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Magnetically Recyclable Fe@Pt Core−Shell Nanoparticles and Their Use as Electrocatalysts for Ammonia Borane Oxidation: The Role of Crystallinity of the Core

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Platinum-group metals, especially Pt, are excellent and versatile catalysts in various important reactions but occur at very low levels of abundance in nature.[1] Therefore, further enhancement of their utilization efficiency, catalytic activity, and recycle strategy has long been of fundamental importance.[2] Arranging noble metals as thin shells on proper non-noble-metal cores not only greatly reduces their usage but also could significantly modify (enhance) their catalytic properties, as a result of the synergistic structural and electronic effects of the two metals (via the so-called strain and ligand effects).[3] Iron is well-known for its abundance and magnetism; when it is successfully employed as the core, the obtained catalysts naturally combine the advantages of low cost and an easy recovery function derived from use of an external magnetic field.[4] Compared with its crystallized counterpart, a metal in an amorphous state holds many more lattice defects and thus could give birth to distinct effects in mediating the electronic structure and/or tuning the atomic arrangement and coordination of the outer shell.[5] On the basis of this concept, localization of Pt as a thin shell on an amorphous Fe core could be expected to not only obviously decrease the usage of Pt but also enhance its catalytic activity.[2g] Although many studies have been focused on core−shell structured nanoparticles (NPs), employing iron as core has been rarely reported, to say nothing of amorphous iron. Thus, the synthesis of Fe@Pt core−shell NPs with iron cores in different crystal states and a comparison of their catalytic activities are of great interest.

Hydrogen represents an important alternative-energy feedstock for both environmental and economic reasons, and when it is combined with fuel-cell technology, very efficient energy conversion can be achieved.[6] Nowadays, proton-exchange membrane fuel cells (PEMFCs) represent the most advanced fuel-cell technology.[2c−e,6c] Although pure H_2 is an ideal fuel for PEMFC systems, hydrogen-storage technologies are still on the way to matching practical requirements.[7] It is now widely admitted that using other liquid fuels to replace hydrogen for feeding fuel-cell anodes would have many advantages in terms of fuel-cell system simplicity, high mass and volume densities, and safety.[8] Besides its high hydrogen density (19.6 wt % H_2, which exceeds that of gasoline), ammonia borane (NH_3BH_3, AB) is safe, nontoxic, chemically stable, easy to transport in its dry state, and highly soluble in water, making it emerge as a potential fuel for fuel cells.[9] In regard to a novel fuel cell using aqueous AB as the fuel, development of efficient and economical catalysts is highly desired for its practical application.[10]

Herein, we report a facile route for synthesizing carbon-supported Fe@Pt core−shell catalysts with Fe cores in different crystal states. Unexpectedly, in contrast to its crystallized counterpart, iron in the amorphous state exerts a distinct and powerful ability as a core for the Fe@Pt NPs. The resultant NPs are far more active for AB oxidation (up to 354%) than the commercial Pt/C catalysts.

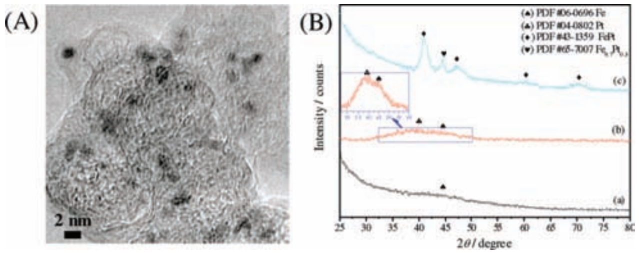

Figure 1. (A) TEM image of carbon-supported Fe@Pt NPs and (B) XRD patterns of (a) Fe cores reduced by $NaBH_4$ and NH_3BH_3 before Pt replacement, (b) Fe@Pt NPs, and (c) Fe@Pt NPs after heat treatment at 823 K for 3 h under an argon atmosphere.

The carbon-supported Fe@Pt NPs were synthesized using a sequential reduction process.[11] The Fe core was first synthesized by reduction of $FeSO_4$ using $NaBH_4$ in an aqueous solution containing well-dispersed carbon in the presence or absence of AB in air at room temperature. Second, the atoms in the outer layer of the Fe core were sacrificed to reduce Pt^{2+}. Under such conditions, a Pt shell can be expected to form around the Fe core.[11]

Figure 1A shows a transmission electron microscopy (TEM) image of a representative sample. It was found that the NPs are isolated from each other with high dispersion on the carbon substrate and that the particle size is ∼2 nm. An X-ray diffraction (XRD) study showed that the Fe core reduced by $NaBH_4$ in the presence of AB is in the amorphous state [Figure 1B, trace (a)], whereas without AB the Fe core is in a crystallized state,[11] which is in good agreement with the corresponding selected-area electron diffraction (SAED) patterns.[11] This difference in crystallinity of the iron core seems to have a dramatic effect on the catalytic activity of the Fe@Pt NPs, as discussed below. Trace (b) in Figure 1B is the XRD pattern of the Fe@Pt NPs, in which the new, broad peak at 39.8° can be attributed to the replacement of Pt. Sharp diffraction peaks of the platinum shell are not detected, possibly because the layer of platinum is too thin to make significant peaks. This XRD data is consistent with both the core−shell structure and phase-separated monometallic particles, because if the NPs were in a FePt alloy phase, the diffraction peaks should lie between those of iron and platinum. However, we can exclude the phase-separated species from consideration on the basis of the following experiments. (1) Annealing the Fe@Pt NPs at 823 K for 3 h under an argon atmosphere converts the sample into FePt alloy. In contrast, this did not occur when intimately mixed physical mixtures of Fe and Pt NPs of the same composition were heated under the conditions described above.[11] (2) The catalytic activity of the physical mixture of the Fe and Pt NPs is quite different from that of the core−shell NPs.[11]

The X-ray photoelectron spectroscopy (XPS) method was employed to further confirm the core−shell structure.[11] The XPS study (Figure S5a) reveals that the as-made NPs include only one type of Pt species. The Pt $4f_{7/2}$ and Pt $4f_{5/2}$ binding energies correspond to Pt^0. On the

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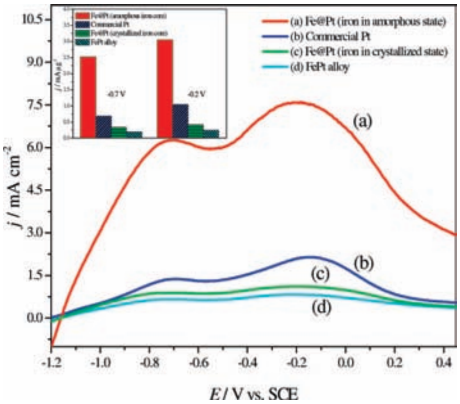

Figure 2. Comparison of catalytic activities for AB oxidation of (a) carbon-supported Fe@Pt NPs with amorphous iron cores, (b) commercial Pt, (c) Fe@Pt NPs with crystallized iron cores, and (d) the FePt alloy. Electrolyte: 0.01 M NH_3BH_3/1 M NaOH; sweep rate: 10 mV s^{-1}; rotation rate: 1600 rpm; room temperature; Pt loading: 24.6 μg cm^{-2}. Inset: Comparison of the mass activities at −0.7 and −0.2 V.

contrary, two types of Fe species are detected (Figure S5b): Fe^0 (Fe $2p_{3/2}$ located at 706.75 eV) and oxidized Fe (Fe $2p_{3/2}$ located at 710.7 eV). These oxidized Fe species are those from the outer layer of the iron core. In order to probe the core−shell structure of the particles, we conducted Ar sputtering experiments. The results show that the Fe/Pt molar ratio increases after Ar sputtering, which indicates that more Pt atoms were etched than Fe atoms. This result is in accordance with a core−shell structure including a core mainly made of Fe and a shell mainly made of Pt.

To compare the activities of the two types of NPs described above, we evaluated the electrooxidation reaction of AB. Figure 2 shows the polarization curves in a 0.01 M AB/1 M NaOH solution obtained using a rotating-disk electrode. Unexpectedly, the Fe@Pt NPs with the amorphous Fe cores exhibit much-enhanced catalytic activity in terms of normalized current per unit surface area of Pt, as determined from hydrogen adsorption (Figure 2a).[11] Its maximum current is more than 3 times (as high as 354%) larger than that of a commercial Pt/C catalyst (Figure 2b). On the contrary, the catalytic activity of Fe@Pt NPs with the crystallized Fe core Figure 2c) is rather poor, even less than that of commercial Pt/C. This is because, compared with its crystalline counterpart, iron in the amorphous state holds many more lattice defects and thus could give birth to distinct effects in mediating the electronic structure and/or tuning the atomic arrangement and coordination of the outer shell. As in a core−shell architecture, the Fe metal is confined and trapped inside the Pt shell, and thus, the conventional bifunctional mechanism cannot be implicated because AB oxidation necessarily occurs entirely on the Pt surface sites. For comparison, after the Fe@Pt NPs with amorphous iron cores were annealed at 823 K for 3 h, the obtained FePt alloy (Figure 2d) suffered an obvious decrease in catalytic activity, to a value even lower than that for Fe@Pt NPs with crystallized Fe cores. This indicates that for AB oxidation, the invoked bifunctionality of the coexisting Fe and Pt on the FePt alloy surface is inferior to the ligand and surface strain effects in the core−shell NPs. Moreover, when mass activity was used as the indicator of electrocatalyst quality (Figure 2 inset), only Fe@Pt NPs with the amorphous Fe cores exhibited catalytic activity greater than that of the commercial Pt/C catalysts. This result further confirms the role of amorphous iron as the core in Fe@Pt core−shell NPs used as electrocatalysts for AB oxidation.

The stability or recycle ability is of great importance for the practical application of catalysts. In this sense, we tested the polarization curves of the Fe@Pt NPs with amorphous iron cores over 100 cycles and after they were kept for three weeks in air. It was found that there was no significant current density (catalytic activity) decrease in either case. In addition, it should be noted that this high-performance catalyst is magnetic and thus can be easily recovered by an external magnetic field.[11]

In summary, we report a facile route for the synthesis of carbon-supported Fe@Pt core−shell NPs. Surprisingly, iron in the amorphous state proved to be a distinct and powerful core for the Pt-based core−shell-structured catalyst. The resultant Fe@Pt NPs combine high catalytic activity, low cost, long-term stability, and easy recovery. These encouraging findings could be expanded to other system or reactions and could open up a new direction in catalysis. In addition, as catalysts, these NPs could be used for optical, magnetic, and electrical applications.

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Supporting Information Available: Experimental procedures and XRD, TEM, electrochemical active surface, stability, and recycle results for the catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) See the Supporting Information.

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