Oxidation Catalysts

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Composition-Dependent Electrocatalytic Activity of Pt-Cu Nanocube Catalysts for Formic Acid Oxidation**

Dan Xu, Stoyan Bliznakov, Zhaoping Liu, Jiye Fang, and Nikolay Dimitrov**

Shape-control synthesis of metallic nanocrystals (NCs) has received extensive interest ever since the catalytic performances of nanoparticles (NPs) were found to be strongly related with the facets terminated the surface of the particles.[1–6] For example, tetrahexahedral platinum NCs exhibit an unusual high electrooxidation activity for formic acid and ethanol compared with spherical Pt NCs.[5] We have also demonstrated that $Pt_{60}Cu_{40}$ nanocubes (NCbs) exhibit superior electrochemical activity towards the methanol oxidation reaction compared to similarly sized spherical Pt NCs.[6] On the other hand, it is an urgent task to develop substitutes for pure platinum catalysts owing to high cost and the rarity. In recent years, less-expensive platinum-based binary alloy NPs have been elaborately prepared and intensively studied.[7–11] Along with particle shape, the alloy composition is also an extremely important characteristic with respect to the catalytic activity.[11–16] Nevertheless, it is still a great challenge to synthesize high-quality platinum-based bimetallic NCbs with a precisely controlled composition. Herein, we present a successful preparation of various compositions of Pt_xCu_{100-x} NCbs using a versatile colloidal method, and also our investigation of their electrochemical activity towards formic acid oxidation.

Pt_xCu_{100-x} NCbs were synthesized using our recently developed strategy.[6] Generally, platinum (II) acetylacetonate [$Pt(acac)_2$] and copper(II) acetylacetonate [$Cu(acac)_2$] in 1-octadecene (ODE) were co-reduced by 1,2-tetradecanediol (TDD) in the presence of tetraoctylammonium bromide (TOAB), oleylamine (OLA), and 1-dodecanethiol (DDT). NCbs of various compositions were prepared by precisely tuning the ratio of metal precursors, the amount of stabilizing/coordination agents, and the reaction temperature. The compositions and morphologies of the products are highly dependent upon the experimental conditions. Table 1 summarizes the experimental parameters.

Table 1: Experimental conditions for preparing $Pt_xCu_{(100-x)}$ nanocubes with different compositions.[a]

Pt_xCu_{100-x}	[$Pt(acac)_2$]	[$Cu(acac)_2$]	TOAB	OLA	DDT	TDD	T [°C]	t [min]
$Pt_{80}Cu_{20}$	0.09	0.01	1.23	0.36	0.06	0.50	220	20
$Pt_{70}Cu_{30}$	0.08	0.02	1.10	0.36	0.05	0.50	220	20
$Pt_{60}Cu_{40}$[b]	0.05	0.05	0.60	0.94	0.05	0.50	230	20
$Pt_{54}Cu_{46}$	0.04	0.05	0.58	0.90	0.04	0.50	230	20

[a] All values are in mmol unless indicated otherwise. acac = acetylacetonate, DDT = 1-dodecanethiol, TDD = 1,2-tetradecanediol. [b] Reference data were taken from our previous report.[6]

Different platinum-based bimetallic alloys show diverse nucleation and growth mechanisms.[11,17–20] First, the as-prepared NCbs may be evolved from platinum atoms as nucleation seeds because only NCbs with a dominant platinum component could be produced. Furthermore, precursors with a Pt/Cu feeding ratio of 1:1 only produce $Pt_{60}Cu_{40}$ NCbs. To further increase the platinum component, much higher concentration of platinum precursor is required in unstoichiometric amounts; for example, $Pt_{70}Cu_{30}$ and $Pt_{80}Cu_{20}$ NCbs need 4:1 and 9:1 of Pt/Cu inputs, respectively.

Second, the amount of stabilizers (TOAB and OLA) and coordination agent (DDT) also need to be finely tuned to generate NCbs with desired composition. Among these factors, we believe that the amount of TOAB is the key to ensure high-quality NCbs.[6] Pt_xCu_{100-x} NCbs with a larger platinum constituent require more TOAB. A good example at this point is that 0.58 mmol TOAB was enough to stabilize $Pt_{54}Cu_{46}$ NCbs, whereas as high as 1.23 mmol of TOAB was necessary to develop $Pt_{80}Cu_{20}$ NCbs. OLA, the other stabilizer used, also plays an important role in the present system. Our results indicate that the alloy NCbs with a larger platinum constituent need less OLA. For example, 0.90 and 0.94 mmol of OLA were required to produce $Pt_{54}Cu_{46}$ and $Pt_{60}Cu_{40}$ NCbs, respectively; however, 0.36 mmol OLA was sufficient for the preparation of $Pt_{70}Cu_{30}$ and $Pt_{80}Cu_{20}$ NCbs. In all of the samples, it was observed that it is difficult to stabilize the NPs in the colloidal system without OLA, whereas excessive OLA

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[*] D. Xu, Dr. S. Bliznakov, Prof. J. Fang, Prof. N. Dimitrov
Department of Chemistry
State University of New York at Binghamton
Binghamton, New York 13902 (USA)
Fax: (+1) 607-777-4478
E-mail: jfang@binghamton.edu
dimitrov@binghamton.edu
Dr. Z. Liu
Ningbo Institute of Materials Technology and Engineering
Chinese Academy of Sciences
Ningbo, Zhejiang 315211 (China)

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results in larger NPs with fewer NCbs. We therefore conclude that OLA and TOAB offer a synergistic stabilizing effect on the development of high-quality NCbs.

Third, the product morphology is also directly associated with the amount of coordination agent DDT, which can synchronize the reduction rate of platinum and copper ions during the reaction. The results indicate that in the present system, the amount of DDT required varies over an extremely narrow region. For $Pt_{54}Cu_{46}$ and $Pt_{80}Cu_{20}$ NCbs, 0.04 and 0.06 mmol of DDT were used to facilitate the uniform products. For NCbs with $54\% < Pt < 80\%$, 0.05 mmol of DDT was enough. Furthermore, less DDT produces smaller NPs with irregular morphology, whereas excessive DDT leads to larger NPs. TDD as a reducing agent can accelerate the nucleation rate, which is also essential in the evolution of high-quality NCbs. In our case, a constant amount of TDD (0.5 mmol) served for preparation of all the NCbs. It is worth mentioning that the effect of TDD on NP growth is opposite to that of DDT: Insufficient TDD leads to produce larger partial-filled octapods, whereas excessive TDD increases the population of smaller NCbs and accordingly broadens the particle size distribution.

Finally, the quality of NCbs are also sensitive to the reaction temperature and time. They should be kept at 230 °C for 20 min to prepare the best $Pt_{54}Cu_{46}$ and $Pt_{60}Cu_{40}$ NCbs, and 220 °C for 20 min for $Pt_{70}Cu_{30}$ and $Pt_{80}Cu_{20}$ NCbs. For $Pt_{54}Cu_{46}$ and $Pt_{60}Cu_{40}$ systems, higher temperatures (up to 250 °C) result in larger NPs with less NCbs, and lower temperatures (down to 210 °C) lead to a certain amount of smaller NPs with irregular shape. Moreover, lower reaction temperatures favor formation of NCbs with a higher platinum content.

Figure 1 shows X-ray diffraction (XRD) patterns of five samples with different compositions, including pure platinum. The well-defined (200) peaks suggest that most of the NPs are cubic in shape and are deposited perfectly flat on the surface-polished silicon wafer. The patterns shift to higher positions of 2θ with increasing copper composition, which is in agreement with Vegard's law.[21,22] On the basis of the full-width at half-maximum (FWHM), the crystalline size was estimated as 7–9 nm, which is in good agreement with the TEM observation. The right panels in Figure 1 show a 100×100 nm^2 square area of TEM images (see also the Supporting Information, Figure S1), thus indicating that all five samples are mainly composed of NCbs with narrow size distributions (Supporting Information, Figure S1). The compositions were evaluated using an energy-dispersive X-ray spectroscopy (EDS), and the results are presented in the Supporting Information, Figure S2.

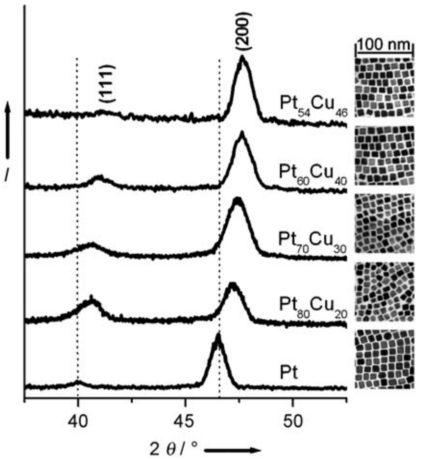

Figure 1. XRD patterns of Pt and Pt_xCu_{100-x} nanocubes of different compositions. Insets: the corresponding TEM images. The scale bar (100 nm) applies for all of the images.

Typical features for hydrogen underpotential formation/stripping (H_{UPD})[23] are clearly observed in the cyclic voltammetry (CV) curves (Supporting Information, Figure S3) that were measured for all catalysts at a sweep rate of 50 mV s^{-1} in 0.1 M $HClO_4$ solution. The electrochemically active surface area (ECASA) for each electrode was calculated from the corresponding charge of H_{UPD} (also known as "hydrogen adsorption") peak divided by the formation charge of a H_{UPD} monolayer deposited on polycrystalline platinum surface (210 μC cm^{-2}).[15] ECASA values determined accordingly were used for normalization of the voltammetric currents, corresponding to the formic acid electrooxidation on the catalyst surfaces. As presented in Figure 3 b, the CV curve for formic acid electrooxidation on $Pt_{80}Cu_{20}$ NCbs is virtually identical to those obtained on pure metallic platinum or palladium surfaces. (For CV curves of all the catalyst compositions, see the Supporting Information, Figure S4.) Generally, the presence of hysteresis between the positive and negative scans in the curves is an indication of CO adsorption. Furthermore, a sharp increase of the current at 0.33 V and decrease at 0.44 V when the potential was swept in the negative and positive direction is attributed to the OH^- desorption and adsorption process, respectively. The electrocatalytic activity in this work is defined as a maximum current density derived from the negative scan of the CV curves at a sweep rate of 50 mV s^{-1}, measured in 0.1 M $HClO_4$ + 2.0 M HCOOH. It should be noted that the catalytic activity of the NCb catalysts examined herein is about one order of magnitude higher than that of Pd NPs,[24] which is most likely due to the nafion-free route in catalyst preparation.

Having a narrow size and shape distribution, it is anticipated that the electrochemical activity of these NCbs towards formic acid oxidation may directly depend on the NC composition. Figure 2 illustrates a compositional dependence of the peak current density towards formic acid oxidation from these Pt_xCu_{100-x} ($x = 54$–80 atom %) NCbs. Furthermore, it was confirmed that the electrocatalytic activity of $Pt_{80}Cu_{20}$ NCbs towards formic acid oxidation exceeds that determined from the pure Pt NCbs. The enhanced activity of this bimetallic alloy could be due to a shift of the onset potentials of OH^- electrosorption to more positive values as a result of alloying, owing to the lower tendency of an alloy surface to chemisorb OH^-.[25] The OH^- ion is a poison for formic acid oxidation, as it most likely blocks adjacent vacant surface sites needed for the decomposition of formate (an intermediate in the oxidation process) to CO_2.[26,27] Figure 2 clearly indicates a decreasing activity of the catalysts with the increase of the copper content in the Pt_xCu_{100-x} NCbs. This tendency is in agreement with the negative shift of the onset potential for OH^- electrosorption with the increase of the

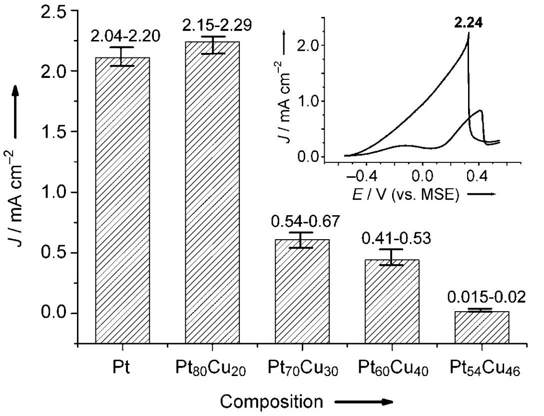

Figure 2. Peak current density of formic acid oxidation as a function of Pt$_x$Cu$_{100-x}$ nanocube composition. (For detailed data see the Supporting Information, Figure S4.) Inset: Cyclic voltammetry curve measured in 0.1 M HClO$_4$ + 2.0 M HCOOH solution at 50 mV s^{-1} on the Pt$_{80}$Cu$_{20}$ nanocube catalyst.

copper content of the samples (see the Supporting Information, Figure S4).

Figure 3 a shows comparative stability test results of electrodes prepared from NCbs of Pt$_{80}$Cu$_{20}$ alloy and of pure platinum with similar size. It can be clearly seen that the catalytic activity of the platinum catalyst rapidly decreases, and its current density reaches values as low as 1.9 mA cm^{-2} after 20.8 h of cycling (1700 cycles) in the potential range of -0.55–$+0.55$ V at a sweep rate of 50 mV s^{-1}. Such behavior for the pure platinum catalysts is generally attributed to a strong CO adsorption and (in turn) poisoning of the active surface. A substantially improved stability is demonstrated by the bimetallic Pt$_{80}$Cu$_{20}$ catalyst, showing that the activity of this catalyst is higher than original activity of the pure Pt NCbs even after 300 h of cycling (24546 cycles) in the working solution. The enhanced CO tolerance from this bimetallic catalyst is most likely due to the electronic ligand-effect mechanism; that is, the electronic properties of platinum are modified by alloy orbital overlapping, resulting in a weakening of the binding strength of CO adsorbed on Pt-Cu catalyst. According to a report of other platinum-based bimetallic catalysts,[28] such overlapping leads to an improved electrocatalytic activity and/or stability of some bimetallic catalysts towards formic acid oxidation. The decrease of the activity after 300 h of cycling for the Pt$_{80}$Cu$_{20}$ NCbs (Figure 3 a) is also expected, and can be attributed to the formation of a platinum skin layer on the surface of NCbs as a result of long-term electrochemical cycling in acidic electrolytes.[15] The platinum skin formation was caused either by dissolution of platinum from the alloy followed by redeposition and rearrangement on the surface,[15] and/or by electrochemical dissolution of the less noble component from the alloy accompanied by regrouping of platinum atoms.[29] In our experiments, a 50 % reduction of the amount of copper after the stability tests is ascertained based on an EDS analysis (Supporting Information, Figure S5). Figure 3 b presents CV curves for Pt NCbs before and after the cycling, and that for Pt$_{80}$Cu$_{20}$ NCbs after a long-term cycling, suggesting that both types of the CV curves, measured on the pure platinum and the Pt$_{80}$Cu$_{20}$ NCbs, are identical after the stability tests. These results further support the formation of a platinum skin on the surface of bimetallic NCbs after a long-term cycling in an acidic solution.

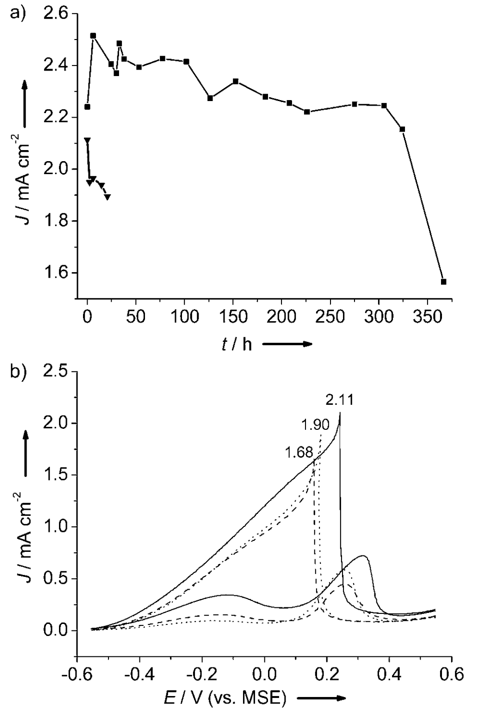

Figure 3. a) I–t characteristics of Pt$_{80}$Cu$_{20}$ (■) and Pt nanocubes (▼). b) Cyclic voltammograms of formic acid oxidation on Pt nanocubes before (——) and after (•••••) a stability test, and on Pt$_{80}$Cu$_{20}$ nanocubes (-----) after a stability test.

In summary, bimetallic Pt$_x$Cu$_{100-x}$ NCbs ($x = 54$–80 atom %) were successfully prepared using a facile colloidal approach, and a comparative investigation of the electrocatalytic activity and long-term NCb stability in the formic acid oxidation process was carried out. As a key finding, we have identified Pt$_{80}$Cu$_{20}$ NCbs as the best electrocatalyst on the basis of the maintainable electrocatalytic activity (which is slightly superior to that of pure Pt NCbs) and remarkable long-term stability (ca. 300 h versus 3 h for Pt NCbs). Such superior overall electrocatalytic performance, and especially the higher CO tolerance, suggests that the Pt$_{80}$Cu$_{20}$ NCbs could be regarded as a promising anode catalyst in the fuel cell industry.

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[1] H. Song, F. Kim, S. Connor, G. A. Somorjai, P. Yang, *J. Phys. Chem. B* **2005**, *109*, 188 – 193.
[2] Y.-J. Zhao, S.-S. Chng, T.-P. Loh, *J. Am. Chem. Soc.* **2007**, *129*, 492 – 493.
[3] R. Narayanan, M. A. El-Sayed, *Nano. Lett.* **2004**, *4*, 1343 – 1348.

[4] M. Subhramannia, K. Ramaiyan, V. K. Pillai, *Langmuir* **2008**, *24*, 3576–3583.
[5] N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding, Z. L. Wang, *Science* **2007**, *316*, 732–735.
[6] D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou, K. Sun, *Angew. Chem.* **2009**, *121*, 4281–4285; *Angew. Chem. Int. Ed.* **2009**, *48*, 4217–4221.
[7] B. Lim, M. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu, Y. Xia, *Science* **2009**, *324*, 1302–1305.
[8] T. Pellegrino, A. Fiore, E. Carlino, C. Giannini, P. D. Cozzoli, G. Ciccarella, M. Respaud, L. Palmirotta, R. Cingolani, L. Manna, *J. Am. Chem. Soc.* **2006**, *128*, 6690–6698.
[9] F. Zhao, M. Rutherford, S. Y. Grisham, X. Peng, *J. Am. Chem. Soc.* **2009**, *131*, 5350–5358.
[10] Z. Peng, H. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 7542–7543.
[11] K. Ahrenstorf, O. Albrecht, H. Heller, A. Kornowski, D. Görlitz, H. Weller, *Small* **2007**, *3*, 271–274.
[12] I.-S. Park, K.-S. Lee, J.-H. Choi, H.-Y. Park, Y.-E. Sung, *J. Phys. Chem. C* **2007**, *111*, 19126–19133.
[13] H. Ye, R. M. Crooks, *J. Am. Chem. Soc.* **2007**, *129*, 3627–3633.
[14] W. Chen, J. Kim, S. Sun, S. Chen, *J. Phys. Chem. C* **2008**, *112*, 3891–3898.
[15] W. Chen, J. Kim, S. Sun, S. Chen, *Langmuir* **2007**, *23*, 11303–11310.
[16] Y. Li, X. L. Zhang, R. Qiu, R. Qiao, Y. S. Kang, *J. Phys. Chem. C* **2007**, *111*, 10747–10750.
[17] K. Ahrenstorf, H. Heller, A. Kornowski, J. A. C. Broekaert, H. Weller, *Adv. Funct. Mater.* **2008**, *18*, 3850–3856.
[18] E. V. Shevchenko, D. V. Talapin, H. Schnablegger, A. Kornowski, Ö. Festin, P. Svedlindh, M. Haase, H. Weller, *J. Am. Chem. Soc.* **2003**, *125*, 9090–9101.
[19] M. Chen, J. P. Liu, S. Sun, *J. Am. Chem. Soc.* **2004**, *126*, 8394–8395.
[20] B. Stahl, J. Ellrich, R. Theissmann, M. Ghafari, S. Bhattacharya, H. Hahn, N. S. Gajbhiye, D. Kramer, R. N. Viswanath, J. Weissmüller, H. Gleiter, *Phys. Rev. B* **2003**, *67*, 014422.
[21] C. Bock, C. Paquet, M. Couillard, G. A. Botton, B. R. MacDougall, *J. Am. Chem. Soc.* **2004**, *126*, 8028–8037.
[22] R. J. Best, W. W. Russell, *J. Am. Chem. Soc.* **1954**, *76*, 838–842.
[23] K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz, N. M. Markovic, *Electrochim. Acta* **2008**, *53*, 3181–3188.
[24] V. Mazumder, S. Sun, *J. Am. Chem. Soc.* **2009**, *131*, 4588–4589.
[25] S. Gottesfeld in *Fuel Cell Catalysis—A Surface Science Approach* (Ed.: M. Koper), Wiley, Hoboken, NJ, **2009**, p. 6 (The Wiley Series on Electrocatalysis and Electrochemistry).
[26] A. Cuesta, M. Escudero, B. Lanova, H. Baltruschat, *Langmuir* **2009**, *25*, 6500–6507.
[27] A. Miki, S. Ye, M. Osawa, *Chem. Commun.* **2002**, 1500–1501.
[28] W. Chen, J. Kim, S. Sun, S. Chen, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2779–2786.
[29] W. Chen, J. Kim, L.-P. Xu, S. Sun, S. Chen, *J. Phys. Chem. C* **2007**, *111*, 13452–13459.