Reduction-Resistant and Reduction-Catalytic Double-Crown Nickel Nanoclusters

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COMMUNICATION

Reduction-Resistant and Reduction-Catalytic Double-Crown Nickel Nanoclusters

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In this work, an attempt to synthesize zero-valent Ni nanoclusters using the Brust method resulted in an unexpected material, $Ni_6(SCH_2CH_2Ph)_{12}$, which is a nanoscale Ni(II)-phenylethanethiolate complex and hexameric, double-crown-like structure, as determined by a series of characterizations, including mass spectrometry (MS), thermal gravimetric analysis (TGA), single-crystal X-ray diffraction (XRD), and X-ray photoelectron spectrometry (XPS). An interesting finding is that this complex is resistant to aqueous BH_4^-. Investigations of other metal-phenylethanethiolate and Ni-thiolate complexes reveal that this property is not universal and only appears in complexes with a double-crown-like structure, indicating a correlation between this interesting property and the complexes' special structure. Another interesting finding is that the reduction-resistant $Ni_6(SCH_2CH_2Ph)_{12}$ exhibits remarkably higher catalytic activity than a well-known catalyst, $Au_{25}(SCH_2CH_2Ph)_{18}$, toward the reduction of 4-nitrophenol at low temperature (e.g., 0 °C). This work will help stimulate more research on the properties and applications of less noble metal nanoclusters.

Because structure–property relationships have long provided guidance in the discovery and optimization of novel materials, investigations into the relationship between physicochemical properties and chemical structure has never ceased. To better understand how materials can be modified and further applied, detailed information about the relationships between different properties and structures of materials is needed. For example, the Steffen P. Graether group reported the correlation of structure and ice-binding properties of a hyperactive antifreeze protein from an insect;[1] Teri Wang Odom and co-workers resolved the structure of the walls of SWNTs (single-walled nanotubes) and demonstrated that the electronic properties do indeed depend on diameter and helicity;[2] Jeffrey M. McMahon et al. reported the relationship between the structure and optical response of silver nanocubes.[3] Herein, we add to these paradigms by providing another example stemming from our recent nanocluster research.

Sub-nanometer-sized metal clusters,[4] which bridge the gap between metal atoms and nanoparticles, have attracted particular research interest in recent years due to their unique electronic structures,[5] interesting physiochemical properties (including optical,[6] electronic,[7] magnetic,[8] and redox properties,[9] etc.), as well as potential applications in many fields, such as nanoelectronics,[10] catalysis,[11] optics,[12] chemical and biological sensing,[13] and biomedicine.[14] Among such materials, gold and silver clusters, particularly thiolate-protected clusters, have been extensively investigated over the past decade. A number of $Au_n(SR)_m$ and $Ag_n(SR)_m$ nanoclusters (SR=thiolate) with molecular purity have been obtained, such as $Au_{19}(SR)_{13}$,[15] $Au_{25}(SR)_{18}$,[16] $Au_{36}(SR)_{23}$,[17] $Au_{38}(SR)_{24}$,[18] $Au_{44}(SR)_{28}$,[19] $Au_{102}(SR)_{44}$,[20] $Au_{144}(SR)_{60}$,[21] $Ag_7(DMSA)_4$[22] and $Ag_{44}(MBA)_{30}$[23] nanoclusters. Nickel, as a less noble and ferromagnetic metal, has received more attention than gold and silver not only for industrial application but also for scientific research. However, to the best of our knowledge, mono-disperse thiolated nickel nanoclusters (analogous to gold and silver nanoclusters) have not been reported, which inspired us to investigate the feasibility of synthesizing such nanoclusters following the versatile Brust-Schiffrin method.[24]

To our surprise, the experimental results demonstrated that a Ni(II) complex $Ni_6(SC_2H_4Ph)_{12}$ (Ni_6 for short) was obtained instead of the expected zero-valent nickel clusters (supported by MALDI-MS, single-crystal XRD, XPS, etc.), which was further confirmed by control experiments performed without the addition of the reducing reagent $NaBH_4$. The unexpected product Ni_6 yielded by the Brust method indicates that Ni_6 is resistant to aqueous BH_4^-, and further experiments corroborate this result. To investigate the universality of this unexpected property, other M-phenylethanethiolate (PET) complexes (M: Fe, Co, Bi) and Ni–SR complexes (SR: 4-(tert-butyl) benzene-1-thiolate, abbreviated as TBBT; tert-butyl thiolate, abbreviated as TBT, ethanethiolate, hexanethiolate) were tested. It was observed that the reduction-resistance property (RRP) is not universal. We attribute this property to the structure shared among these complexes – a double-crown-like structure. This type of relationship has not been reported previously to the best of our knowledge and provides another example of the aforementioned structure-property correlation. Another interesting finding obtained in this work is that the reduction-resistant Ni_6 shows greatly higher catalytic activity than a well-known catalyst, $Au_{25}(SCH_2CH_2Ph)_{18}$, toward the reduction of 4-nitrophenol at low temperature (e.g., 0 °C), which indicates the potential application of Ni_6 as a hydrogenation catalyst. In the following, we provide more detailed information and further discussion.

The synthesis of $Ni_6(SCH_2CH_2Ph)_{12}$ follows a modified Brust-Schiffrin method (details in the Supporting Information). Briefly,

$Ni(NO_3)_2$•$6H_2O$ (0.42 mmol) and tetraoctylammonium bromide (TOAB, 2 equivalents per mole of nickel) were dissolved in 25 ml of THF. Phenylethanethiol (6 equivalents) was then slowly added to this solution, and the resulting mixture was stirred for 3 hours. Subsequently, an aqueous solution of sodium borohydride (10 equivalents per mole of nickel, freshly dissolved with 5 ml of ice-cold Nanopure water) was rapidly added all at once under vigorous stirring. After stirring for 20 hours, the THF was removed to obtain a large amount of precipitate. The precipitate was washed with water and methanol and recrystallized from CH_2Cl_2/ethanol solution at least three times. The role of TOAB in this reaction is comparable to that in synthesizing Au_{25}.[25] As a phase-transfer catalyst, TOAB can make the aqueous and non-aqueous reactants well-mixed, thus facilitate (or accelerate) the forming of products. The control experiment reveals that without TOAB the yield was decreased from 30% to 20% (other reaction conditions are unchanged). Thiol etching is also nontrivial in our reaction.[26,27] Generally speaking, adequately long etching time and largely excessive ligands are beneficial to the forming of high-yield product. For instances, when the etching time was prolonged from 2 hours to 20 hours, the yield was improved from 11% to 30%; when the molar ratio of thiol to Ni was lifted from 3: 1 to 6: 1, the yield was dramatically increased from 3.5% to 30%. However, longer etching time than 20 hours and higher S/Ni molar ratio than 6: 1 contribute little to the further improvement of yield. Transmission electron microscopy (TEM) imaging demonstrated that the as-prepared particles were nanometer-sized (see Figure 1a). A diluted solution was required to prepare the TEM specimen to prevent cluster aggregation during TEM imaging because densely distributed particles can quickly agglomerate and grow larger upon electron beam irradiation. The ultra-small particles (dissolved in dichloromethane) showed three distinct absorption bands centered at 540, 408 and 338 nm (Figure 2a), similar to those previously reported for $Ni_6(SCH_2CH_2Ph)_{12}$.[28] MALDI-MS analysis, which is a very powerful and well-recognized technique for identifying compounds, revealed a distinct peak at 1998 Da (Figure 1b). The peak corresponds to the formula $Ni_6(SCH_2CH_2Ph)_{12}$ (expected m/z 1998), and the isotopic pattern is in good agreement with the simulated one. To confirm the composition, thermal gravimetric analysis (TGA) was performed. A weight loss of 72 wt % is in perfect agreement with the previously reported result (weight loss: 72 wt %[28]) (Figure 2d). Single-crystal X-ray diffraction further confirmed the cluster formula. The structure revealed by single crystal X-ray diffraction is similar to that indicated in a previous report.[28] The crystal was observed to be in the $P2_1/c$ space group with a = 11.3662(2) Å, b = 12.5415(3) Å, c = 32.7762(8) Å, α = 90.00(0)°, β = 91.676(2)°, and γ = 90.00(0)° (see the SI for detailed structural data). Briefly, the six nickel atoms form a hexagonal ring with pairs of sulfur atoms uniformly situated above and below the plane of the nickel ring. Each nickel atom is coordinated to four sulfur atoms with an approximately square planar geometry (Figure 3).

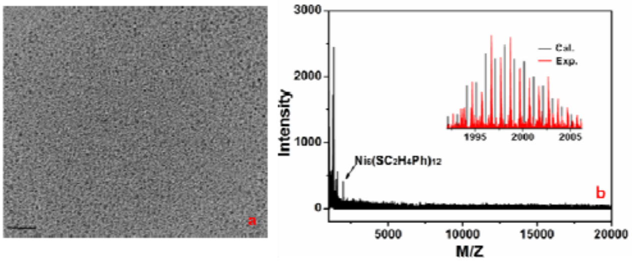

Fig.1 TEM image of $Ni_6(SCH_2CH_2Ph)_{12}$ (the scale bar is 20 nm) (a). MALDI-TOF mass spectrum of $Ni_6(SCH_2CH_2Ph)_{12}$. (Inset) The comparison of simulated and experimentally obtained isotopic patterns (b).

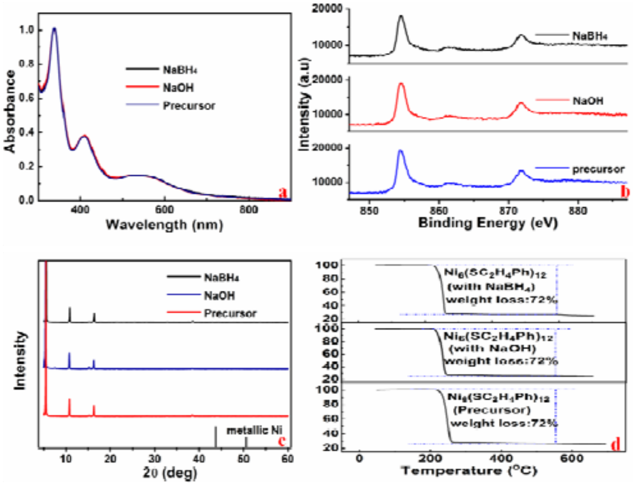

Fig.2 Comparison of the UV/Vis/NIR spectra (a), the XPS analysis (b), the XRD analysis (c) (the stick pattern corresponds to bulk nickel) and the thermogravimetric analysis (d) (N_2 atmosphere, 10 °C min^{-1}) of the products made using three different synthetic methods.

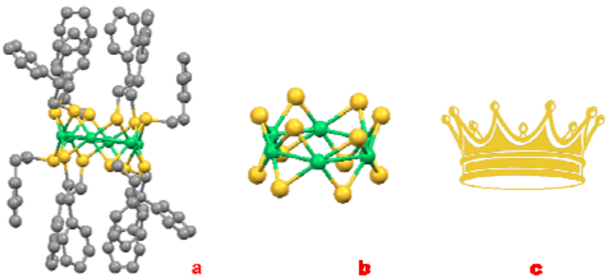

Fig.3 Crystal structure of $Ni_6(SCH_2CH_2Ph)_{12}$ (a), magnified view of the Ni_6S_{12} core after removing the carbon atoms (b), and illustrative depiction of a crown (c). Green, Ni; yellow, S; gray, C

Surprisingly, we observed that the composition of the product is quite different from that of the gold and silver clusters reported previously. Furthermore, the atomic number ratio of Ni/S corresponds to 1:2, less than 1, which indicates that Ni_6 may not be simply described as a zero-valent Ni cluster. In fact, the complex may be a large coordination complex. XPS was performed to investigate the valence state of nickel in the product. The binding energies of 854.3 eV and 871.4 eV (assigned to $Ni2p_{3/2}$ and $Ni2p_{1/2}$, respectively) indicate that the incorporated nickel is not neutral but close to being divalent ($Ni2p_{3/2}$ and $Ni2p_{1/2}$ for Ni(II)-dodecanethiolate complex: approximately 854.2

eV and 871.5 eV, respectively[29]) (Figure 2b). For neutral nickel, the theoretical binding energies of $2p_{3/2}$ and $2p_{1/2}$ are 852.7 eV and 869.6 eV, respectively. If this result is correct, the Ni in the precursor Ni-phenylethanethiolate complex was not reduced at all by the strong reducing reagent $NaBH_4$. To confirm this result, a control experiment was conducted in which the Ni-phenylethanethiolate complex was synthesized without $NaBH_4$ (the details of the synthesis are provided in the Supporting Information). The as-prepared complex shows a UV/Vis/NIR spectrum that closely matches that of Ni_6 (see Figure 2a). All of the other data (including those obtained by XPS, TGA and XRD) (see Figure 2) are completely identical to those of Ni_6. For further verification, the Ni-phenylethanethiolate complex was also synthesized by reacting $Ni(NO_3)_2$ with 2-phenylethanethiol sped up by NaOH (see method II of the control experiments in the Supporting Information). Interestingly, all of the data (including those obtained by UV/Vis/NIR, XPS, XRD and TGA, see Figure 2) also demonstrate that the product is Ni_6. The above mentioned results indicate that the Ni-phenylethanethiolate complex, Ni_6, is resistant to the strong reducing reagent $NaBH_4$, which was confirmed via further experiments: the addition of up to 3.78 mg (0.1 mmol) $NaBH_4$ does not lead to any distinct change in the UV/Vis/NIR spectra of Ni_6 (Figure 4a). Electrochemical measurements provide thermodynamic evidence for the RRP (see Figure 4b). A highly negative reduction potential at -1.56 V (vs SCE) theoretically suggests that Ni_6 is difficult to reduce. The RRP of the metal-phenylethanethiolate complex, which is not observed in noble metal-phenylethanethiolate complexes (e.g., Au, Ag-phenylethanethiolate complexes[30]) and has not been previously reported, inspired us to investigate its universality among other less noble metal analogues. Metals that are more active than Ni, i.e., Co and Fe, and the less active metal Bi were chosen for the test. First, the metal-phenylethanethiolate complexes were synthesized using the same method used to synthesize Ni_6 (see the Supporting Information); then, hydrated $NaBH_4$ was added into the THF solution of the metal-phenylethanethiolate complexes. Distinct changes in the UV/Vis/NIR spectra were observed upon the addition of the reducing reagent (see Figures 5a, 5b, 5c) in all cases, indicating that these metal salts cannot form stable complexes with phenylethanethiol that are resistant to $NaBH_4$. Thus, the reduction resistance should not be shared by all less noble metal-phenylethanethiolate complexes. A question that naturally arises concerns whether the RRP is shared by all thiolated Ni complexes. To answer this question, we tested the RRP of other Ni-SR complexes (SR: TBBT, TBT, ethanethiolate, hexanethiolate). It was observed that the Ni-TBBT complex has a distinctly different absorption spectrum, see Figure 6a, hinting that it has a different structure than that of Ni_6. After the addition of hydrated $NaBH_4$, the maximum absorption peak was red-shifted by ~10 nm and the absorption intensity decreased notably, demonstrating that Ni-TBBT complex is not stable against hydrated $NaBH_4$ (see Figure 6a). The Ni-TBT complex is even unstable under ambient conditions without the addition of $NaBH_4$ (see Figure 6b). On the other hand, for the Ni-alkanethiolate complexes, the absorption spectra are observed to be the same as the absorption spectrum of Ni_6, indicating structural similarity among the complexes. Indeed, the Ni-ethanethiolate complex was previously revealed to have a similar double-crown structure.[31] Interestingly, it was observed that both the spectral shape and absorption intensity of the Ni-alkanethiolate complex barely change after the addition of hydrated $NaBH_4$ (Figure 6c, d). These experimental results demonstrate that the RRP is not only metal dependent but also thiolate-dependent. For the other three

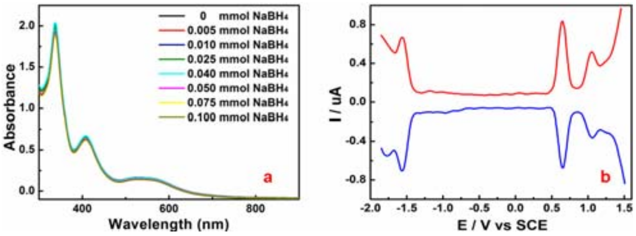

Fig.4 UV/Vis/NIR spectra of $Ni_6(SCH_2CH_2Ph)_{12}$ (in THF) following the successive addition of BH_4^- (a). Differential pulse voltammetry (DPV) of Ni_6 (b).

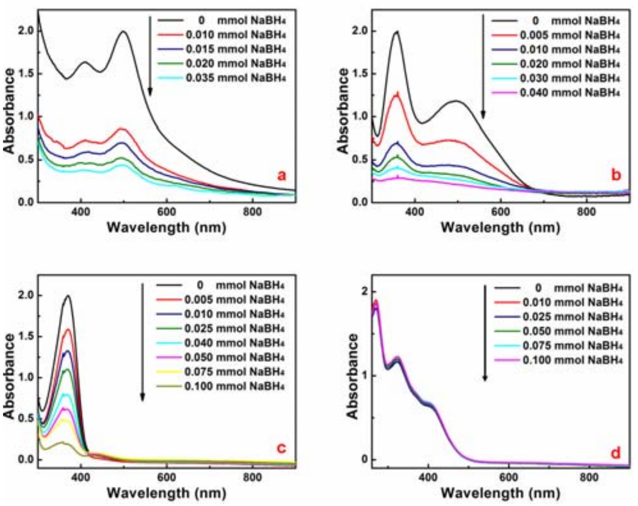

Fig.5 UV/Vis/NIR spectra of Co-PET (a), Fe-PET (b), Bi-PET (c), and Pd-dodecanethiolate (d) complexes (in THF) obtained following the successive addition of BH_4^-.

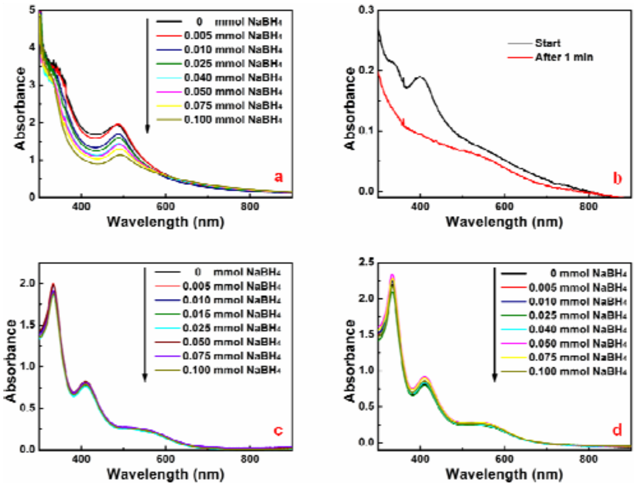

Fig.6 UV-Vis spectra of Ni-TBBT (a), Ni-ethanethiolate (c), and Ni-hexanethiolate (d) complexes (in THF) obtained following the successive addition of BH_4^-. The Ni-TBT complex is very unstable and deteriorates fast (b).

metal complexes in Figure 5a-c, the intrinsic structures are unknown due to the difficulty to grow high qualified single crystal for X-ray diffraction analysis. However, the MALDI-TOF-MS analyses indicate the composition and structure of M-phenylethanethiolate (M: Fe, Co, Bi) complexes are totally different from those of Ni_6, see Figure S1. It is known that both $Ni_6(SCH_2CH_2Ph)_{12}$ and $Ni_6(SC_2H_5)_{12}$[31] have hexameric double-crown-like Ni_6S_{12} cores; thus, it is proposed that the RRP may be related to the exceptional stability of such a structure. It is difficult for Ni-TBBT and Ni-TBT complexes to form hexameric double-crown-like structures due to the steric hindrance caused by tertiary-butyl groups. Therefore, the complexes do not possess the same properties as Ni_6. The double-crown structure of the Ni-thiolate complex has long been known and has attracted great interest over the past five decades,[31-34] but the exceptional stability of the complex has not been fully recognized by the scientific community. At least two facts illustrate the ultra-stability of such a structure. One is that the absorption spectrum of $Ni_6(SCH_2CH_2Ph)_{12}$ (in CH_2Cl_2) does not change dramatically after left standing for seven days under ambient conditions (see Figure S2); the other is that $Ni_6(SCH_2CH_2Ph)_{12}$ does not decompose until reaching a temperature of 205 °C, whereas another stable nanocluster, $Au_{25}(SCH_2CH_2Ph)_{18}$, starts to collapse at 180 °C, as indicated by thermal gravimetric analysis (see Figure S3). The interesting finding that the Pd-dodecanethiolate complex with a double-crown structure[35] is also resistant to aqueous BH_4^- provides further evidence of the structure-property correlation (see Figure 5d).

To the best of our knowledge, Ni(II)-thiolate complexes as catalysts have rarely reported. Herein, we found that reduction-resistant Ni_6 exhibits high catalytic activity toward the reduction of 4-nitrophenol. Importantly, Ni_6 shows remarkably higher catalytic activity than a well-known catalyst, $Au_{25}(SCH_2CH_2Ph)_{18}$,[36-38] at low temperature (0 °C), see figure 7 and Figure S4. At least two additional factors (besides the intrinsic catalysis property of Ni complex) contribute to the superior catalytic properties of $Ni_6(SR)_{12}$. First, the RRP guarantees that the catalytic activity of Ni_6 is kept without any loss during the catalysis process. Secondly, the cavity in the double crown structure of Ni_6 can trap the electron-rich $-NO_2$ of nitrophenol[31] and facilitate the hydrogenation of it. Further investigation on the intriguing catalysis properties of Ni_6 need to be conducted in future. The low-temperature catalytic activity is greatly beneficial to practical applications due to energy savings. In addition, the low cost of Ni gives Ni_6 a remarkable advantage over some noble metal catalysts like $Au_{25}(SCH_2CH_2Ph)_{18}$.

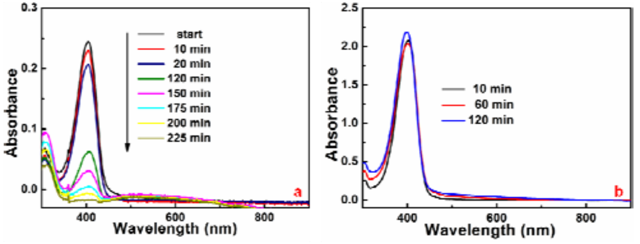

Fig.7 UV/Vis/NIR spectra monitoring the reduction of 4-nitrophenol to 4-aminophenol catalyzed by $Ni_6(SCH_2CH_2Ph)_{12}$ (a) or $Au_{25}(SCH_2CH_2Ph)_{18}$ (b) at approximately 0 °C.

Conclusions

In summary, attempts to synthesize zero-valent Ni nanoclusters using the Brust method resulted in an unexpected material, whose composition was determined to be $Ni_6(SCH_2CH_2Ph)_{12}$ based on MALDI-MS analysis in conjunction with other analytical techniques, including XRD, XPS, and TGA, and whose structure was revealed to be double-crown-like. An interesting finding obtained in this work is the RRP of Ni_6, which has not been previously reported. This property is not universal for all M-phenylethanethiolate complexes (M: metal) or Ni-thiolate complexes but is related to the ultra-stable, double-crown-like structure. Another interesting finding is that the reduction-resistant Ni_6 exhibits greater catalytic activity than a well-known catalyst, $Au_{25}(SCH_2CH_2Ph)_{18}$, at low temperature (0 °C). The low cost and low-temperature catalysis activity of the complex should be greatly beneficial in practical applications and should impart remarkable advantages to Ni_6 over certain existing catalysts (e.g., $Au_{25}(SCH_2CH_2Ph)_{18}$). It is expected that our work will prompt future studies of the synthesis, properties and potential applications of less noble metal nanoclusters.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental section, detailed structural data, stability study of Ni_6 and TGA analysis of $Au_{25}(SCH_2CH_2Ph)_{18}$]. See DOI:10.1039/b000000x/

1 S. P. Graether, M. J. Kuipei, S. M. Gagne, V. K. Walker, Z. C. Jia, B. D. Sykes and P. L. Davies, Nature, 2000, **406**, 325.
2 T. W. Odom, J. L. Huang, P. Kim and C. M. Lieber, Nature, 1998, **391**, 62.
3 J. M. McMahon, Y. M. Wang, L. J. Sherry, R. P. Van Duyne, L. D. Marks, S. K. Gray and G. C. Schatz, J. Phys. Chem. C, 2009, **113**, 2731.
4 Y. Z. Lu and W. Chen, Chem. Soc. Rev., 2012, **41**, 3594.
5 Z. Wu and R. Jin, Acs Nano, 2009, **3**, 2036.
6 S. A. Miller, C. A. Fields-Zinna, R. W. Murray and A. M. Moran, J. Phys. Chem. L., 2010, **1**, 1383.
7 K. Kaya, M. Hashimoto, A. Kato, Y. Nakamura, K. Miyajima, Y. Negishi, S. Nagao and A. Nakajima, Physics and Chemistry of Clusters, 2001, **117**, 12.
8 D. T. Miles and R. W. Murray, Analy. Chem., 2001, **73**, 921.
9 S. Antonello, N. V. Perera, M. Ruzzi, J. A. Gascón and F. Maran, J. Am. Chem. Soc., 2013, **135**, 15585.
10 T. Lee, J. Liu, N. Chen, R. P. Andres, D. B. Janes and R. J. Reifenberger, Nanopart. Res., 2000, **2**, 345.
11 X. Nie, H. Qian, Q. Ge, H. Xu and R. Jin, Acs Nano, 2012, **6**, 6014.

12 X. L. Chen, X. M. Meng, S. X. Wang, Y. L. Cai, Y. F. Wu, Y. Feng, M. Z. Zhu and Q. X. Guo, Dalton Trans., 2013, **42**, 14819.
13 M. Wang, Z. Wu, J. Yang, G. Z. Wang, H. Z. Wang and W. P. Cai, Nanoscale, 2012, **4**, 4087.
14 D. Maity, P. Chandrasekharan, P. Pradhan, K. H. Chuang, J. M. Xue, S. S. Feng and J. Ding, J. Mater. Chem., 2011, **21**, 14717.
15 Z. Wu, M. A. MacDonald, J. Chen, P. Zhang and R. Jin, J. Am. Chem. Soc., 2011, **133**, 9670.
16 M. Zhu, E. Lanni, N. Garg, M. E. Bier and R. Jin, J. Am. Chem. Soc., 2008, **130**, 1138.
17 P. R. Nimmala and A. Dass, J. Am. Chem. Soc., 2011, **133**, 9175.
18 I. Dolamic, S. Knoppe, A. Dass and T. Burgi, Nature Commun., 2012, **3**, 798.
19 C. Zeng, Y. Chen, G. Li and R. Jin, Chem. Commun., 2014, **50**, 55.
20 E. G. Mednikov and L. F. Dahl, Small, 2008, **4**, 534.
21 H. Qian and R. Jin, Chem. Mater., 2011, **23**, 2209.
22 Z. Wu, E. Lanni, W. Chen, M. E. Bier, D. Ly and R. Jin, J. Am. Chem. Soc., 2009, **131**, 16672.
23 A. Desireddy, B. E. Conn, J. S. Guo, B. Yoon, R. N. Barnett, B. M. Monahan, K. Kirschbaum, W. P. Griffith, R. L. Whetten, U. Landman and T. P. Bigioni, Nature, 2013, **501**, 399.
24 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, J. Chem. Soc. Chem. Commun., 1944, **3**, 801.
25 F. Parker, J. E. F. Weaver, F. McCallum, C. A. Fields-Zinna, and R.W. Murray, Langmuir 2010, **26**, 13650.
26 R. Jin, H. Qian, Z.Wu, Y. Zhu, M. Zhu, A. Mohanty, N. Garg, J. Phys. Chem. Lett. 2010, 1, 2903.
27 X．Yuan, B. Zhang, Z. Luo, Q. Yao, D. T. Leong, Ning Yan, and J. Xie, Angew. Chem. Int. Ed. 2014, 53, 4623.
28 H. N. Kagalwala, E. Gottlieb, G. Li, T. Li, R. Jin and S. Bern-hard, Inorg. Chem., 2013, **52**, 9094\.
29 S. Noel, F. Houze, L. Boyer, Z. Mekhalif, J. Delhalle and R. Caudano, IEEE Transactions on Components and Packaging Technology, 1999, **22**, 79.
30 Wu, Angew. Chem. Int. Ed., 2012, **51**, 2934.
31 P. Woodward, L. F. Dahl, E. W. Abel and B. C. Crosse, J. Am. Chem. Soc., 1965, **87**, 5251.
32 P. Alemanyt and R. Hoffmann, J. Am. Chem. Soc., 1993, **115**, 8290.
33 F. F. Jian, K. Jiao, Y. Li, P. S. Zhao and L. D. Lu, Angew. Chem. Int. Ed., 2003, **42**, 5722.
34 H. L. Xiao, F. F. Jian and K. J. Zhang, Bull. Korean Chem. Soc., 2009, **30**, 846.
35 Z. Q. Yang, A. B. Smetana, C. M. Sorensen and K. J. Klabunde, Inorg. Chem., 2007, **46**, 2427.
36 Y. Zhu, H. Qian, B. A. Drake and R. Jin, Angew. Chem. Int. Ed. 2010, **49**, 1295.
37 A. Shivhare, J. Ambrose, H. Zhang, R. W. Purves and R. W. J. Scott, Chem. Commun., 2013, **49**, 276.
38 M.-B. Li, S.-K. Tian and Z.Wu, Nanoscale, 2014, **6**, 5714.

TOC

$Ni_6(SCH_2CH_2Ph)_{12}(Ni_6)$ was synthesized using three different methods and fully characterized, importantly, the reduction-resistance and reduction-catalysis properties of Ni_6 were revealed.