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Fullerene-linked Pt nanoparticle assemblies

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Fullerene–Pt nanoparticle assemblies were prepared by attachment and immobilisation of different Pt nanoparticles on a gold electrode using molecular layers of C_{60} as a linker system. These assemblies were active for the methanol oxidation following treatment with CO.

Materials structured on the nanoscale can have physical properties which differ significantly from their bulk counterparts.[1,2] A major challenge is the preparation of well-defined nanostructures exhibiting promising catalytic properties.[3–7] Supported nanoparticle electrocatalysts can be very difficult to address by using electrochemical techniques. By contrast, studies with single crystals provide an excellent means to achieve further insight into fundamental mechanisms[8] but cannot be used to investigate particle size effects. The present work contributes to bridging the gap between single crystal studies and investigations employing supported nanoparticulate systems by the use of newly-developed fullerene–nanoparticle assemblies.[9]

These assemblies were prepared by attachment and immobilisation of different Pt nanoparticles on a gold electrode using C_{60} as a linker. Fullerene provides strong attachment to metals[10] and chemical inertness. Previous work has demonstrated the strong adsorption of C_{60} on Au.[11] Using pre-prepared colloidal Pt the size and shape of the nanoparticles can be controlled by the synthesis conditions.[12–14] Stabilised nanoparticles can be used to promote electrocatalytic reactions by the adsorption of CO and subsequent oxidative stripping.[15,16]

Colloidal Pt solutions were prepared in water and in toluene and characterised by elemental analysis and transmission electron microscopy (TEM, JEOL 2000-EX). The nanoparticles were then attached to a Au electrode using fullerene as a linker (Fig. 1). The assemblies were tested for their activity in the methanol oxidation reaction (MOR). Three preparations were employed; the first (TOAB–Pt) was prepared by the Brust method[17] using tetraoctylammonium bromide as both the phase-transfer agent and stabiliser, and aqueous sodium borohydride for the reduction of the hexachloroplatinic acid transferred to the organic phase. For the second synthesis, aqueous polyvinylpyrrolidone was added to aqueous H_2PtCl_6, stirred vigorously in an ice bath and reduced with aqueous borohydride for 4 h (PVP–Pt).[18] The third preparation was of naked-Pt nanoparticles prepared by aqueous borohydride reduction of H_2PtCl_6 in water. These were used as a reference to distinguish between ligand and linker effects.[19]
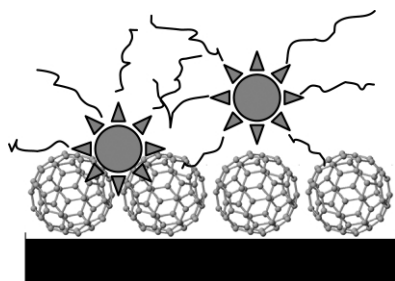
All nanoparticle preparations contained $(1–2) \times 10^{-3}$ M Pt as determined by elemental analysis. TEM images of the TOAB–Pt nanoparticles appear rather homogeneous, with sizes of approximately 10 nm and a narrow size distribution (Fig. 2, left).

The PVP–Pt preparation (Fig. 2, right), however, reveals significant heterogeneities; the nanocrystallites are of different shapes and display a wider size distribution centred at 4 nm. The electrocatalytic activity of the different systems was checked by cyclic voltammetry (CV) in 0.1 M perchloric acid (puriss. p.a.®, ACS, Fluka) containing 1 M methanol. All measurements are referred to the saturated calomel electrode (SCE). The working electrode was prepared as follows: a polycrystalline Au disk electrode (geometric area = 0.79 cm²) was cleaned by brief immersion into *aqua regia* (care, strong oxidant), polished with alumina powder (Buehler GmbH, Germany; down to 0.05 μm) and rinsed with MilliQ® water (Millipore system). A drop of 1 mM C_{60} in toluene was placed on the cleaned Au surface for 5 s, excess was removed with ultrapure water, and a droplet of the colloidal Pt solution put on top. The electrode was rinsed with ultrapure water and immersed into the electrolyte deaerated with argon. The bare gold surface (Au) and Au with adsorbed C_{60} (Au|C_{60}) displayed no activity for methanol oxidation. A Pt wire (ϕ = 0.5 mm, Alfa Aesar) and a commercial carbon-supported 20 wt.% Pt on Vulcan XC-72 catalyst (E-TEK Inc.) were also used as electrodes for comparison.

Fig. 3 compares CVs for the different surfaces investigated before activation with CO. A characteristic feature appears at approximately −0.35 to 0.30 V which does not appear for bare Au and Au with adsorbed fullerene electrodes (insert in Fig. 3), and is associated with hydrogen evolution and oxidation on the attached Pt nanoparticles. However, no indication of the typical structure of electrochemical hydrogen adsorption on Pt surfaces was observed. Similar behaviour was noted for all Pt preparations, although the oxidation currents are at their largest for naked-Pt–fullerene assemblies (Au|C_{60}|naked-Pt). This is as expected, since the naked particles would contain the greatest number of accessible sites. This feature becomes significantly suppressed on addition of 1 M methanol, but no evidence of any activity for the MOR was obtained, as shown in Fig. 3c considering the PVP–Pt–fullerene assembly as an example (Au|C_{60}|PVP–Pt).

It is proposed that the platinum surface is effectively covered by both the ligands and the linker molecules and is thus inactive for methanol oxidation. While the evolution and oxidation of hydrogen can proceed to a certain extent, methanol oxidation is expected to
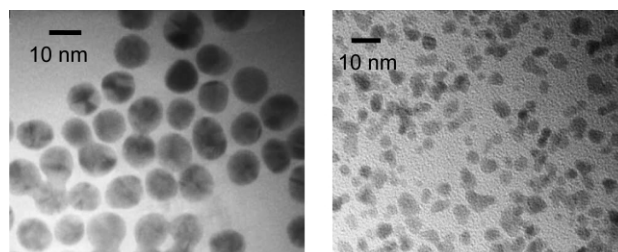
Fig. 1 Schematic representation of the ligand-stabilised Pt nanoparticles attached to a polycrystalline Au electrode by fullerene.

Fig. 2 Transmission electron micrographs of TOAB–Pt in toluene (left) and PVP–Pt in water (right)

require three adsorption sites, which cannot be provided by the (partially) blocked surface.

The preceding results show that the ligand-stabilised nanoparticles are ineffective electrocatalysts for methanol oxidation. This is a general problem in the design of well-defined surfaces based on colloidal nanoparticles, since there are conflicting requirements between stability in solution and the availability of accessible active sites. To obviate this drawback platinum sites were activated for the methanol oxidation reaction by a CO activation treatment (Fig. 4a, b).[16] In contrast to the voltammogram in Fig. 3c, a distinct methanol oxidation peak at approximately 0.35 V was observed, in good agreement with the onset of methanol oxidation both on polycrystalline Pt and on a commercial carbon-supported Pt catalyst (data not shown). Table 1 summarises the results obtained.
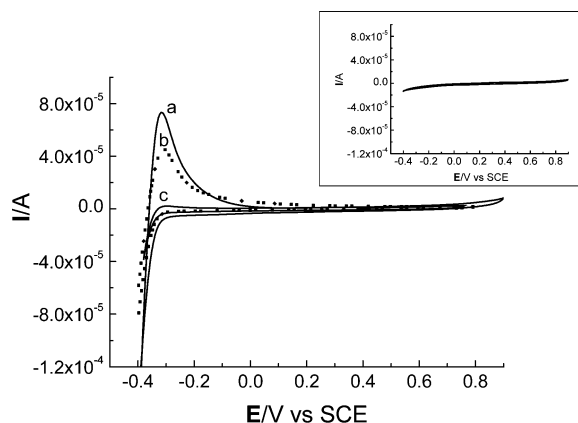
Fig. 3 Cyclic voltammetry for (a) Au|C_{60}|naked-Pt and (b) Au|C_{60}|PVP–Pt, both in perchloric acid, and (c) Au|C_{60}|PVP-Pt with the addition of 1 M methanol. All data is before CO activation; scan rate = 20 mV s^{-1}; the third sweep is shown in all cases. The insert shows the results for the bare Au surface for comparison.
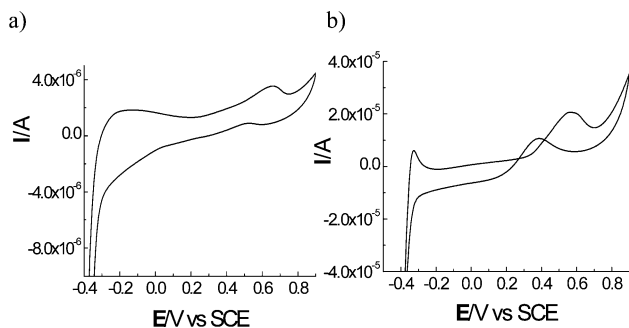
Fig. 4 Au|C_{60}|PVP–Pt (a) and Au|C_{60}|naked-Pt (b) both in 1 M methanol after CO treatment; scan rate = 20 mV s^{-1}; the third sweep is shown in all cases.

Table 1 Onset of methanol oxidation in the different fullerene–nanoparticle assemblies; values for a Pt wire and a commercially available 20 wt.% Pt on carbon catalyst purchased from E-TEK (see ref 20 for preparation) are listed for comparison

System Onset	TOAB–Pt	PVP–Pt	Naked-Pt	Pt wire	Supported catalyst
MOR/mV	384	360	324	319	361

More pronounced oxidation currents and a shift of the current onset to less positive potentials were found for the naked Pt nanoparticles (Fig. 4b), although these, too, had to be activated using the CO treatment. This result suggests that the linker molecules might also block part of the active surface but are probably less strongly attached than the ligand shell.

The present work is of importance for three reasons: (1) the attachment and immobilisation of Pt nanoparticles to a Au surface using fullerene as a linker molecule has been demonstrated; (2) it is shown that the fullerene–nanoparticle assemblies provide active sites for electrocatalytic reactions involving small molecules; and (3) the CO treatment is successful for activating the ligand-stabilised nanoparticles for methanol oxidation. The relevance of these observations is to open up a novel way for the investigation of well-defined electrocatalytic surfaces. These surfaces have a closer resemblance to real catalysts than single crystals, but in contrast to conventional supported nanoparticle catalysts, pre-prepared colloidal nanoparticles can be immobilised in a well-defined manner for electrochemical evaluation. Using fullerene–nanoparticle assemblies the synthesis of tailor-made model systems becomes feasible thus allowing the investigation of size effects[21] or basic mechanisms in fuel cell catalysts by changing only one parameter at a time.

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