Silver nanoparticles deposited on glassy carbon. Electrocatalytic activity for reduction of benzyl chloride

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Abstract

A potentiostatic single-pulse technique was employed to prepare silver nanoclusters deposited on glassy carbon (GC) from $CH_3CN + 0.1$ M $LiCO_4$ plating solutions containing 1–2 mM $AgClO_4$. The morphology of the particles, obtained at a constant voltage pulse of variable duration, was examined by scanning electron microscopy. Clusters with particle diameter of 100–400 nm, which are uniformly distributed over the GC surface, can be prepared on a time-scale of 30–90 s. The Ag clusters exhibit remarkable electrocatalytic activity for the reduction of benzyl chloride. The supported Ag nanoclusters and bulk Ag metal have comparable electrocatalytic activities, both anticipating the reduction potential of $PhCH_2Cl$ by ca. 0.5 V with respect to bare GC. The Ag-modified electrode was used in preparative scale electrocatalytic reduction of benzyl chloride in different experimental conditions. Good yields of toluene or phenylacetic acid were obtained, depending on experimental conditions, whereas no loss of catalytic activity could be observed, even when the electrode was repeatedly used over a period of several days.
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1. Introduction

There is substantial interest in the electrochemistry of organic halides, due to the importance of C–X bond activation in organic synthesis [1], abatement of environmental pollution [2,3] and understanding of the dissociative electron transfer mechanism [4]. Direct electrochemical reduction of RX in aprotic media generally proceeds via two-electron cleavage of the C–X bond, occurring at very negative potentials at non-catalytic electrode surfaces. This process was therefore extensively studied in catalytic conditions, both homogeneous and heterogeneous. Although a large number of efficient homogeneous catalysts, especially transition metal complexes, have been reported [5], only a few metal electrodes, including Ag, Pd, Au and Hg, are known to have catalytic properties towards the reduction of RX [6–8]. Among the latter, much attention has been devoted to Ag, due to its powerful catalytic properties, which appears to be applicable to a large variety of organic halides [9]. Such an electrode material has recently been used to activate the C–X bond for both synthetic and pollution abatement purposes [10–13].

Metal nanoparticles display interesting optical, electronic and chemical properties which differ significantly from those of the corresponding bulk metal [14]. Much effort is devoted to research on such systems, because of the many potential applications in various areas such as catalysis [15–17], electroanalysis [18], surface-enhanced Raman spectroscopy (SERS) [19,20], development of optical and biological nanosensors [21–23], etc.. In the field of electrocatalysis, metal nanoparticles arouse much attention, owing to their extraordinary catalytic properties over bulk metal electrodes [24–27]. Metal nanoparticle-modified electrodes are increasingly being used in many electrocatalytic processes, mainly related to fuel cells. Thus, nanoparticles of precious metals such as Au, Pt and Pd, as well as

their alloys with less noble metals, have been reported as electrocatalysts for the reduction of oxygen [28–31], hydrogen evolution reaction [32,33] and oxidation of carbon monoxide and small organic compounds such as methanol [27,34,35].

This paper reports the results of a study on the electrocatalytic properties of supported silver clusters towards the reduction of organic halides in non-aqueous media. Metal nanoparticles deposited on solid surfaces can be prepared by a wide variety of methods including, for example, vacuum deposition of metals, inert gas evaporation, diffusion-controlled aggregation, and chemical and electrochemical deposition [36]. In particular, a simple, fast electrochemical method has recently been developed and applied to the preparation of Ag, Pt and Au nanocrystallites deposited on graphite surfaces [36–38]. In this work, supported Ag clusters on glassy carbon were prepared by a potentiostatic pulse method, and their electrocatalytic activities towards the electrochemical reduction of benzyl chloride, chosen as a model compound, were examined.

2. Experimental

2.1. Chemicals

Acetonitrile (Fluka, HPLC grade) was distilled over CaH_2 and stored under an argon atmosphere. Tetraethylammonium perchlorate (Fluka, >98%) was recrystallised from H_2O + ethanol mixture (2:1 v/v) and dried in a vacuum oven at 70 °C. All other reagents, benzyl chloride (Fluka, $\geqslant$99.5%), $LiClO_4$ (Janssen) and $AgClO_4$ (Aldrich, $\geqslant$99.5%) were used without further purification.

2.2. Instrumentation

Electrochemical measurements were carried out by a computer-controlled Autolab PGSTAT30 potentiostat or an EG&G PARC Model 173 potentiostat equipped with a digital coulometer. All experiments were carried out at 25 °C in a three-electrode cell system with a bare glassy carbon disc (GC), silver deposited glassy carbon (Ag/GC) or an Ag disc as working electrode, a Pt counter-electrode, and either $Ag|AgI|I^-$ or $Ag|Ag^+$ as the reference electrode. Electrodeposition of Ag clusters on GC was accomplished in CH_3CN + 0.1 M $LiClO_4$ containing 1–2 mM $AgClO_4$, by a single potential pulse method. A silver wire directly immersed in the silver plating solution was used as reference electrode ($Ag|Ag^+$). Its equilibrium potential was 0.2 V vs a saturated calomel electrode (SCE). Study of the electrocatalytic properties of the silver nanoparticles was carried out in CH_3CN containing tetraethylammonium perchlorate (TEAP) as background electrolyte. In these experiments, an $Ag|AgI|0.1$ M $(C_4H_9)_4NI$ in DMF was used as reference electrode. The equilibrium potential of this reference system (which was about −0.44 V vs SCE) was always measured after each experiment against the ferricenium/ferrocene couple ($E^o_{Fc^+/Fc} = 0.391$ V vs

SCE in CH_3CN) and, hence, the potentials were converted to the SCE scale.

Working electrodes used for cyclic voltammetry studies were built from a 6-mm diameter GC rod (Tokai GC-20) or a 2-mm diameter Ag wire (Alfa Aesar, 99.999%) and were polished to a mirror finish with silicon carbide papers of decreasing grain size (Struers, grit: 500, 1000, 2400, 4000) followed by diamond paste (3-, 1-, 0.25-μm particle size). They were then cleaned in ethanol (GC) or CH_3CN (Ag) in an ultrasonic bath for about 5 min. Prior to each experiment, the Ag and unmodified GC electrodes were refreshed by polishing with 0.25-μm diamond paste followed by ultrasonic rinsing. Instead, the Ag-modified electrodes required more drastic cleaning to remove deposited Ag completely. A clean GC surface was obtained by the polishing procedure described above, starting from the 1000 grit paper down to the 0.25-μm diamond paste.

Controlled-potential electrolyses were carried out in a divided cell with a silver-deposited GC plate of ca. 4.5 cm^2 area, which was polished and cleaned according to the above procedure, and a Pt anode. The products of electrolyses were analysed on a JASCO HPLC model PU-2080, equipped with a JASCO UV detector and a 25 cm × 4.6 mm Discovery HS C18 Supelco column. The eluent was a mixture of CH_3CN and H_2O containing 5 g/L of CH_3CO_2H. Authentic compounds were used for identification and quantification of products. All quantitative determinations were based on calibration curves.

The morphological characterisation of Ag particles deposited onto glassy carbon was performed by field emission scanning electron microscopy (Zeiss Supra 40 VP). Immediately after preparation, the Ag-modified GC electrodes were rinsed with CH_3CN, dried with a stream of hot air, and analysed by SEM.

3. Results and discussion

3.1. Ag/GC electrodes

Cyclic voltammetry (CV) of $AgClO_4$ was examined in CH_3CN + 0.1 M $LiClO_4$, with GC as working electrode and a silver wire directly immersed in the electrolytic solution as reference electrode. Fig. 1 shows two successive cyclic voltammograms, displaying the characteristic features of diffusion-controlled electrodeposition in the cathodic branch and stripping of the metal from the electrode surface in the anodic branch. The reduction peak in scan 2 is positively shifted with respect to the first scan. If we define the nucleation overpotential, η_{dep}, as the difference between a potential corresponding to the foot of the reduction wave (inset of Fig. 1) and the equilibrium potential, i.e., $E = 0$ V vs $Ag|Ag^+$, the $|\eta_{dep}|$ for the first and second scans are 126 and 42 mV, respectively. Equilibrating the electrode at the turning potential (0.5 V in Fig. 1) strongly influences the nucleation overpotential for silver. The effect of the equilibration time on η_{dep} is illustrated by the linear scan voltammograms of Fig. 2, each of which was obtained
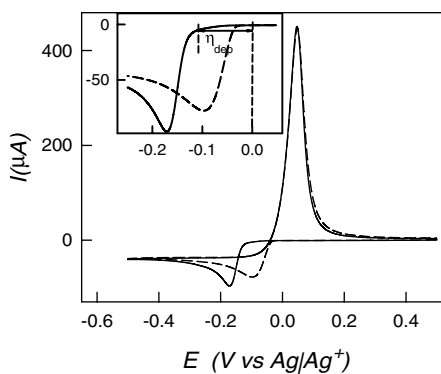
Fig. 1. Cyclic voltammetry of 1.3 mM AgClO$_4$ in CH$_3$CN + 0.1 M LiClO$_4$ at a glassy carbon electrode at $v = 0.02$ V s^{-1}, showing first (full line) and second (dashed line) cycles. Inset: detail of cathodic branch of CV curves and definition of deposition overpotential η_{dep}.
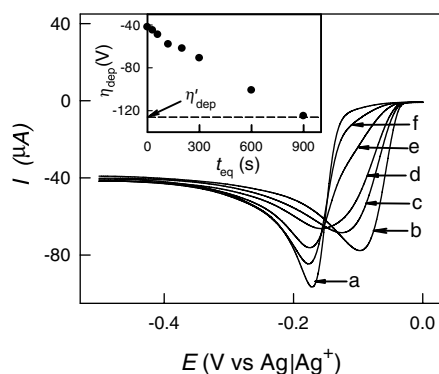

Fig. 2. Cathodic branch of cyclic voltammograms obtained for 1.3 mM AgClO$_4$ in CH$_3$CN + 0.1 M LiClO$_4$ at GC at $v = 0.02$ V s^{-1}, as a function of equilibration time t_{eq}, at 0.5 V vs Ag|Ag$^+$: (a) first cycle and (b–f) successive cycles recorded after equilibration times of (b) 0 s, (c) 60 s, (d) 120 s, (e) 300 s, (f) 600 s. Inset: variations of deposition overpotential as a function of t_{eq}.

after deposition and stripping of silver from the GC surface, and equilibration of the surface at 0.5 V vs Ag|Ag$^+$ for a certain time t_{eq}. As t_{eq} increased, the nucleation overpotential also increased, approaching that of a fresh GC electrode on which silver had never been deposited. The inset of Fig. 2 shows the variation of η_{dep} as a function of t_{eq}; after an equilibration time of 15 min, η_{dep} becomes identical to that obtained on a fresh GC electrode in the first scan.

Voltammetric study of Ag$^+$ reduction on GC showed that successive voltammograms were not reproducible, the electrodeposition reaction taking place more readily in the second and subsequent scans. Similar results have previously been reported at GC [39,40] and highly oriented pyrolytic graphite (HOPG) [41] electrodes for Ag. A reasonable explanation of this is that, in the first cyclic voltammetry, deposited Ag is not completely anodically stripped, and the presence of residual Ag on GC therefore facilitates the nucleation and deposition of silver in the second and subsequent scans. The reason for the partial anodic dissolution of Ag has been proposed to be due to intercalation
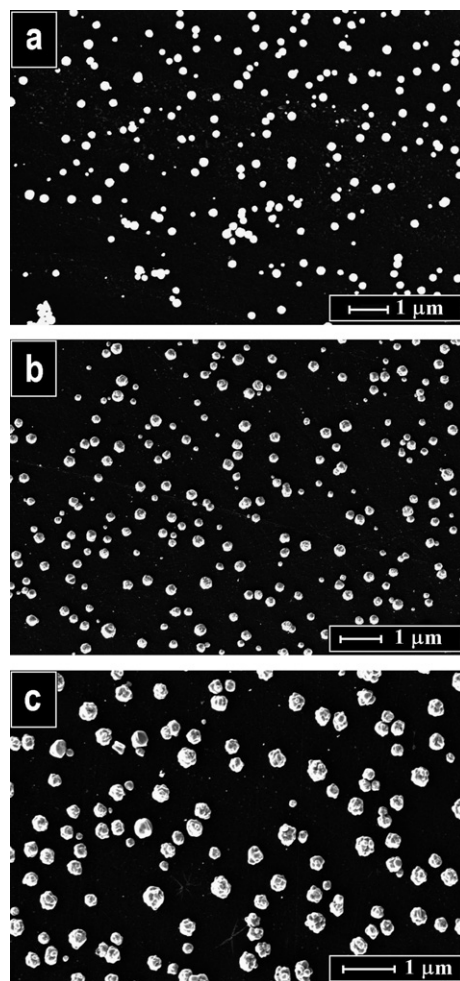

Fig. 3. SEM images and particle size distributions of Ag nanoparticles electrodeposited on GC by potential steps from 0.5 V to −0.4 V vs Ag|Ag$^+$, with pulse durations of (a, d) 30 s, (b, e) 50 s, (c, f) 90 s.

of the metal in the graphite matrix [39]. This hypothesis does not explain how the intercalation could facilitate nucleation of Ag in successive scans, whereas Penner and
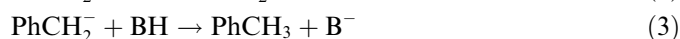
coworkers [41] have shown that anodic dissolution of silver microparticles from the HOPG electrode surface occurs rapidly until the mean diameter of these particles is reduced to 0.4–1 nm. At this subnanometer level, the dissolution rate decreases drastically, resulting in metastable clusters with a half-life on the graphite surface of the order of 1 h. Facilitated renucleation of Ag on HOPG has therefore been attributed to the presence of such silver clusters on the electrode surface. Residual Ag particles on the GC surface after cyclic voltammetry of Ag^+ has also been reported [40]. We attribute the decrease of η_{dep} of Ag on GC, observed here, to be due to incomplete dissolution of Ag in the anodic scan. However, the dissolution rate of subnanometer particles of Ag on GC should be faster than on HOPG, because, on GC, η_{dep} returns to its initial value after 15 min of oxidation at 0.5 V vs $Ag|Ag^+$, instead of 1 h as reported for HOPG.

The potentiostatic deposition of silver particles on GC was accomplished by pulsing the potential of the electrode from 0.5 V to −0.4 V vs $Ag|Ag^+$. In these conditions, the process is diffusion-controlled and, hence, instantaneous nucleation of Ag occurs on the GC surface. SEM images of Ag particles deposited on GC at the same potential but during different deposition times, t_{dep}, are shown in Fig. 3, together with particle size distributions in the form of histograms. The particles are roughly spherical in shape, and are uniformly distributed over the GC surface. They are polydisperse, the relative standard deviation, RSD, of their mean diameter being in the range 22–27%. Areal number densities as well as average diameter and standard

deviation of cluster distributions were determined from the SEM micrographs by approximating the shape of the particles to a sphere. Whereas areal number density N was found to be little affected by t_{dep}, the mean diameter of the clusters increased with increasing deposition time. For example, the N values obtained for t_{dep} values of 30, 50 and 90 s are 2.6×10^8, 3.1×10^8 and 2.5×10^8 cm^{-2}, respectively. This result fits that of previous reports, showing that the number density of active sites on GC depends on deposition overpotential, rather than on t_{dep} [36].

3.2. Cyclic voltammetry of benzyl chloride at Ag/GC

The electrocatalytic activity of silver clusters was tested for the reduction of benzyl chloride, chosen as a model process for electroreduction of organic halides. Fig. 4 shows cyclic voltammetry of $PhCH_2Cl$ at bulk silver, bare GC and Ag-deposited GC electrodes. A single irreversible reduction peak is observed in all cases. The reduction mechanism of $PhCH_2Cl$ at bulk Ag and GC has previously been reported [42], showing that, on both electrodes, the process involves two successive one-electron transfers leading to the carbanion $PhCH_2^-$, which is then rapidly protonated to give toluene by any proton donor, BH, in solution.

$$PhCH_2Cl + e^- \rightarrow PhCH_2^{\cdot} + Cl^- \tag{1}$$

$$PhCH_2^{\cdot} + e^- \rightleftarrows PhCH_2^- \tag{2}$$

$$PhCH_2^- + BH \rightarrow PhCH_3 + B^- \tag{3}$$

As shown in Fig. 4, the bulk Ag electrode exhibits a remarkable electrocatalytic effect, with a positive shift of E_p of 0.49 V with respect to GC. The Ag-modified GC electrode also has electrocatalytic activity which, however, depends on surface coverage. As deposition time increases, the reduction peak at bare GC decreases, while a new peak, attributed to the reduction of $PhCH_2Cl$ at the Ag nanoparticles deposited on GC, appears at less negative potentials. At small t_{dep} values ($t_{dep} \leqslant 30$ s), both processes contribute to the overall reduction of $PhCH_2Cl$, so that a broad peak is observed but, at higher t_{dep} values, the halide is exclusively reduced at the Ag surface. In these conditions, a well-defined reduction peak with a peak potential comparable to that obtained at bulk Ag is observed. For example, at $v = 0.2$ V s^{-1}, E_p values measured at GC, Ag and Ag/GC electrodes are −2.21, −1.72 and −1.73 V vs SCE, respectively.

So far, we had found that Ag clusters, easily prepared by a potentiostatic pulse of 90 s, have the same catalytic activity as that of the bulk metal. Next, we examined the long-term stability of the clusters and their catalytic efficiency, by means of two separate voltammetric experiments aimed at examining the stability of Ag/GC electrode both in solution and in air. Silver particles prepared with a pulse duration of 90 s were used in both cases, and electrocatalytic activity for the reduction of benzyl chloride was monitored for 3 h. In one case, the electrode was kept immersed in the test solution and cyclic voltammograms were recorded at
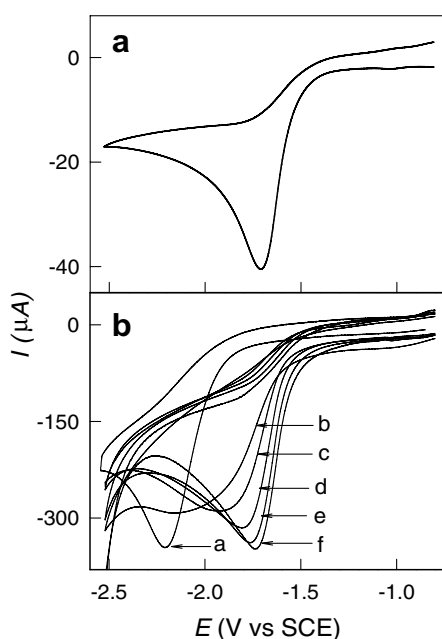

Fig. 4. Cyclic voltammetry of 1.0 mM $PhCH_2Cl$ in $CH_3CN + 0.1$ M TEAP obtained at $v = 0.2$ V s^{-1} at various cathode materials. (A) 2-mm diameter silver disc; (B) 6-mm diameter GC disc used as bare electrode (a) or modified with Ag nanoparticles via electrodeposition for (b) 20 s, (c) 30 s, (d) 50 s, (e) 70 s, (f) 90 s.
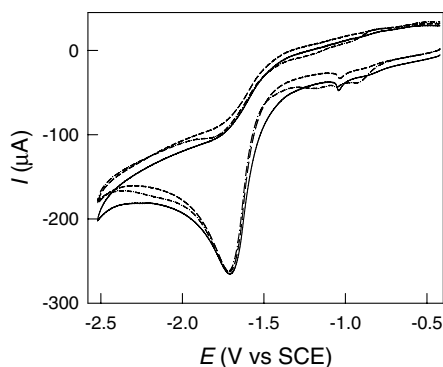
Fig. 5. Cyclic voltammetry of 1.0 mM PhCH$_2$Cl in CH$_3$CN + 0.1 M TEAP obtained at $v = 0.2$ V s^{-1} at Ag-modified GC electrode (90 s electrodeposition): CV curves obtained at freshly prepared electrode (full) and at same electrode after exposure to air for 1 h (dash) or 3 h (dash and dot).

fixed intervals of 10 min; in the other experiment, the electrode was stored in air and a cyclic voltammogram of PhCH$_2$Cl was recorded every 30 min. Both experiments showed reproducible voltammetric peaks for PhCH$_2$Cl reduction. Comparison of CV curves, obtained at a freshly prepared Ag/GC electrode and at the same electrode after exposure to air for 1 h or 3 h, is shown in Fig. 5.

3.3. Preparative-scale reduction of benzyl chloride at Ag/GC

As a further test of the good electrocatalytic properties of the Ag clusters, a series of controlled-potential electrolyses were carried out for preparative-scale reduction of benzyl chloride. Ag clusters were electrodeposited on a glassy carbon plate of 4.5 cm^2 area by a potential pulse of 90 s. The Ag-modified electrode was examined by SEM, which showed that both surface coverage and morphology of Ag clusters were the same as those obtained on GC discs. Except in a few experiments, in which the aging effect of the deposit was under examination, a freshly prepared electrode was used in each experiment. Before preparing a new deposit, the GC support was always cleaned by the mechanical polishing procedure (see section 2).

Electrolyses were conducted under potential control and were interrupted after the current had dropped to ca. 5% of its initial value, which corresponded to total conversion of the halide. Results are listed in Table 1. They compare well with those reported in the literature for reduction of halides at bulk Ag [42]. The main products of the electrolyses, performed in various conditions, were toluene and hydrocinnamonitrile. Small amounts of PhCH$_2$OH were also detected, but were not quantitatively determined. Reduction of PhCH$_2$Cl involves reactions (1)–(3), the residual water in CH$_3$CN and also the solvent itself acting as proton donors. Although in principle PhCH$_2^-$ may react with PhCH$_2$Cl via nucleophilic substitution leading to bibenzyl, the latter was not found among the reaction products. This may be attributed to at least two factors. First, since PhCH$_2$Cl reduction was performed in diffusion limit conditions, its concentration in the reaction layer adjacent to the electrode surface was very low. Second, protonation reaction (3) is very fast, because the pK_a of toluene is more than 10 orders of magnitude greater than those of acetonitrile and water [43]. Therefore, the S$_N$2 reaction between PhCH$_2$Cl and PhCH$_2^-$ is overcome by protonation of the latter by H$_2$O or CH$_3$CN. The conjugate bases of these proton donors, especially NCCH$_2^-$, react in the bulk with PhCH$_2$Cl by a nucleophilic substitution reaction, leading to PhCH$_2$OH and PhCH$_2$CH$_2$CN. The production of toluene is a two-electron process, but neither of the two other products requires charge consumption. Thus, the low charge stoichiometry shown in Table 1 reflects the fact that not all of the starting halide undergoes electron transfer.

In order to test the long-term stability of the Ag clusters, some electrolyses were repeatedly carried out on the same Ag/GC electrode, without renewal of the Ag deposit. The results were highly reproducible and compared well with those obtained using a freshly prepared electrode. The average values from three experiments performed within a period of one week are included in Table 1 (entry 4). After exhaustive reduction of PhCH$_2$Cl, a total charge of 23 C was consumed in each experiment. In addition, similar current-time characteristics were always observed, except for a slight decrease in initial current with electrode aging. Therefore, no significant aging effect on the electro-

Table 1
Preparative-scale electroreduction of benzyl chloride (10 mM) at Ag nanoparticles deposited on GC in CH$_3$CN + 0.1 M TEAP

Entry	E_{app} (V)[a]	n (F/mol)	PhCH$_3$ (%)[b]	PhCH$_2$CH$_2$CN (%)[b]	PhCH$_2$CO$_2$H (%)[b]
1	−1.9	1.1	58	28	
2	−1.8	1.2	59	26	
3	−1.7	1.2	60	22	
4[c]	−1.7	1.2	60	22	
5[d]	−1.5	2.0	89		
6[e]	−1.5	2.0	23		62

[a] Applied potential (vs SCE).
[b] Yield calculated with respect to PhCH$_2$Cl consumed.
[c] Average of results on an aged electrode.
[d] Electrolysis conducted with 20 mM CH$_3$CO$_2$H added.
[e] Electrolysis conducted in CO$_2$-saturated solvent.

catalytic properties of Ag/GC emerged from our experiments, at least within a period of one week.

The last two entries of Table 1 shows results obtained from electrolyses carried out in the presence of strong carbanion scavengers such as acetic acid and carbon dioxide. The main effect of both compounds was to suppress nucleophilic substitution reactions, which subtract part of the starting molecule from the reduction reaction. As expected, in the presence of CH_3CO_2H, the toluene yield increases considerably, while charge consumption becomes $2e^-$/molecule of $PhCH_2Cl$. Charge consumption increases to $2e^-$/molecule of $PhCH_2Cl$ also in the presence of CO_2, but now the main reduction product becomes phenylacetic acid. These results show how well supported Ag nanoclusters can function as electrocatalysts in reducing benzyl chloride, even in conditions suitable for electrosynthesis.

4. Conclusions

Mechanically and chemically stable Ag nanoclusters deposited on GC can easily be prepared by a single potential pulse method in $CH_3CN + 0.1$ M $LiCO_4$ containing millimolar amounts of $AgClO_4$. The particles obtained by applying a pulse from rest potential to -0.4 V vs $Ag|Ag^+$, are spherical in shape and are uniformly distributed over the GC surface. Areal density number depends on applied deposition potential, whereas particle size depends on deposition time.

Ag clusters have remarkable electrocatalytic activity, which is comparable to that of the bulk metal, at least for the reduction of benzyl chloride. Ag/GC electrodes of suitable active surface can be employed in macroscale electrolyses for important catalytic electrosyntheses. For example, electrocatalytic reduction of benzyl chloride gives satisfactory yields of toluene or phenylacetic acid, the latter being the main product obtained in electrocaboxylation conditions, i.e., in CO_2-saturated CH_3CN. It is important to note that the performance of the Ag-modified GC electrode described here is comparable to those of bulk silver, but the catalyst metal load is very different, only a few micrograms of Ag per cm^2 being present in the former. This is a very important economic aspect, which should be taken into consideration in large-scale electrosynthesis processes.

Acknowledgement

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