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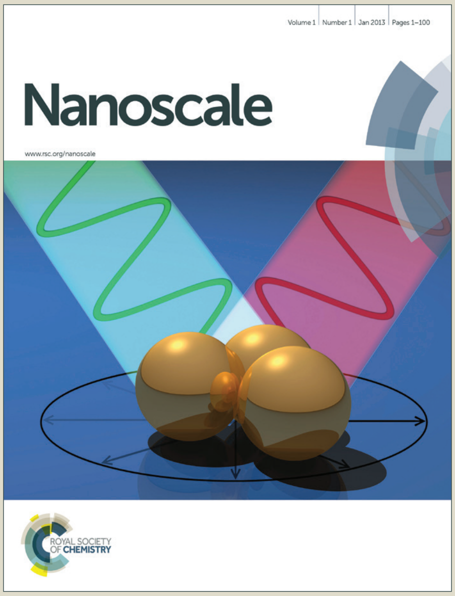

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Enhanced catalytic electrochemical reduction of dissolved oxygen with ultraclean cucurbituril[7]-capped gold nanoparticles

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Gold nanoparticles capped with cucurbituril[7] have been prepared in the absence of metallic cations and organic ligands. Remarkably, these nanohybrids encapsulate dissolved oxygen and are highly active in its electrochemical reduction. The effect of the presence of sodium and ammonium salts on this catalysed process is also analysed.

Cucurbiturils (CBs) are methylene-linked macrocyclic molecules made of glycoluril ($C_4H_4N_4O_2$) monomers (Fig. 1).[1] They are water-soluble macrocyclic hosts with a hydrophobic cavity that form strong inclusion complexes with many types of guests (e.g. positively charged organic guests[2]), they can also interact with metallic cations[3, 4] and bind to gold surfaces,[5] as well as to the surface of silver,[6] platinum,[7] palladium,[8] and gold nanoparticles (AuNPs),[9-12] through the carbonyl groups at their edges.

Up to now, supramolecular assemblies of AuNPs with CB have been made by in situ reduction of gold salts with sodium borohydride in the presence of CB,[9, 10, 13] by employing metastable AuNPs as labile intermediate combined with a dilute NaCl solution,[10] or by using AuNPs capped with organic ligands, such as citrate[12] or thiols, that include moieties able to complex CB (e.g. diaminohexane[14] or methyl viologen[15]). Unfortunately, the binding dynamics of the guests are influenced by the presence of cations that bind to CB portals[3, 16] and so could be the catalytic performance of a nanohybrid containing CB[7].

We presumed that cucurbit[7]uril (CB[7]), which has seven glycouril units, could give rise to CB-capped AuNPs (NP@CB, Fig. 1) via polydentate binding to "ultraclean" AuNPs. Interestingly, Scaiano *et al.* have synthesised "ultraclean", narrow-sized, water-dispersible AuNPs by UVA irradiation of $HAuCl_4$ in the presence of H_2O_2 followed by ablation of the as-prepared AuNPs by 532 nm laser irradiation.[17,18]

We report here an alternative one-pot protocol to make "ultraclean" AuNPs and their subsequent capping with CB[7] to produce highly stable NP@CB systems without needing additional organic ligands or metallic cations. These nanohybrids are more catalytically active in the electrochemical reduction of dissolved O_2 than the AuNPs alone. Remarkably, we demonstrate that sodium and ammonium salts stop oxygen entering the CB cavity of the NP@CB systems.

The protocol for the preparation of the AuNPs combines the capacity of H_2O_2 to thermally reduce Au(III)[19] to Au(0)[20] and that of 532 nm-laser light (18-20 mJ per pulse) to ablate the AuNPs generated in situ, thus modulating their size (see details in ESI). We have checked the reproducibility of the method by repeating the synthesis of the AuNPs more than twenty times.

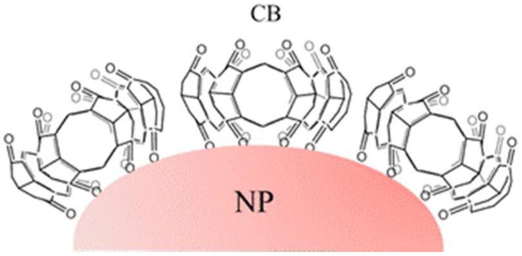

Fig. 1. Binding of cucurbit[7]uril to "ultraclean" AuNPs. Not in real scale.

Remarkably, after dilution in milli-Q water and elimination of the residual H_2O_2 (see ESI) the samples remained stable under ambient conditions for more than six months. Transmission electron microscopy revealed the formation of quasi-spherical monodisperse AuNPs (sized ca. 17±5 nm) (see Fig. S1).

Afterwards, the AuNP and CB concentrations as well as their relative ratio were varied to find the conditions for the preparation of stable, non-aggregated NP@CB systems. We found that a AuNP concentration well below 1nM was required to avoid the formation of aggregates (see Fig. S2 and Table S1).

Cyclic voltammetry was then used to demonstrate the binding of CB to AuNPs. The voltammetric response of CB or AuNPs, as well as those containing AuNPs capped with different CB concentrations, was studied in aqueous solution. In order to avoid interferences, experiments were performed without a supporting electrolyte using microelectrodes.[21,‡] Although the electrochemistry of host-guest complexes of CB with electroactive guests has been widely studied,[22] no detailed description of the CB electrochemistry has been provided so far.

Fig. 2 compares the cyclic voltammetric response, after deconvolution, of i) CB and ii) CB in the presence of AuNPs, CB/NP = 4000. An anodic peak appears at +1.0 V *vs* Ag|AgCl (A1) for CB (Fig. 2a); this signal can be attributed to the oxidation of urea motifs, a process occurring at high potentials with considerable kinetic constraints,[21, 23] so that the electrochemical oxidation of CB appears as an irreversible process, as denoted by the absence of cathodic peaks coupled with the anodic wave.

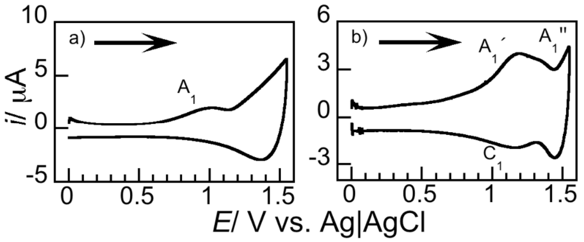

Fig. 2 Cyclic voltammograms at GCE after deconvolution of: a) CB (0.72 μM) and b) AuNPs (0.18 nM) and CB (0.72 μM) in milliQ water. Potential scan initiated at 0.0 V in the positive direction (marked by arrows); potential scan rate 50 mV/s.

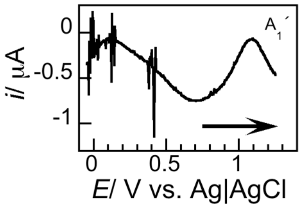

Fig. 3. Square wave voltammograms at the GCE for AuNPs (0.18 nM) with CB (0.72 μM) after subtracting that from a CB solution (0.72 μM) in milliQ water. Potential scan initiated at 0.0 V in the positive direction (marked by the arrow); potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

Under identical conditions, the naked AuNPs remained electrochemically silent. The solution containing CB (0.72 μM) and the AuNPs (0.18 nM) showed two anodic peaks at +1.20 (A1') and +1.35 V (A1'') followed, in the subsequent cathodic scan, by a reduction peak at *ca.* +1.15 V (C1). The existence of binding between CB and the AuNPs was evidenced by the significant peak potential shift in the anodic signal for the CB oxidation and even by the appearance of a peak splitting. These are typical features when both 'weak' and 'strong' coordination occur.[24] Additionally, the appearance of a cathodic signal (C1), absent in the voltammograms of 'free' CB, was indicative of the increase in the reversibility of the electrochemical process and confirmed the existence of a significant CB-AuNP interaction. Consistently, if the voltammogram for CB solution is subtracted from that of the AuNPs plus CB solution, one obtains a unique, definite peak at +1.20 V (see Fig. 3), which can be considered as representative of the CB binding to the AuNP surface. Equivalent results were obtained in the absence and in the presence of $NaClO_4$ supporting electrolyte (not shown).

Pyrrolidone units of poly(vinylpyrrolidone), which have a similar structure that the glycouril units, interact with AuNPs via oxygen (by ligand-to-metal charge transfer interaction), nitrogen (less favoured due to steric hindrance effects) or via both of them oxygen and nitrogen.[25] Therefore, it is expected that CBs become attached to the AuNP similarly. The peak potential value (E_p) recorded in the absence of a supporting electrolyte for a 0.72 μM CB solution was 1000 mV, while in the presence of AuNPs (0.18 nM) the value was 1200 mV (obtained from CB-centred process A1 and A1').

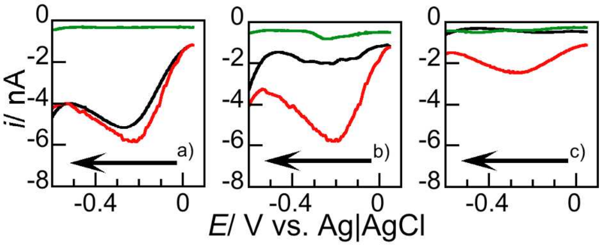

Fig. 4. Square wave voltammograms at Pt microdisk electrode of 0.46 nM AuNPs aqueous solutions of: a) air-saturated (black), id. and CB (red), N_2-saturated (green); b) air-saturated CB and NaCl (red), N_2-saturated CB and NaCl before (black) and after equilibration (green) with air; c) air-saturated CB and ammonium acetate (red), N_2-saturated CB and ammonium acetate before (green) and after (black) equilibration with air. The concentration of CB, NaCl, and ammonium salt was 0.64 μM. Potential scan initiated at +0.05 V in the negative direction (see arrow); potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

The performance of the NP@CB nanohybrids in the electrochemical reduction of dissolved O_2 (ORR) was compared to that of the naked AuNPs. The CB-AuNP interaction can be further confirmed by the distinctive catalytic effect on the electrochemical reduction of dissolved oxygen (ORR); this effect has been recently studied in different NP-modified electrodes.[26]

Figure 4a compares the linear potential scan voltammogram using a Pt microdisk electrode of an air-saturated nanopure water solution containing AuNP (0.46 nM) with those of i) an air-saturated solution containing AuNP (0.46 nM) plus CB (0.64 μM) and ii) a nitrogen-saturated solution containing AuNP (0.46 nM). The reduction peak at −0.25 V vs. Ag|AgCl, which is characteristic of O_2 reduction, was enhanced in the solution containing both the CB and the AuNP. This result revealed a synergistic effect of the AuNP and the CB to enhance the electrochemical reduction of oxygen. As expected, the O_2 reduction signal disappeared in a degasified solution of NP@CB (Fig. 4a).

The effect of NaCl, ammonium acetate, and adamantylammonium chloride on the catalytic response of the nanohybrid was assessed. Remarkably, the O_2 reduction peak vanished when the NP@CB solution was prepared in degasified water containing 0.64 μM NaCl and was subsequently equilibrated with air (ca. 20 min), see Fig 4b. The near complete absence of the O_2 reduction wave was consistent with Na^+ blocking the entrance of O_2, thus avoiding the formation of an O_2@CB inclusion complex.

Similarly, the addition of ammonium acetate to a deaerated solution of NP@CB blocked the subsequent entrance of O_2 (Fig 4c). Although there exists presently no experimental evidence for the encapsulation of guests as small as oxygen in a CB[7], the capacity of ammonium cations as lids of cucurbiturils has previously been applied to the encapsulation of N_2 and O_2 in decamethylcucurbit[5]uril$(NH_4^+)_2$.[27]

As expected, adamantylammonium cations caused removal of the O_2 from the CB cavity of the NP@CB (Fig. not shown), due to the complementarity between this cavity and the adamantyl moiety (binding constant ca. 10^{12} M^{-1}).[28]. Consequently, the O_2 reduction peak practically vanished. The binding of H_3O^+ to the vacant carbonyl portal of the CB is considerably less efficient.[3]

In short, ultraclean AuNPs have been prepared by a one-pot procedure in which only one by-product, specifically HCl, remained in the water solution. These nanoparticles can be capped with CB[7] without any additional organic ligand or metal ions. These nanohybrids showed an enhanced catalytic activity towards reduction of dissolved O_2 due to a cooperative effect between their components by fixing oxygen to the nanoparticle surface and increasing the local concentration of oxygen.

Remarkably, sodium and ammonium cations can block the entrance of oxygen to the CB cavity of NP@CB. The importance in catalysis of removing ligands or polymers used for the preparation of metallic nanoparticles has been highlighted when supporting the nanoparticles in solid supports[29] but has never been proved before for nanohybrids in solution. Therefore, preparation of nanoparticles free of organic ligands and metal cations should be a must in order to design more efficient catalytic nanohybrids in solution.

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Notes and references

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‡ Microelectrodes permits to obtain voltammetric data in the absence of supporting electrolyte. Satisfactory voltammetric responses (although with resistive distortions) were also obtained using macroelectrodes.

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