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COMMUNICATION

One-step and rapid synthesis of "clean" and monodisperse dendritic Pt nanoparticles and their high performance toward methanol oxidation and *p*-nitrophenol reduction†

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Well-defined and monodisperse dendritic platinum nanoparticles (DPNs) are successfully prepared by a rapid, one-step, and efficient route with high yield in aqueous solution, wherein neither organic solvents nor surfactants are employed, ensuring the as-made DPNs definitely have "clean" surfaces, allowing them to exhibit high activity for both methanol oxidation and *p*-nitrophenol reduction. This proposed strategy for simple and facile preparation of "clean" metal nanocatalysts paves the way for accurately evaluating and further improving their intrinsic catalytic activity.

Platinum-group metals (PGMs), especially Pt, are excellent and versatile catalysts in various important reactions, such as fuel cells and synthesis of fine chemicals, but they occur at very low levels of abundance in nature.[1] Therefore, further enhancement of their catalytic efficiency and utilization efficiency by fine tuning the size, shape, surface morphology, *etc.*, has long been of fundamental importance.[2] In this regard, Pt nanostructures with specific structural features, such as nanospheres,[3] nanofibers,[4] nanowires,[5] nanotubes[6] and nanosheets,[7] have been synthesized. However, most of the synthetic methods reported to date rely heavily on organic solvents and surfactants, which are uneconomic, are not environmentally friendly, and most seriously would poison the sample surface. The surface is vital for applications such as catalysis, where surface active sites are urgently needed.[8] Consequently, additional thermal and oxidative approaches are indispensable to "clean" the catalyst, which not only complicate and prolong the synthesis process, but also lead to unwanted size and shape changes, and are not highly reproducible.[8a,b] Although efforts to develop synthesis protocols free of post-treatment processes have led to significant successes,[2a,9] some novel type of Pt nanostructures, *e.g.*, monodisperse dendritic Pt nanoparticles (DPNs), providing new alternatives for scientists to obtain high-efficiency catalysts, could only be prepared with multistep and complex procedures in the presence of pre-synthesized seeds, organic solvents, and especially surfactants as structure-directing agents.[10] Therefore, the development of a mild, template- and surfactant-free strategy for one-step synthesis of "clean" DPNs in aqueous solution and further discovering the intrinsically catalytic activities of DPNs are highly desirable and technologically important.

Herein, we propose a rapid, one-step, and efficient route to synthesize surfactant-free DPNs with high yield in aqueous solution. The as-synthesized DPNs catalysts possess definitely "clean" surfaces and thus exert excellent catalytic activity in both methanol oxidation and *p*-nitrophenol reduction.

In a typical synthesis, the DPNs were generated as a black suspension just by mixing the aqueous solution of chloroplatinic acid (H_2PtCl_6), sodium hydroxide (NaOH) and ascorbic acid (AA) together and then heating the mixture in a water-bath at 60 °C for only 10 min without disturbance. This is a truly simple and unique process which is quite different from the traditional seed-mediated growth strategy. The details of the synthetic procedure are given in the Supporting Information.†

The morphology and structure of the as-synthesized sample were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Fig. 1A and 1B obviously show that the entire resulting sample is definitely endowed with dendritic morphology, indicating that the production yield of DPNs is nearly 100%. The DPNs are almost monodisperse with a mean particle size of 31.1 nm (Fig. S1A†), which is further confirmed by the dynamic light scattering data (Fig. S2†). The high-magnification TEM image (Fig. 1B) clearly shows that each of the DPNs is assembled with a primary Pt nanoparticle (NP) having an average dimension of 3.7 nm in diameter (Fig. S1B†). The high-resolution TEM (HRTEM) image shows that the DPNs are in the polycrystalline state, of which the *d* spacings are 0.232 and 0.194 nm, which can be assigned to the {111} and {200} planes of Pt, respectively (Fig. 1C). This is further confirmed by the corresponding selected-area electron diffraction (SAED) pattern for single DPNs (Fig. 1D). The XRD pattern of the DPNs shows that the peaks can be referenced to a face-centered cubic unit cell with lattice constant a = 3.923 Å (Fig. S3†). The 2θ values of 39.75°,

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† Electronic supplementary information (ESI) available: Synthesis conditions; experimental procedures; XRD, SEM, TEM, DLS and XPS analyses of the NPs; FT-IR and Raman spectra, electrochemical activity. See DOI: 10.1039/c2nr11912a

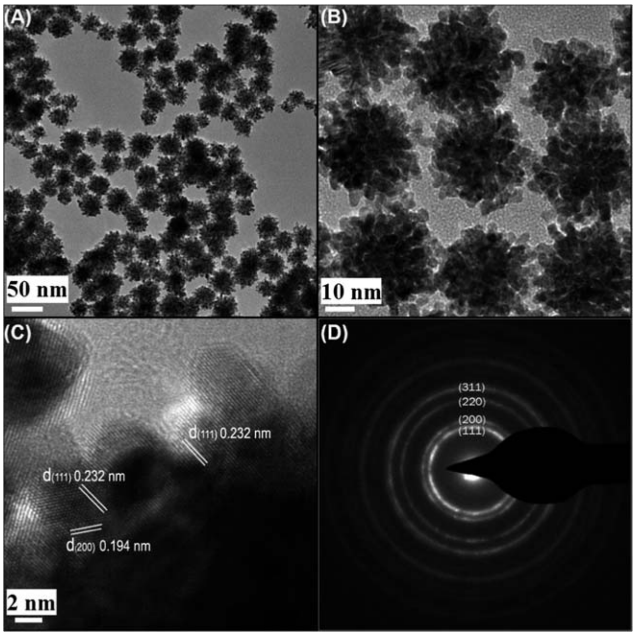

Fig. 1 (A, B) TEM, (C) HRTEM images, and (D) corresponding SAED pattern of single DPNs.

46.23°, 67.45°, and 81.24° can be indexed to diffraction of the (111), (200), (220), and (311) planes, respectively (PDF #65-2868).

To clearly figure out the mechanism of formation of DPNs, the intermediate products at different time intervals were extracted and characterized by TEM (Fig. 2). At the initial stage of reduction of the precursor, the primary Pt NPs are formed (Fig. 2A). Then, the secondary NPs are generated *via* depositing Pt atoms onto the active sites of the primary NPs along with continuous reduction (Fig. 2B, C). As the step-by-step growth proceeds, the increasing active sites result in the accelerating reduction rate until the complete consumption of the precursor (Fig. 2D, E). These phenomena indicate the obtained DPNs follow an overgrowth mode, as opposed to an aggregated growth mode, which can be reasonably attributed to the slow and continuous nucleation, and fast autocatalytic growth.[10,11]

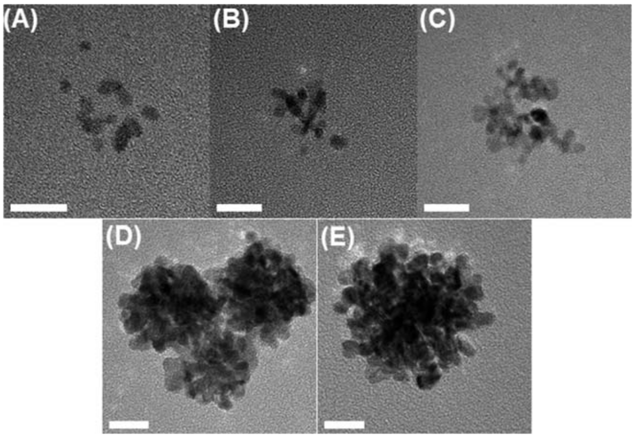

Fig. 2 TEM images of the intermediate products sampled at different reaction times: (A) 4, (B) 5, (C) 6, (D) 8, and (E) 10 min, respectively. The scale bar is 10 nm.

For discovering the underlying factors that dominate the formation of the obtained monodisperse DPNs with well-defined shape and size, different control experiments were performed by changing the amount of the H_2PtCl_6, the reaction temperature and the amount of NaOH. Firstly, we find that the morphology of the products changes obviously when varying the amount of the precursor solution (Fig. S4†). High precursor concentration is favorable for the formation of a highly branched morphology. When the precursor concentration was decreased, only lots of irregular and primary Pt NPs were obtained, revealing that the precursor concentration was too low to obtain mature dendritic structures. Secondly, the reaction temperatures were changed and the obtained results reveal that well-dispersed DPNs are able to form in a wide range of temperatures from 0 to 90 °C (Fig. S5†). And it should be noted that low temperature leads to DPNs with small dimensions, which might be attributed to the slow kinetic and low thermodynamic factors during the growth process, even though their diameters are not very uniform in size. Thirdly, through increasing the amount of NaOH to tailor the reduction capability of AA, we find that the dimensions of DPNs tend to decrease (Fig. S6†). However, when the amount of NaOH reaches 40 μL, the immature Pt particles still exist at the completion of the reaction (Fig. S6C†), which might be because the static interparticle repulsion, deriving from the adsorption of hydroxide ions on the primary NP surface, is so strong that it prevents them from further growing into the dendritic structure.[12] Meanwhile, the fact that more primary NPs are generated by the increasing reduction capability of AA with the increasing amount of NaOH might be another important factor. As such, the optimized prerequisites for the synthesis of well-defined DPNs with high yield are a truly simple and unique process that is quite different from the traditional seed-mediated growth strategy.

We then checked the efficacy of the proposed method for endowing DNPs with "clean" surface. Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy were employed to evaluate the surface function groups of the obtained DPNs (Fig. S7†). Interestingly, it is found that no characteristic absorption peak is observed, which confirms the definitely "clean" surface of the DPNs even after only simple washing with water. For comparison, DPNs were also synthesized in the presence of polyvinylpyrrolidone (PVP), a commonly used structure-directing agent, according to the literature[10b] and characterized by X-ray photoelectron spectrometry (Fig. S8A†). The strong N1s peak reveals that PVP is still firmly adsorbed on the surface of DPNs even after a consecutive centrifugation and washing cycle with water and ethanol for many times, which is consistent with the FT-IR spectrum (Fig. S8B†). This surface uncleanness would degrade their active activity (*vide infra*).[8a] In contrast, DPNs prepared with our strategy have no N1s peak after only washing with water twice, highlighting the benefit of our method again (Fig. S8A†).

Inspired by their "clean" surface, the DPNs were then employed as electrocatalysts for the methanol oxidation reaction. The catalytic reaction was carried out with a catalyst which was prepared by depositing DPNs evenly on activated carbon (Vulcan XC-72*R*) (Fig. S9†). The catalytic activity was further benchmarked against a commercial Pt/C catalyst. Unexpectedly, the DPNs/XC-72R catalyst exhibits much-enhanced catalytic activity in terms of the normalized current per unit surface area (Fig. 3). Its maximum current (forward scan) is nearly four times (up to 396%) as high as that of the commercial Pt/C catalyst. The superior catalytic activity of

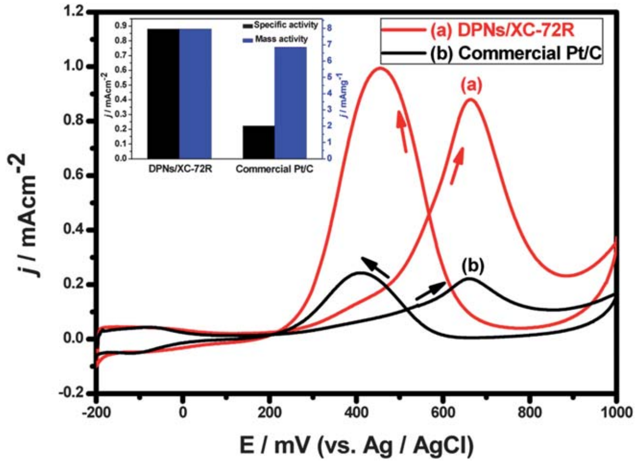

Fig. 3 Stable CV curves obtained for the DPNs/XC-72R and commercial Pt/C catalyst in the electrolyte of 0.5 M H_2SO_4 and 0.5 M CH_3OH at a sweep rate of 50 mV s^{-1}. Inset: comparison of specific activity and mass activity of the DPNs/XC-72R and the commercial Pt/C catalyst.

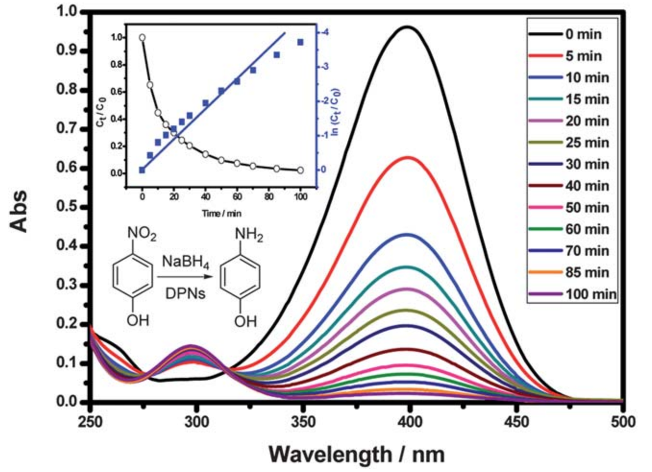

Fig. 4 UV–Vis spectra taken at different times for the reduction of *p*-nitrophenol in the presence of $NaBH_4$ and the as-prepared DPNs solution: [*p*-nitrophenol] = 2 mM; [$NaBH_4$] = 0.3 M; [DPNs] = 0.0187 mM. Inset: plots of C_t/C_0 and ln (C_t/C_0) *versus* time for the reduction of *p*-nitrophenol over the DPNs. C_0 and C_t are associated with the absorption peak at 400 nm initially and at time *t*, respectively.

the DPNs/XC-72R reveals that the dendritic structure is very suitable for use as an electrocatalyst, mainly due to the inherent nature of the abundant grain boundaries and the three-dimensional structure inhibiting the undesirable agglomeration of the active sites.[13] This is further reinforced by the higher performance of DPNs/XC-72R compared to that of the commercial Pt/C catalyst, when mass activity is used as the indictor of electrocatalyst activity (Fig. 3, inset). Note that the catalytic activity of PVP-contaminated DPNs, although with smaller size (Fig. S8A, inset†), is still inferior to that of DPNs synthesized by our method (Fig. S11†), highlighting the role of surface cleanness and the advantage of our strategy again. Moreover, the chronoamperometric curves recorded at 0.67 V for 1800 s (Fig. S12†) indicate that the current densities of the DPNs/XC-72R are higher than those of the commercial Pt/C catalyst over the entire time range, suggesting the good stability of DPNs/XC-72R.

It is highly desirable if the superiority of the as-prepared DPNs is not only embodied in the electrochemical reactions but also in the synthesis of fine chemicals. In this regard, we tested the reduction reaction of *p*-nitrophenol into *p*-aminophenol with $NaBH_4$ catalyzed by the DPNs, which is generally employed as a model reaction for the analysis of the catalytic activity of Pt-based catalysts.[1f,14] To exclude the influence of the concentration of $NaBH_4$ on the reduction rate, an excess amount of $NaBH_4$ was added. The reduction process can be monitored by the disappearance of the 400 nm peak with the concomitant appearance of a new peak at 290 nm. As the reaction proceeds, the peak at 400 nm gradually reduces (Fig. 4), which is associated with the reduction of *p*-nitrophenol as a function of time. The apparent rate constant, *k*app, is found to be proportional to the concentration (M, mol L^{-1}) of DPNs present in the system:

$$-dct/dt = kappct = k1Mct$$

where *ct* is the concentration of *p*-nitrophenol at time *t* and *k*1 is the rate constant normalized to *M*. When 0.05 mL of the as-prepared DPNs suspension is applied to catalytic reduction of *p*-nitrophenol, the value of *k*app is calculated to be 7.5×10^{-4} s^{-1} at room temperature and the according *k*1 data is 40.1 s^{-1} mol^{-1} L (Fig. 4, inset). Compared with some other catalysts, the results obviously indicate the excellent catalytic activity of DPNs toward the reduction of *p*-nitrophenol.[15]

In summary, we propose a rapid, one-step, and efficient route to synthesize well-defined and high yielding DPNs in aqueous solution without using any organic solvents and surfactants as protecting and structure-directing agents. The "clean" surface of the as-synthesized DPNs endows them with excellent catalytic activity toward both methanol oxidation and *p*-nitrophenol reduction. These encouraging findings would certainly assist the long-term endeavors to further enhance the catalytic activity of PGMs. In addition to catalysis, these NPs could be used in broad fields including optical, magnetic, and electrical applications.

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