)30035-6		
DOI:	http://dx.doi.org/10.1016/j.tetlet.2015.08.081		
Reference:	TETL 46665		
To appear in:	Tetrahedron Letters		
Received Date:	23 June 2015		
Revised Date:	18 August 2015		
Accepted Date:	27 August 2015		



Please cite this article as: Padma Latha, P., Bhatt, M., Jain, S.L., Sustainable catalysis using magnetic chicken feathers decorated with Pd(0) for Suzuki-cross coupling reaction, *Tetrahedron Letters* (2015), doi: http://dx.doi.org/10.1016/j.tetlet.2015.08.081

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### **Graphical Abstract**

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Sustainable catalysis using magnetic chicken feathers decorated with Pd(0) for Suzuki-cross coupling reaction	Leave this area blank for abstract info.
P. Padma Latha, Mukesh Bhatt and Suman L. Jain <sup>*</sup>	0
Fe <sub>1</sub> O <sub>4</sub> @CF-Pd (0)	SG
K2CO3, H2O, 80 °C	<u></u>
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# Sustainable catalysis using magnetic chicken feathers decorated with Pd(0) for Suzuki-cross coupling reaction

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ABSTRACT

#### ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: Biodegradable catalyst Magnetic separable catalyst Chicken feather C-C coupling Palladium Magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) coated with chicken feather (CF) were synthesized and subsequently grafted with palladium nanoparticles (Pd NPs) using *in situ* preparation approach. The synthesized catalyst showed excellent activity for Suzuki cross coupling reaction between aryl halides and phenylboronic acid. After completion of the reaction, the catalyst could conveniently be separated via magnetic separation. More importantly, the presence of amino and carboxyl groups on the surface due to chicken feather, provided sufficient binding sites for Pd NPs, and therefore make the synthesized material highly stable. No leaching was observed during the reaction as ascertained by ICP-AES analysis. Furthermore, the catalytic activity of this supported catalyst did not show any significant loss after being used for at least six times.

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Chicken feathers (CF), a poultry waste, produced worldwide 8.5 billion tonnes annually from feather meal industry.<sup>1</sup> In general, these poultry waste are often disposed by methods like burning in incineration plants, buried in landfills, or recycled into low quality animal feeds, which are limited options of disposal. Furthermore, these methods of disposal generate green house gases which are detrimental to the environment. Therefore, the utilization of chicken feathers to develop new materials and products is highly desired not only to add value to this waste<sup>2-7</sup> but also to reduce the pollution caused by disposal in landfills. In this regard, main efforts have been made to develop biodegradable thermoplastics from chicken feathers through graft polymerization with methyl acrylates.<sup>8</sup> In addition Senoz et al.<sup>9</sup> synthesized pyrolyzed chicken

In addition Senoz et al.<sup>9</sup> synthesized pyrolyzed chicken feather fibres from a two-step process (215 °C/15 h + 400–450 °C/1 h) and demonstrated to be as adsorbents for strong H<sub>2</sub> adsorption at low pressures and 77 K. Brandelli et al.<sup>10</sup> produced keratinases from diverse microorganisms including Eucarya, Bacteria, and Archea domains, which have been used to be promising candidates to degrade keratin and possess potential applications in agro-industrial, pharmaceutical and biomedical fields. However, in the area of catalysis the use of chicken feathers as support matrix to develop heterogeneous catalysts is rarely been known. Zheng et al.<sup>11</sup> reported a feather-palladium complex for hydrogenation of anisole and benzaldehyde.

Recently, magnetic nanoparticles (MNPs) have been established to be robust, easily accessible and important catalyst support which offers an additional advantage of being magnetic recovery of the catalyst, thereby eliminating the requirement of catalyst filtration after completion of the reaction. However, the naked MNPs possess higher chemical activity and are easily oxidized in air, resulting in loss of magnetism. Therefore, the surface functionalization of magnetic nanoparticles to keep their stability is an important process. In this regard, various strategies including grafting of or coating with small organic molecules, surfactants, polymers, and biomolecules, or coating with an inorganic layer, such as silica, metal oxide etc. have been developed.<sup>12</sup>

<sup>15</sup> Owing to the growing environmental and economical considerations, utilization of readily available, inexpensive and biodegradable materials as a greener substitute of various metal and non-metal catalyst supports are gaining particular interest in recent decades.

Recently, palladium-catalyzed cross coupling reactions such as Suzuki-Miyaura, Heck coupling of aryl halides has been considered to be an effective method for the construction of C-C bonds in the modern chemical transformations. Although homogeneous palladium catalysts have been extensively investigated, their practical uses remained limited due to the non-recycling ability and tedious separation of catalyst from the products. Thus, the heterogenization of homogeneous palladium catalysts or grafting of palladium nanoparticles to solid organic or inorganic support matrix offers an attractive solution to overcome these limitations. In this regard, a number of catalysts supports for grafting of palladium nanoparticles for constructing C-C bond through cross coupling reactions have been investigated.<sup>16-25</sup>

In continuation to our on-going research herein, we report a simple, cost effective and efficient  $Fe_3O_4$ @/CF-Pd catalyst synthesized via grafting of Pd(0) nanoparticles to magnetically separable chicken feather for catalyzing Suzuki cross coupling reaction (Scheme 1). Importantly, magnetic core provides convenient separation of the catalyst from the reaction mixture in quantitative yield without any loss.

Tetrahedron



Scheme 1: Palladium catalyzed Suzuki cross coupling reaction

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#### Synthesis and characterization of the catalyst

The schematic representation of the catalyst synthesis is depicted in Scheme 2. The catalyst was prepared by sonicating magnetic nano-ferrite (Fe<sub>3</sub>O<sub>4</sub>) with powdered chicken feathers (CF) in water for 5 h, followed by the addition of palladium acetate which subsequently treated with NaBH<sub>4</sub> to get Pd(0) immobilized magnetic chicken feather Fe<sub>3</sub>O<sub>4</sub>@/CF-Pd(0) catalyst in excellent yield.



Scheme 2: Synthesis of Fe<sub>3</sub>O<sub>4</sub>@/CF-Pd(0) catalyst

The FT-IR spectra of CF, Fe<sub>3</sub>O<sub>4</sub>@CF and Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) were recorded to confirm the chemical modification during the immobilization process as shown in panels a, b and c of Figure 1, respectively. In FTIR spectrum of CF (Figure 1a) the absorption peaks at 1647, 1536 and 3423  $\text{cm}^{-1}$ are attributed to the characteristic absorption bands of the amide I and amide II and (-NH, -OH) stretching, respectively. The FTIR spectrum of Fe<sub>3</sub>O<sub>4</sub>@CF showed an additional peak at around 579 cm<sup>-1</sup>, corresponding to the Fe-O vibrations (Figure 1b). The peak shifting of bending vibration of amide I and amide II from 1647 and 1536 cm<sup>-1</sup> to 1640 and 1535 cm<sup>-1</sup> was most likely due to the interaction of amide groups of feather with metal nanoparticles (Figure 1b). Moreover, the band at around 1072 cm<sup>-1</sup>, corresponding to C-S bond of the chicken feather (Figure 1a), was found to be significantly reduced in Fe<sub>3</sub>O<sub>4</sub>@CF (Figure 1b) indicating the strong interaction between sulfur groups and metal NPs. Further shifting in the characteristic bands of CF and Fe-O bond was observed in  $Fe_3O_4@CF-Pd(0)$  (Figure 1c). Taking the above observations into consideration, it can be concluded that the  $Fe_3O_4@CF$  and  $Fe_3O_4@CF-Pd(0)$  nanoparticles were successfully obtained along with a strong interaction between sulfur and amino-group functionalities of the CF with Fe<sub>3</sub>O<sub>4</sub> and Pd NPs.



Figure 1: FTIR spectra of a) CF; b) Fe<sub>3</sub>O<sub>4</sub>@CF; c) Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0).

Afterwards, the crystalline structures of Fe<sub>3</sub>O<sub>4</sub>@CF and Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) were determined by XRD. As displayed in Figure 2a, chicken feather has amorphous structure, whereas in Figure 2b additional six characteristic diffraction peaks ( $2\theta$ = 30.2°, 35.6°, 43.3°, 53.8°, 57.3° and 63°) corresponding to the (220), (111), (400), (422), (551) and (440) reflections of inverse spinal Fe<sub>3</sub>O<sub>4</sub> were in well accordance with the previous literatures.<sup>26</sup> After anchoring the Pd NPs to Fe<sub>3</sub>O<sub>4</sub>@CF, four characteristic diffraction peaks ( $2\theta$  = 34°, 40°, 46° and 52°) corresponding to the (311), (111), (200) and (422) planes for face-centered cubic Pd (0)were observed (Figure 2c). Additional crystalline phase of Fe<sub>3</sub>O<sub>4</sub> and Pd (0) in amorphous chicken feather is another conformation. Here, the diffraction peaks of Pd NPs are very weak due to amount of Pd NPs is very low relative to the carriers.



Figure 2: XRD patterns of: a) CF; b) Fe<sub>3</sub>O<sub>4</sub>@CF and c) Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0).

Surface morphology and the presence of palladium in the synthesized catalyst were further confirmed by transmission electron microscopy (TEM) analysis. The TEM image of Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) revealed the core-shell structure with the homogeneous distribution of the CF coated MNPs (Figure S1a). Figure S1b showed diffraction pattern of Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) having fcc and bcc structures of Fe<sub>3</sub>O<sub>4</sub>, Pd NPs respectively. The size of the Pd NPs was found to be about 3–10 nm and were successfully grafted on the surface of Fe<sub>3</sub>O<sub>4</sub>@CF with uniform distribution.

Furthermore, the appearance of C, O, Fe and Pd in EDX analysis of synthesized catalyst clearly indicated the presence of these elements (Figure S1c and S2). Moreover, elemental mapping of C, Fe, Pd and the combined composition (Figure S3a-d) clearly indicated the homogeneous distribution of the palladium nanoparticles in the chicken feather coated magnetic core. The loading of palladium in the synthesized catalyst was found to be 0.27 mmol/g determined by inductively coupled plasma optical emission spectrometry (ICP-AES).

The surface textural properties of the synthesized materials i.e.  $Fe_3O_4@CF$ ,  $Fe_3O_4@CF$ -Pd(0) was determined by  $N_2$  adsorption/desorption as shown in Figure S4. The  $N_2$  adsorption/desorption isotherms of the core–shell magnetic  $Fe_3O_4@CF$  nanoparticles (Figure S4a) showed a smooth curve, and the BET surface area, BJH pore volume and pore size was found to be 59.71 m<sup>2</sup>/g, 0.16 cm<sup>3</sup> g<sup>-1</sup> and 3-10 nm, respectively. As expected the significant reduction in  $N_2$  adsorption was achieved after the immobilization of Pd NPs on the surface (Figure S4b). In addition, the measured BET surface area, BJH pore volume and pore size for  $Fe_3O_4@CF$ -Pd(0) was found to be 31.93 m<sup>2</sup> g<sup>-1</sup>, 0.1479 cm<sup>3</sup> g<sup>-1</sup> and 3–18 nm, respectively.

## Catalytic activity of $Fe_3O_4@CF-Pd(0)$ in the Suzuki–cross coupling reaction

The catalytic activity of the synthesized Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) catalyst was tested in Suzuki-Miyaura cross coupling reaction by considering bromobenzene and phenylboronic acid as model substrates. At first the reaction was performed in water by varying the amount of the catalyst, using  $K_2CO_3$  as a base at 80 °C under nitrogen atmosphere (Table 1, entry 1-4). As shown the yield of the product was found to be increased with increasing the catalyst amount, in the range of 0.1 to 1 mol %. The reaction afforded a yield of 92%, using 0.5 mol % of [Pd] within 5h. Further increase in catalyst amount showed no significant enhancement in the yield of the product (entry 4). Further, we checked the effect of various bases including K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, KOH, and Cs<sub>2</sub>CO<sub>3</sub> under described experimental conditions (Table 1, entry 2, 5-7). Among the various bases studied, K<sub>2</sub>CO<sub>3</sub> gave maximum yield of the desired product at 80 °C in 5 h. Furthermore, the reaction was found to be very slow at room temperature, 80 °C was found to be optimum and further increase in temperature beyond 80 °C did not improve the results to any significant extent (Table 1, entry 8-9). In the controlled blank experiments, the reaction did not occur neither in the absence of palladium nor by using the magnetically separable CF as catalyst under identical reaction conditions (Table 1, entry 10-11). Moreover, we investigated the effect of various solvents such as THF, CH<sub>3</sub>CN, and EtOH: H<sub>2</sub>O (4:1) and water. Among these solvents, the reaction did not occur in THF and acetonitrile solvent. However, the reaction was found to be slow in ethanol-water mixture and gave slightly lower product yield (88% isolated yield). The maximum activity of the catalyst in water is most likely due to the possibly strong hydrogen bonding between water molecules and amino acid chain. Owing to this bonding the amino acid chain may get stretched and provide more accessibility of active palladium sites to the substrate molecules.

Table 1:	Results of	the optimization	experiments. <sup>a</sup>
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Entry	Catalyst	Base	Temperature	Time	Yield
	(mol %)		(°C)	(h)	$(\%)^{D}$
1	0.1	$K_2CO_3$	80	5	58
2	0.2	$K_2CO_3$	80	5	75
3	0.5	$K_2CO_3$	80	5	92
4	1.0	$K_2CO_3$	80	5	93
5	0.5	Na <sub>2</sub> CO <sub>3</sub>	80	5	81
6	0.5	KOH	80	5	67
7	0.5	$Cs_2CO_3$	80	5	87
8	0.5	$K_2CO_3$	RT	24	20
9	0.5	K <sub>2</sub> CO <sub>3</sub>	50	24	26
10 <sup>c</sup>	0.5	K <sub>2</sub> CO <sub>3</sub>	80	24	-
11 <sup>d</sup>	0.5	K <sub>2</sub> CO <sub>3</sub>	80	24	-
12 <sup>e</sup>	0.5	K <sub>2</sub> CO <sub>3</sub>	80	5	80, 32 <sup>f</sup>
13	0.5	K <sub>2</sub> CO <sub>3</sub>	80	5	88 <sup>g</sup>

<sup>a</sup>Reaction conditions: bromobenzene (2 mmol), phenylboronic acid (3 mmol), base (4 mmol) under a nitrogen atmosphere; <sup>b</sup>Isolated product; <sup>c</sup>In the absence of catalyst; <sup>d</sup>using magnetic chicken feather as catalyst; <sup>c</sup>using Pd@Fe<sub>3</sub>O<sub>4</sub> as catalyst; <sup>f</sup>isolated yield after three cycles; <sup>g</sup>EtOH: H<sub>2</sub>O (4:1) as a solvent.

The recyclability, a key issue of heterogeneous catalysts from both the economical and environmental points of view, was also checked for the developed Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) catalyst using bromobenzene and phenyl boronic acid as model substrates. After completion of the reaction the catalyst was readily separated by external magnet as shown in Figure 3, and the recovered catalyst was reused as such for subsequent runs under optimized experimental conditions. The recycling ability of the recovered catalyst was checked for subsequent six runs (Figure 4). As shown in Figure 4 the catalyst maintained its activity and provided almost similar product yield in all cases. These results confirmed that the developed catalyst was quite stable and could be recycled for several runs without any significant loss in the catalytic activity. The ICP-AES analysis of the recovered catalyst revealed that the Pd content of the recovered catalyst after six cycles (Pd, 0.26 mmol/g) did not change significantly, which implied that the catalyst was highly stable.



Figure 3: Magnetic separation of the catalyst

Tetrahedron



In addition, we also tested the Pd NPs immobilized to magnetic core (Pd@Fe<sub>3</sub>O<sub>4</sub>) to establish the effect of CF coating onto the magnetic nanoparticles (Table 1, entry 12). As shown in results, the comparison among these two catalysts clearly indicated the positive effect of CF coating in the Suzuki cross coupling reaction in terms of both reactivity and recyclability, in particular to the recyclability issue. The improved catalytic performance of Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) is most likely due to the presence of amino and carboxyl group functionalities on the surface which efficiently stabilized the Pd NPs and played a crucial role towards preventing the leaching of Pd NPs or part of it from the support.

Furthermore, to ascertain the catalytic activity originated from the grafted Pd NPs not from leached Pd, a control experiment between bromobenzene and phenylboronic acid in the presence of  $Fe_3O_4$ @CF-Pd(0) was performed to proceed for 2 h under the optimized conditions providing the desired cross-coupling product in 32% yield. Subsequently, the catalyst was magnetically separated at 80 °C; the remaining reaction solution was stirred again for next 22 h. In this case the isolated yield of the biphenyl product was remained 32 % yield, which showed that almost no yield increase had occurred after removing the immobilized Pd NP catalyst. The result of the hot magnetic separation experiment confirmed that the developed catalyst was truly heterogeneous in nature.

Encouraged by the efficiency of the reaction protocol described above, the scope of the Suzuki–cross coupling reaction was studied with Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) (0.5 mol % of [Pd]) and K<sub>2</sub>CO<sub>3</sub> as base using water as a reaction medium under nitrogen atmosphere at 80 °C (Table 2). A series of bromobenzenes bearing various substituents were tested in reaction with phenylboronic acid. During the present study, it was observed that the bromobenzenes containing electron-withdrawing (NO<sub>2</sub>, CHO, CH<sub>3</sub>CO) and electron-donating (NH<sub>2</sub>, CH<sub>3</sub>O, CH<sub>3</sub>) groups in the para position were efficiently converted to the corresponding coupling products in 84–92 % yields. However, the unactivated chlorobenzene under the described reaction condition provided poor product yield (34 %) even in the prolonged reaction time (72 h).

**Table 2**: Investigation of the substrate scope in the presence of  $Fe_3O_4@CF-Pd(0)$  in the Suzuki–cross coupling reaction<sup>a</sup>



<sup>a</sup>Reaction conditions: substrate (2 mmol), phenylboronic acid (3 mmol) in the presence of  $K_2CO_3$  (2 eq), catalyst Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0) (0.5 mol% of [Pd] in H<sub>2</sub>O under a nitrogen atmosphere for 5 h; <sup>b</sup>Isolated yields.

We have demonstrated the first successful synthesis of magnetically separable chicken feather grafted with palladium nanoparticles for catalyzing Suzuki cross coupling reaction using water as reaction medium. The developed catalyst was found to be quite stable and could be readily recovered by external magnet. The catalyst showed consistent activity for six subsequent runs without showing any detectable leaching of metal particles. Facile recovery of the catalyst, use of biodegradable waste such as chicken feather as support matrix and water as environmentally benign reaction media make this method green and attractive for sustainable development of organic synthesis.

#### Acknowledgments

We are thankful to the Director, IIP for his permission to publish these results. MB is thankful to CSIR, New Delhi for providing technical HR under the XII five year projects.

#### **References and notes**

### Preparation of magnetic nanoparticles coated with chicken feathers ( $Fe_3O_4@CF$ )

Magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) were synthesized by coprecipitation method by following the literature procedure. In a typical synthesis, NaOH (4.8g, 0.12 mol) solution was slowly added to the round bottomed flask containing 40 ml mixed solution of ferric chloride (4.86 g, 0.03 mol), ferrous chloride (2.976g, 0.015 mol) were stirred at temperature 60 <sup>o</sup>C under nitrogen atmosphere. During this process, iron oxide nanoparticles were precipitated, which were separated by an external magnet and washed with methanol, acetone and deionized water. The collected nanoparticles were dried under vacuum. The dried nanoparticles were dispersed in deionized water containing 3g of feather powder and the mixture was sonicated for approximately 2h and then stirred for 5 h at room temperature. During this process magnetic NPs were coated with chicken feather (Fe<sub>3</sub>O<sub>4</sub>@CF), which were separated by centrifugation and then washed with methanol, acetone and deionized water to remove impurities and finally at 80 °C for 6h under vacuum.

### Preparation of palladium NPs decorated magnetic chicken feather (Fe<sub>3</sub>O<sub>4</sub>@CF-Pd(0))

Feather coated magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@CF) were dispersed in a solution of palladium acetate (0.2g, 0.89 mmol) for 1h under sonication. The sonicated mixture was stirred at

room temperature for additional 2 h, and then added with a solution of NaBH<sub>4</sub> (500 mg) in water (20 ml) followed by stirring the above suspension for 10 h at room temperature. During this, the colour of the mixture changed from brown to black, which indicated the reduction Pd (II) to Pd (0) and successful formation of Pd NPs. The loading of palladium in the synthesized catalyst was found to be 0.26 mmol/g determined by inductively coupled plasma optical emission spectrometry (ICP-AES).

#### **Typical experimental procedure**

In a typical experiment, bromobenzene (2 mmol), phenyl boronic acid (3 mmol), potassium carbonate ( $K_2CO_3$ , 4 mmol), and catalyst (0.5 mol % of [Pd]) were taken in 20 ml of water; the resulting mixture was stirred at 80 °C under nitrogen atmosphere. The progress of the reaction was monitored by TLC using hexane: ethyl acetate (10:1) as the eluent. After completion of the reaction, the reaction mixture was cooled to room temperature and catalyst was separated by external magnet. The obtained filtrate was concentrated under reduced pressure. The crude reaction mixture was further purified by column chromatography to obtain pure products. All the products were confirmed by comparing their physical and spectral data with those of authentic compounds.

- (<u>http://www.thepoultrysite.com/poultrynews/18275/new-solution-found-to-disposal-of-feather-waste</u>).
- 2 M. Zhan, R. P. Wool, and J. Q. Xiao, *Composites Part A*, 2011, 42(3), 229.
- 3 N. Fakhfakh-Zouari, N. Hmidet, A. Haddar, S. Kanoun, and M. Nasri, *Appl. Biochem. Biotechnol.*, **2010**, *162*(2), 329.
- 4 S. Agrahari and N. Wadhwa, Int. J. Poult. Sci., 2010, 9(5), 482.
- 5 S. Cheng, K. Lau, T. Liu, Y. Zhao, P. M. Lam and Y. Yin, Composites Part B, 2009, 40(7), 650.
- 6 P. M. Schrooyen, P. J. Dijkstra, R. C. Oberthur, A. Bantjes and J. Feijen, J. Agric. Food Chem., 2001, 49(1), 221.
- 7 C. Hu, N. Reddy, K. Yan and Y. Yang, J. Agric. Food Chem., 2011, 59, 10517.
- 8 E. Jin, N. Reddy, Z. Zhu and Y. Yang, J. Agric. Food Chem., 2011, 59(5), 1729.
- 9 E. Senoz and R. P. Wool, Int. J. Hydrogen Energy, 2011, 36(12), 7122.

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- 10 K. Janaranjani, G. Praveenkumar and V. Suneetha, *RJPBCS*, **2015**, *6*(2), 1802.
- 11 M. Zheng, X. Li, S. Mao, M.Huang and Y. Jiang, *Polym. Adv. Technol*, **1997**, *8*, 638.
- 12 S. Zhang, H. Niu, Z. Hu, Y. Cai and Y. Shi, J. Chromatogr. A, 2010, 1217, 4757.
- 13 C. W. Lim and I. S. Lee, Nano Today, 2010, 5, 412.
- 14 R. Narayanan and M. A. EI Sayed, J. Phys. Chem. B, 2005, 109, 12663.
- 15 H. Bae, T. Ahmad, I. Rhee, Y. Chang, S. Jin and S. Hong, Nanoscale Res. Lett., 2012, 7, 44.
- 16 F. Wen, W. Zhang, G. Wei, Y. Wang, J. Zhang, M. Zhang and L. Shi, *Chem. Mater*, **2008**, 20, 2144.
- 17 D. A. Alonso and C. Najera, Chem. Soc. Rev., 2010, 39, 2891.
- 18 N. Karbass, V. Sans, E. Garcia-Verdugo, M. Burguete and S. V. Luis, *Chem. Commun.*, 2006, 29, 3095.
- 19 S. Ogasawara and S. Kato, J. Am. Chem. Soc., 2010, 132, 4608.
- 20 Z. Zheng, H. LI, T. Liu and R. Cao, J. Catal., 2010, 270, 268.
- 21 H. Kochkar, M. Aouine, A. Ghorbel and G. Berhault, J. *Phys. Chem.*, **2011**, *115*, 11364.
- 22 W. X. Niu, L. Zhang and G. G. Xu, ACS Nano, 2010, 4, 1987.
- 23 M. Crespo-quesada, J. M. Andanson, A. Yarulin, B. K. Lim, Y. N. Xia and L. KIWI-Minsker, *Langmuir*, **2011**, *27*, 7909.
- 24 B. Karimi and P. F. Akhavan, Inorg. Chem., 2011, 50, 6063.
- 25 F. Wen, W. Zhang, G. Wei, Y. Wang, J. Zhang, M. Zhang and L. Shi, *Chem. Mater*, **2008**, *20*, 2144.
- 26 W. Li, Y. Tian, B. Zhang, L.Tian, X. Li, H. Zhang, N. Ali and Q. Zhang, *New J. Chem.*, **2015**, *39*, 2767.
- 28. T. Koutzarova, S. Kolev, C. Ghelev, D. Paneva and I.Nedkov, *Phys. Stat. Sol.*(*c*), **2006**, *3*(*5*), 1302.
- 29. X. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, second edn., *Wiley*, New York, **2000**.

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