

DOI:10.1002/ejic.201402173

Compositionally Controlled Self-Assembly of Hierarchical Pd–Ni Bimetallic Chains

Peiyu Jin,^[a] Xin Liang,^{*[b]} Yeheng He,^[a] Sijia Liu,^[a] and Xiaolin Zhu^[a]

Keywords: Self-assembly / Palladium / Nickel / Nanoparticles / Heterogeneous catalysis

Magnetic Pd–Ni bimetals with various compositions were synthesized by a one-pot reaction, in which chain-like Pd–Ni bimetals formed through the self-assembly of Pd–Ni nanoparticles. The self-assembly behaviour of the Pd–Ni bimetals gradually changes with the changes in composition. The Pd– Ni nanoparticles form simple chains at lower Pd content, while the Pd–Ni bimetals take on a beads-on-string structure composed of sphere-shaped Pd–Ni-nanoparticle assemblies

Introduction

The self-assembly of small building blocks into hierarchical nano- or microstructures is an efficient approach for constructing advanced artificial materials with the desired structures and functionalities.^[1] Generally, the self-assembly of the building blocks can be driven by the noncovalent interactions between components, such as hydrogen bonding interactions, charge-transfer interactions, van der Waals forces, and electric/magnetic dipole interactions.^[2] The control of the interaction between components is a powerful strategy for controlling the assembling modes of the building blocks. For example, the assemblies tend to reach the equilibrium state under weak non-covalent interactions and form a non-equilibrium system under strong non-covalent interactions.^[3] The interaction is significantly influenced by the properties of the building blocks, such as the size,^[4] shape,^[5] magnetic properties and the capped organics.^[6] Thus, investigations on the effect of factors on the self-assembly behaviours of the building blocks lead to the design and synthesis of complicated assemblies by modulating the building blocks.

Bimetallic nanocrystals, which are distinct from those of their parent metals, show a composition-dependent surface structure and atomic segregation behaviour, and offer the

[b] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 100029 Beijing, P. R. China E-mail: liangxin@mail.buct.edu.cn at higher Pd content. Magnetic hysteresis loops show that Ni-rich assemblies have a higher saturation magnetization than Pd-rich assemblies. The formation mechanism for these Pd–Ni assemblies is proposed, in which the self-assembly behaviours are controlled by the competition of the surfactant interaction and the magnetic dipole interaction. The catalytic activity and selectivity of the hydrogenation of acetophenone over these Pd–Ni bimetals depend on their compositions.

opportunity to obtain novel catalysts with enhanced selectivity, activity and stability.^[7] Various bimetals with the combination of 3d transition metals (e.g. Fe, Co and Ni) along with nearly magnetic 4d metals (e.g. Rh, Pd and Ag) have been extensively investigated,^[8] in which the Pd–Ni bimetal is one of the most promising materials with significant potential in catalysis. It has been realized that Pd–Ni bimetals are magnetic materials and their properties are strongly composition dependent. Thus, Pd–Ni bimetallic systems could serve as an ideal system to investigate the self-assembly behaviours under tunable non-covalent interactions by controlling their compositions.

Herein, an example of compositionally controlled selfassembly has been demonstrated in which hierarchical Pd– Ni bimetallic chains with different assembling modes have been achieved. This paper shows how the composition factor governs the structural, morphological and magnetic properties of Pd–Ni bimetals, the non-covalent interactions between components, and the self-assembly of the hierarchical chains. The catalytic properties of these Pd–Ni bimetallic assemblies were systematically investigated by the hydrogenation of the acetophenone (ACP) reaction, which shows that the catalytic hydrogenation performance of these Pd–Ni assemblies is strongly dependent on their compositions.

Results and Discussion

Pd–Ni bimetallic assemblies with tunable compositions were obtained by the one-pot reduction of $Pd(Ac)_2$ and Ni(Ac)₂·4H₂O in the presence of oleylamine and tetrabutyl ammonium bromide (TBAB), in which the samples derived

 [[]a] Department of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201402173.



Figure 1. (a) X-ray diffraction patterns of Pd–Ni bimetallic assemblies, and (b) the enlarged parts within the range from 2θ values 38° to 43°.

as Pd²⁺/Ni²⁺ in molar ratios of 1:3, 2:3, 1:1 and 3:1 were denoted as Pd₂₅Ni₇₅, Pd₄₀Ni₆₀, Pd₅₀Ni₅₀ and Pd₇₅Ni₂₅, respectively. The X-ray diffraction (XRD) patterns of the prepared series of Pd-Ni alloys are demonstrated in Figure 1. For Pd₅₀Ni₅₀ and Pd₇₅Ni₂₅, the X-ray diffractive peaks can be assigned to {111}, {200} and {220} diffractions of a pure phase of face-centered cubic crystal structures, in which the peaks are located between the corresponding standard peaks of pure Pd (JCPD-65-6174) and Ni (JCPD-04-0850), arising from the formation of Pd-Ni alloys. The peaks shift from the palladium standard peaks to the nickel standard peaks with the increase of nickel content from Pd₅₀Ni₅₀ to Pd₇₅Ni₂₅, and no other peaks were observed in the XRD patterns, revealing that only Pd-Ni alloys formed in these cases. For Ni-rich samples (Pd₄₀Ni₆₀ and Pd₂₅Ni₇₅), two sets of X-ray diffractive peaks can be observed from the XRD patterns, which can be attributed to the cubic phase of Pd and Ni crystal structures. The diffractive peaks at 2θ values of 44.5°, 51.8° and 76.4° are well assigned to the nickel standard peaks. With the increase of nickel content from Pd₄₀Ni₆₀ to Pd₂₅Ni₇₅, the intensity of these Ni peaks gradually strengthens, and the shift of the Pd₁₁₁ peaks weakens. The reinforced cubic nickel structures accompanied with the weakened intermetallic alloy structure resulted in a mixed heterogeneous structure for the Nirich samples.

The morphologies and size of the as-prepared Pd–Ni bimetals were observed by TEM and SEM images. TEM images in Figure 2 show that all the Pd–Ni bimetals display hierarchical chain-like structures that are composed of small primary Pd and Ni nanoparticles. The composition of these Pd–Ni bimetals plays a vital role in controlling the self-assembly modes of these Pd–Ni chains. For the Ni-rich samples, the Pd–Ni short chains were formed through random assembly of Pd–Ni nanoparticles with the particle size of 15–20 nm. The assembling modes of these Pd–Ni chains become more hierarchical along with the increase of palladium content. For $Pd_{50}Ni_{50}$ – see Figure 2 (c) – the small primary Pd–Ni alloy nanoparticles assemble into bigger spheres with a diameter of about 150 nm, and then, these secondary spheres link together to shape the unique and more hierarchical beads-on-string chain-like structure. For Pd₇₅Ni₂₅, the sample also takes on the beads-on-string structure, while the secondary spheres became larger, at the rough range of 200-400 nm, see Figure 2 (d). The unique and complex structures of these chain-like Pd-Ni bimetals were further confirmed by SEM characterization (Figure 3). The compositionally controlled morphology evolution from the randomly assembled chains of the Ni-rich samples to the hierarchical beads-on-string chain-like structures of the Pd-rich samples can be observed. Obviously, the compositions control the phase, morphology and the self-assembly behaviour of the as-prepared Pd-Ni bimetals. The accurate compositions of the as-prepared Pd-Ni bimetallic chains were determined by SEM-EDX spectroscopy. The results show that Pd/Ni molar ratios in the Pd-Ni chains are similar to the input Pd/Ni molar ratios of reac-



Figure 2. TEM images accompanied by the different magnifications (lower left inset) of the as-prepared (a) $Pd_{25}Ni_{75}$, (b) $Pd_{40}Ni_{60}$, (c) $Pd_{50}Ni_{50}$ and (d) $Pd_{75}Ni_{25}$.



FULL PAPER

tants (Table S1, Supporting Information). The EDX spectra are shown in Figure S2.



Figure 3. SEM images of prepared (a) $Pd_{25}Ni_{75},$ (b) $Pd_{40}Ni_{60},$ (c) $Pd_{50}Ni_{50}$ and (d) $Pd_{75}Ni_{25}.$

Generally, the possible non-covalent interactions between the building blocks include hydrogen bonding interactions, charge-transfer interactions, Van der Waals forces and electric/magnetic dipole interactions. For the as-prepared Pd-Ni bimetals, oleylamine and cationic surfactant TBAB were applied as both stabilizer agent and surfactant, which are significant for the control of the nucleation and growth process of the Pd-Ni nanoparticles. Comparison experiments also show that only irregular nanoparticles form in the absence of TBAB (Figure S3 in SI). Studies have demonstrated that interactions between the surfactants could induce the self-assembly of the nanoparticles.^[9] It can be concluded that the surfactant in the synthetic systems is responsible for the self-assembly behaviour of these Pd-Ni bimetals. On the other hand, the magnetic properties of Pd-Ni are also crucial for the formation of such chain-like assemblies. Many nanoparticle chains have been demonstrated in the ferromagnetic or superparamagnetic materials, such as FePt and NiCo magnetic materials.^[10] To understand the underlying self-assembly mechanism of these Pd–Ni hierarchical chain-like assemblies, the formation and assembly processes are carefully explored by using Fourier transform infrared spectroscopy (FTIR) and vibration sample magnetometry (VSM).

Figure 4 shows FTIR spectra of the prepared Pd–Ni bimetallic powders with various compositions. The spectra show characteristic peaks of the absorbed oleylamine group: the bands at 2920 and 2852 cm⁻¹ can be assigned to the symmetric and asymmetric methylene stretching modes, the peaks at around 1628 cm⁻¹ can be assigned to the v(C=C) stretching modes of the oleylamine molecules and the wide absorption band around 3430 cm⁻¹ is from the v(N–H) stretching mode. The strong absorption bands at around 1458, 1445 and 1404 cm⁻¹ can be attributed to tetrabutyl ammonium cations.^[11] FTIR spectra confirm that both oleyl group and tetrabutyl ammonium cations are coated on the surface of the Pd–Ni bimetals.

Figure 5 shows the field-dependent magnetization (M-H) curves of these Pd-Ni bimetals with different compositions recorded at 300 K. The M-H curves exhibit clear hysteresis loops for all the samples, demonstrating the ferromagnetic behaviours of these Pd-Ni bimetallic materials. The particle sizes of the as-prepared Pd-Ni nanoparticles (15-20 nm) are in the range of a single magnetic domain, thus, the primary Pd-Ni nanoparticles can be considered as mini-magnets with substantial magnetic moments. Because of the magnetic dipole-dipole interaction of these minimagnets,^[12] these Pd-Ni nanoparticles have a tendency to attract each other to form assemblies. Linear chains will form along the magnetic anisotropy direction if the magnetic dipolar interactions outweigh the thermal motion. Otherwise, the direction of these mini-magnets would be randomly distributed because of the strong thermal motion. Thus, the strength of the magnetism has a great influence on the self-assembly behaviour of these Pd-Ni nanoparticles. The stronger magnetism favours the self-assembly tendency of the nanoparticles because of the higher magnetic dipolar interaction. The magnetic measurements show that the saturation magnetization values (Ms) are 26.92,



Figure 4. FTIR spectra of the prepared Pd-Ni bimetallic powders, (a) Pd₂₅Ni₇₅, (b) Pd₄₀Ni₆₀, (c) Pd₅₀Ni₅₀ and (d) Pd₇₅Ni₂₅.



12.26, 9.55 and 9.15 emug^{-1} for $\text{Pd}_{25}\text{Ni}_{75}$, $\text{Pd}_{40}\text{Ni}_{60}$, $\text{Pd}_{50}\text{Ni}_{50}$ and $\text{Pd}_{75}\text{Ni}_{25}$, respectively. Basically, the higher the proportion of Ni is, the higher the Ms is. By adjusting the Pd/Ni molar ratio in Pd–Ni bimetals, the magnetic strength of these ferromagnetic materials could be well controlled.



Figure 5. Magnetic hysteresis loops of (a) $Pd_{25}Ni_{75}$, (b) $Pd_{40}Ni_{60}$, (c) $Pd_{50}Ni_{50}$ and (d) $Pd_{75}Ni_{25}$ at 300 K.

On the basis of the above analyses of XRD patterns, TEM and SEM images, FTIR spectra and M–H curves, the mechanism of the composition controlling self-assembly can be illustrated clearly in Figure 6. The assembly of chain-like structures resulted from the magnetic properties and the aggregation of micelles for the surfactant should be taken into consideration simultaneously during the growth. In the synthetic system, oleylamine with a long alkyl chain could be linked to the surface of the Pd–Ni nanoparticles through a coordination bond, to make the surface hydrophobic; while the TBAB could be absorbed on the Pd–Ni surface by creating an electrostatic double layer, making a hydrophilic surface.^[13] As studied by FTIR spectra, the oleyl group interdigitate with TBAB on the surface of Pd–

Ni nanoparticles, which bring an amphipathic nature to the Pd-Ni nanoparticles. These amphipathic nanoparticles have a tendency to form spherical assemblies because of the formation of microemulsion droplets in the ethanol/toluene mixed solution. Thus, the self-assembly behaviours are believed to be affected by the competition between the surfactant interaction and the magnetic dipolar interaction. Because the magnetic strength is relatively low for Pd-rich samples, the surfactant interactions play a leading role in these cases, in which the Pd-Ni nanoparticles assemble to the spherical beads because of the surfactant interactions, and then the spherical beads link with each other to form the beads-on-string structure because of the magnetic dipolar interaction. For Ni-rich samples, the magnetic dipolar interactions are strong enough to outweigh the surfactant interactions to induce the chain-like self-assembly. It can be concluded that the composition controls the competition between surfactant interaction and magnetic dipolar interaction, and then controls the self-assembly behaviours of the Pd-Ni nanoparticles.



Figure 6. Schematic illustration of the growth process for the formation of such structures.

In order to study the surface states of such Pd–Ni bimetals, X-ray photoelectron spectroscopy (XPS) was conducted. XPS raw spectra of Ni 2p and Pd 3d are shown in Figure 7. The Ni $2p_{3/2}$ XPS peaks at a binding energy (B.E.) of ca. 852 eV can be assigned to Ni⁰, while the peak located



Figure 7. XPS spectra of the Ni 2p (A) and Pd 3d (B) photoelectron peaks in the investigated samples, (a) $Pd_{25}Ni_{75}$, (b) $Pd_{40}Ni_{60}$, (c) $Pd_{50}Ni_{50}$ and (d) $Pd_{75}Ni_{25}$.



at B.E. ca. 856 eV is assigned to Ni^{2+} or Ni^{3+} ions,^[14] implying that the Ni species were partially oxidized on the surface of the samples. The Pd $3d_{5/2}$ peaks at around 335 eV could be assigned to the zerovalent metallic Pd^[15] and have a slight shift from Ni-rich to Pd-rich samples, perhaps because of an electronic effect.

Recently, Pd-Ni bimetals have shown potential as hydrogenation catalysts for their excellent performance and relatively low cost compared with pure noble metals.^[16] Their composition-dependent surface structure shows great potential in the catalytic reactions. Here, the hydrogenation catalytic activities of these Pd-Ni assemblies were tested by the model hydrogenation reaction: the hydrogenation of acetophenone (AP) to 1-phenylethanol (PE). The reaction scheme is shown in Scheme 1. The performances of these Pd-Ni assemblies with various compositions have been compared by using a batch reactor under the same catalytic conditions (the mass concentration of catalyst was 0.95 gL^{-1} ; the concentration of acetophenone was $0.41 \text{ mol } L^{-1}$). The target hydrogenation product, 1-phenylethanol, is detected along with a small amount of ethylbenzene (EB) as a byproduct from the over-hydrogenation side reaction.



Scheme 1. Reaction scheme for the hydrogenation of acetophenone for the target product PE. (AP: acetophenone, PE: 1-phenyl-ethanol).

As summarized in Table 1, the conversions of AP are 79%, 75%, 93% and 99% for Pd₂₅Ni₇₅, Pd₄₀Ni₆₀, Pd₅₀Ni₅₀ and Pd₇₅Ni₂₅, respectively. The Pd-rich catalysts show better hydrogenation catalytic activity than the Ni-rich catalysts. However, the selectivity of PE decreases and the yield of EB increases over the Pd-rich catalyst (Pd75Ni25) because of the over-hydrogenation side reaction. When considering the AP conversion and the selectivity of PE, the Pd₅₀Ni₅₀ catalyst shows the highest yield of PE (89%) among these Pd-Ni bimetal catalysts. The composition-dependent catalysis may be caused by the variation on the active sites on the surface and electronic effect. XPS results show that Pd in the catalysts consists of Pd⁰ in contrast to various chemical states of Ni. The increase of Pd⁰ on the surface of the catalysts provides more active sites for hydrogenation, which leads to an increase in the conversion of AP, as well as a decrease in selectivity due to the over-hydrogenation from AP to EB.^[17]

The surface areas of the samples are 39.2, 37.6, 67.1 and 72.3 m^2g^{-1} for $Pd_{25}Ni_{75}$, $Pd_{40}Ni_{60}$, $Pd_{50}Ni_{50}$ and $Pd_{75}Ni_{25}$, respectively. The catalytic performance of these catalysts can also be greatly influenced by their surface area. It can be concluded that the performance of the Pd–Ni bimetallic catalysts depends on their compositions, and careful investigations on the composition effect could give a suggestive

Table 1. Comparison of the catalytic activity of different proportions of the Ni–Pd alloy in the hydrogenation of acetophenone. $^{[a]}$

Samples	Conversion of AP [%]	Selectivity of PE [%]	Yield of PE [%]	Yield of EB [%]
Pd ₂₅ Ni ₇₅	79	95	76	3
Pd ₄₀ Ni ₆₀	75	90	72	3
Pd ₅₀ Ni ₅₀	93	95	89	4
Pd ₇₅ Ni ₂₅	99	83	83	16

[a] Reaction conditions: 10 mL of absolute ethyl alcohol, 0.5 mL of acetophenone, 10 mg of catalyst. The reaction was carried out for 4 h under 15 bars of H_2 at 80 °C.

guidance on the design and development of Pd–Ni bimetal hydrogenation catalysts. Moreover, compared with pure noble metals, these Pd–Ni bimetal catalysts could easily be separated from the catalytic reaction solutions for recycling by using an external magnetic field because of the ferromagnetic properties of these Pd–Ni assemblies.

Conclusions

Hierarchical Pd-Ni bimetallic chains have been synthesized by a one-pot synthetic approach in an ethanol/toluene solution in the presence of oleylamine and TBAB. With the change of the composition, these Pd-Ni bimetallic assemblies show different self-assembly behaviours. For the Nirich sample, the Pd-Ni nanoparticles form simple chainlike structures, while the Pd-Ni bimetallic chains display a beads-in-string structure for the Pd-rich samples. The mechanisms underlying the compositionally controlled selfassembly have been investigated by XRD, TEM, SEM, FTIR spectroscopy and VSM analysis. Sufficient evidences show that the self-assembly of Pd-Ni nanoparticles is governed by both the surfactant interactions and the magnetic dipole interactions among the building blocks. The composition controls the competition of surfactant interactions and the magnetic dipole interactions, resulting in the diversity of the self-assembly behaviours. The composition also shows significant influence on the performance of these Pd-Ni assemblies in the hydrogenation of acetophonene.

Experimental Section

Chemicals: Analytical grade ethanol, toluene and oleylamine were obtained from Beijing Chemical Reagents, China. Ni(Ac)₂·4H₂O, Acetophenone (C₈H₈O, 99.5%), cyclohexane and tetrabutyl ammonium bromide (TBAB) were purchased from TianJin GuangFu Fine Chemical Research Institute, China. Palladium(II) acetate [Pd (Ac)₂, GR, ≥46 wt.-% Pd] was obtained from Sinopharm Chemical Reagent Co. Ltd., China. And all the reagents were used without further purification.

Synthesis of Composition Controlled Pd–Ni Alloys: $Pd(Ac)_2$ (0.2 g) was dissolved in toluene (25 mL) to form a $Pd(Ac)_2$ solution (8.0 mgmL⁻¹) (a transparent yellow solution A). Then



 $Ni(Ac)_2$ ·4H₂O (0.665 g) was dissolved in ethanol (50 mL) to form a $Ni(Ac)_2$ ·4H₂O (13.3 mgmL⁻¹) solution (a transparent green solution **B**).

We will use Pd₂₅Ni₇₅ as the example. TBAB (0.1 mmol) was placed in a 50-mL autoclave and solution A (1 mL) and solution B (2 mL) were injected into the autoclave, and stirred to dissolve the TBAB. Later oleylamine (10 mL) was added into the autoclave while stirring. The autoclave was then sealed and kept at 200 °C for 24 h in an oven. The autoclave was cooled down naturally to room temperature after the reaction. The product was washed with the mixture of ethanol and cyclohexane and separated by centrifugation at 10000 rpm for 25 min several times. When collecting the product, a little bit was redispersed in cyclohexane for TEM analysis and the rest was dried at 60 °C overnight. For the synthesis of Pd-Ni bimetals with various compositions, such as Pd40Ni60, Pd50Ni50 and Pd₇₅Ni₂₅, we changed the dosage of solution **B** and additional ethanol was added to maintain the volume ratio of toluene and ethanol as 1:2. Other steps of the synthetic procedures were the same as those for the synthesis of Pd₂₅Ni₇₅.

Characterization: The powder X-ray diffraction (XRD) was accomplished with a D8 Focus diffractometer (Bruker) with a Cu- K_{α} radiation source. A JTEM-1230 (Japan) transmission electron microscope (TEM) and S-4700 (Japan) scanning electron microscope (SEM) were employed to obtain the morphology and size of the as-synthesized samples. HRTEM was measured with an FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope at 200 kV. Energy dispersive X-ray (EDX) analysis was carried out with an FEI scanning electron microscope (JSM-6700F). The Fourier transform infrared (FTIR) spectra were measured with a Nicolet6700 spectrometer with a deuterated triglyceride sulfate (DTGS) detector at room temperature. 32 scans were collected for each spectrum with a resolution of 4 cm⁻¹. Vibration sample magnetometry (VSM) was used to examine the magnetic properties of the obtained Pd-Ni nanocrystals with Lakeshore 7410. The chemical composition was confirmed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 Xi) using Al-K_a radiation. The surface areas (BET) were measured with a JW-RB24 static nitrogen adsorption instrument.

Catalysis for the Hydrogenation of Acetophenone: The catalytic reaction was carried out with a stainless steel reactor (50 mL) at 80 °C for 4 h. The catalyst (10 mg), absolute ethanol (10 mL) and acetophenone (0.5 mL) were all added into the reactor. The batch reactor was then purged with hydrogen to exhaust air several times, pressurized up to 15 bars, heated to the set temperature and kept at about 400 rpm while stirring. After the reaction time, the autoclave was cooled to room temperature, the liquid product was collected for analysis by gas chromatography with a DongXi GC4000A apparatus with a FID director and an SE-54 capillary column.

Supporting Information (see footnote on the first page of this article): HRTEM, SEM-EDX spectra and accurate compositions of Pd–Ni in the investigated samples, TEM images of Pd–Ni nanoparticles in the absence of TBAB, FTIR characterization of pure TBAB and XPS curve-fitting of the Ni 2p and Pd 3d photoelectron peaks in $Pd_{40}Ni_{60}$ and $Pd_{75}Ni_{25}$ samples are shown in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (NSFC) (grant number 21121064),

Beijing Higher Education Young Elite Teacher Project (grant number YETP0484) and the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (grant number 2011CB932402).

- a) J. F. Fei, L. Gao, J. Zhao, C. L. Du, J. B. Li, Small 2013, 9, 1021–1024; b) S. Mann, H. Clfen, Angew. Chem. Int. Ed. 2003, 42, 2350–2365; Angew. Chem. 2003, 115, 2452.
- [2] a) J. N. Hohman, M. Kim, G. A. Wadsworth, H. R. Bednar, J. Jiang, M. A. LeThai, P. S. Weiss, *Nano Lett.* 2011, *11*, 5104–5110; b) M. Grzelczak, J. Vermant, E. M. Furst, L. M. Liz-Marzán, *ACS Nano* 2010, *4*, 3591–3605; c) B. H. Sohn, J. M. Choi, S. I. Yoo, S. H. Yun, W. C. Zin, J. C. Jung, M. Kanehara, T. Hirata, T. Teranishi, *J. Am. Chem. Soc. Commun.* 2003, *125*, 6368–6369; d) J. Y. Ku, D. M. Aruguete, A. P. Alivisatos, P. L. Geissler, *J. Am. Chem. Soc.* 2011, *133*, 838–848.
- [3] a) Y. Zhao, K. Thorkelsson, A. J. Mastroianni, T. Schilling, B. J. Rancatore, T. Xu, J. M. Luther, Y. Wu, D. Poulsen, J. M. J. Fréchet, *Nat. Mater.* 2009, *8*, 979–985; b) Y. Tidhar, H. Weissman, S. G. Wolf, A. Gulino, B. Rybtchinski, *Chem. Eur. J.* 2011, *17*, 6068–6075.
- [4] J. P. Ge, Y. X. Hu, M. Biasini, L. Dong, J. H. Guo, W. P. Beyermann, Y. D. Yin, *Chem. Eur. J.* 2007, 13, 7153–7161.
- [5] Y. Wu, S. F. Cai, D. S. Wang, W. He, Y. D. Li, J. Am. Chem. Soc. 2012, 134, 8975–8981.
- [6] a) F. Bai, D. S. Wang, Z. Y. Huo, W. Chen, L. P. Liu, X. Liang, C. Chen, X. Wang, Q. Peng, Y. D. Li, *Angew. Chem. Int. Ed.* **2007**, *46*, 6650–6653; *Angew. Chem.* **2007**, *119*, 6770; b) H. Yang, X. L. Wu, M. H. Cao, Y. G. Guo, *J. Phys. Chem. C* **2009**, *113*, 3345–3351; c) S. H. Sun, E. E. Fullerton, D. Weller, C. B. Murray, *IEEE Transactions on Magnetics* **2001**, *37*, 1239–1243.
- [7] a) D. S. Wang, Y. D. Li, Adv. Mater. 2011, 23, 1044–1060; b)
 Y. Wu, D. S. Wang, P. Zhao, Z. Q. Niu, Q. Peng, Y. D. Li, Inorg. Chem. 2011, 50, 2046–2048.
- [8] a) J. Guevaraa, A. M. Llois, F. Aguilera-Granjad, J. M. Montejano-Carrizales, *Phys. B* 2004, *354*, 300–302; b) D. L. Wang, H. L. Xin, H. S. Wang, Y. C. Yu, E. Rus, D. A. Mulle, F. J. DiSalvo, H. D. Abruna, *Chem. Mater.* 2012, *24*, 2274–2281; c) Z. Y. Zhang, T. M. Nenoff, K. Leung, S. R. Ferreira, J. Y. Huang, D. T. Berry, P. P. Provencio, R. Stumpf, *J. Phys. Chem. C* 2010, *114*, 14309–14318.
- [9] a) M. Li, H. Schnablegger, S. Mann, *Nature* 1999, 402, 393–395; b) N. Shukla, C. Liu, P. M. Jones, D. Weller, *J. Magn. Magn. Mater.* 2003, 266, 178–184.
- [10] a) S. H. Sun, Adv. Mater. 2006, 18, 393–403; b) M. Raula, Md. H. Rashid, S. Lai, M. Roy, T. K. Mandal, ACS Appl. Mater. Interfaces 2012, 4, 878–889.
- [11] a) R. A. Campbell, S. R. W. Parker, J. P. R. Day, C. D. Bain, Langmuir 2004, 20, 8740–8753; b) M. Akçay, J. Colloid Interface Sci. 2006, 296, 16–21.
- [12] a) L. Dong, Y. Liu, Y. Lu, L. Zhang, N. Man, L. Cao, K. Ma, D. An, J. Lin, Y. J. Xu, W. P. Xu, W. B. Wu, S. H. Yu, L. P. Wen, *Adv. Funct. Mater.* 2013, 23, 5930–5940; b) M. R. Gao, S. R. Zhang, Y. F. Xu, Y. R. Zheng, J. Jiang, S. H. Yu, *Adv. Funct. Mater.* 2013, 23, 1–8; c) J. S. Chen, T. Zhu, C. M. Li, X. W. Lou, *Angew. Chem. Int. Ed.* 2011, 50, 650–653; *Angew. Chem.* 2011, 123, 676.
- [13] V. Salgueirino-Maceira, L. M. Liz-Marzán, M. Farle, *Lang-muir* 2004, 20, 6946–6950.
- [14] a) L. Sciortino, F. Giannici, A. Martorana, A. M. Ruggirello, V. T. Liveri, G. Portale, M. P. Casaletto, A. Longo, *J. Phys. Chem. C* 2011, *115*, 6360–6366; b) E. L. Ratcliff, J. Meyer, K. X. Steirer, A. Garcia, J. J. Berry, D. S. Ginley, D. C. Olson, A. Kahn, N. R. Armstrong, *Chem. Mater.* 2011, *23*, 4988–5000; c) K. W. Park, J. H. Choi, B. K. Kwon, S. A. Lee, Y. E. Sung, H. Y. Ha, S. A. Hong, H. Kim, A. Wieckowski, *J. Phys. Chem. B* 2002, *106*, 1869–1877.
- [15] a) G. B. Hoflund, H. A. E. Hagelin, J. F. Weaver, G. N. Salaita, *Appl. Surf. Sci.* **2003**, 205, 102–112; b) M. Brun, A. Berthet,



J. C. Bertolini, J. Electron Spectrosc. Relat. Phenom. **1999**, 104, 55–60; c) J. M. Tura, P. Regull, L. Victori, M. Dolors De Castellar, Surf. Interface Anal. **1988**, 11, 447–449; d) C. J. Powell, J. Electron Spectrosc. Relat. Phenom. **2012**, 1, 185.

[16] a) K. Fuku, T. Sakano, T. Kamegawa, K. Mori, H. Yamashita, J. Mater. Chem. 2012, 22, 16243; b) Ö. Metin, S. F. Ho, C. Alp, H. Can, M. N. Mankin, M. S. Gültekin, M. F. Chi, S. H. Sun, *Nano Res.* **2013**, *6*, 10–18.

[17] a) C. S. Chen, H. W. Chen, *Appl. Catal. A* **2004**, *260*, 207; b) M. Lenarda, M. Casagrande, E. Moretti, L. Storaro, R. Frattini, S. Polizzi, *Catal. Lett.* **2007**, *114*, 79–84.

Received: March 12, 2014 Published Online: July 23, 2014