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A Disordered Copper-Palladium Alloy Used as a Cathode Material

THE ONE-ELECTRON CLEAVAGE OF CARBON–HALOGEN BONDS

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A novel method of forming a palladised copper (Cu/Pd) interface of well defined structure is described. The CuPd alloy is straightforwardly obtained by immersing a copper substrate in acidic solutions of palladium salts. Depending on the composition of the salt/acid solution, the copper surface is virtually instantly covered with a CuPd deposit. With nitric and sulfuric acid solutions and the corresponding Pd(II)-based salt, the deposit is composed of nanoparticles of disordered CuPd alloy dispersed at the copper interface. The alloy-modified surface was successfully used as an efficient promoter of bond cleavage reactions, especially those of carbon–iodide and carbon–bromide bonds in alkyl halides. The catalytic activity is specifically characterised by a very large shift in potential as between the use of a regular glassy carbon surface and the palladised copper interface. With alkyl halides (RBr and RI), the shift toward less cathodic potentials is so large that it enables the one-electron cleavage of C–I and C–Br bonds. This method should enable the heterogeneous generation of free alkyl radicals as transients in electrochemical reactions. These novel cathodic materials could also be of considerable interest for the disposal of halogenated waste.

For achieving novel reactions in organic electrochemistry the design and construction of an ideal, multi-purpose electrode remains a perennial goal (1). Within the cathodic range, the use of mercury is now banned for environmental reasons (2). Platinum, owing to both its cost and its weak hydrogen over-voltage, is difficult to use over a wide cathodic domain. Various carbon interfaces (such as graphite, glassy carbon and carbon felts) may provide useful working electrodes but they are not always inactive. Their neutrality towards electrochemical insertion of ions as well as their tendency to graft free radicals have been noted (3). Electrodes modified with functionalised conductive polymers have been claimed to be useful in interfacial synthesis since they can mimic some of the mechanisms of organic chemistry on solid supports (4). Consequently, some new insights in electrochemical synthesis may be linked to the

development of solid electrodes with very specific properties. Following this approach, pure silver (5) as well as other solid metal electrodes modified by adatoms (6) could offer interesting prospects when tailored to specific reactions.

Two-electron cathodic cleavage reactions involving halides, sulfones, sulfonamides or tosylates are of importance in organic synthesis, since they can be applied to deprotection processes, see for example (7). However, most of these reactions have been reported as slow electrochemical processes, depending on the electrochemical potential necessary to cleave the carbon–heteroatom bonds. Such cleavage reactions have been shown to occur at quite negative potentials – basically lower than -2 V *vs.* SCE. Thus the use of aqueous or water-wet organic solvents is inappropriate when considering most solid metals for use as cathodes.

The tailoring of surfaces by means of a specific deposit of catalyst is an alternative approach to novel electrode design. Here, the activation potential may become so large as to transform the nature of the cathodic reactions. Large potential shifts can be observed, which in principle enable the overall reaction process to be fundamentally changed. Following this approach, we have developed a very convenient method to produce a modified electrode based on a copper-palladium alloy (8). Preliminary results have shown that the as-obtained Cu/Pd interface appears particularly efficient in accelerating the cleavage of carbon-halogen bonds. These cleavage reactions have often been noted as possessing a high activation energy to achieve the first electron transfer (9–14).

In the present paper, we intend to fully define the characteristics of the copper-palladium layer produced onto copper substrates by displacement reactions from several Pd(II)-based precursors, and to investigate the efficiency of the as-produced surface towards the electrochemical cleavage of several alkyl halides RX (with X = Cl, Br and I). At regular solid metallic electrodes, these cleavages are commonly reported to occur with very large activation energies. A series of organic halides were therefore used as probes to compare their cleavage modes as conventionally observed at glassy carbon electrodes (GCEs) with those at palladised surfaces. The palladised surfaces were prepared by electrochemical deposition (onto platinum or glassy carbon substrates under the same experimental conditions). The advantages of this Cu-Pd surface, such as its great catalytic activity, its stability, and its simplicity of synthesis will be presented. The use and specificity of this new interface are discussed in terms of potential shift values related to its catalytic efficiency. It must be borne in mind that these interfaces specifically promote unexpected one-electron processes, which involve the transient formation of free alkyl radicals. With aryl halides, however, reduction processes retain a two-electron mechanism. This is in agreement with the observed high reactivity of aryl radicals (15, 16).

Experimental

Formation of the Palladised Copper Interface

The copper/palladium interface was simply prepared by dipping into a fresh acidic solution of Pd(II) for 15 s a copper substrate (grid or sheet) previously cleaned with acetone. Three different solutions were prepared by dissolving a palladium salt $\text{Pd}(\text{Y}^n)_{2/n}$ (with $\text{Y} = \text{SO}_4^{2-}, \text{NO}_3^-$ and Cl^-) into the corresponding acid. For example, 1 g of palladium(II) sulfate dihydrate ($\text{Pd}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$) (Alfa Aesar) was dissolved in 100 cm^3 of 0.1 N H_2SO_4 solution. The dipping procedure produced a virtually instant deposit onto the copper surface, due to the displacement of copper by palladium cations, together with the unexpected formation of a palladised copper interface. The shiny layer appeared to be quite stable, and sonication had no visible effect on its adhesion to the copper substrate. To prevent any residue of acidic impurities more or less strongly adsorbed onto the surface, a preliminary cleaning step is recommended; the modified electrode is dipped into a dilute aqueous solution of tetramethylammonium hydroxide, followed by rinsing with water, alcohol and finally acetone before drying with a hot air flow (at about 60°C). Such electrodes were easily reused, giving coherent data, since they were rinsed regularly following the above procedure.

Texture and Structure Analysis

Modified surface samples were first examined by X-ray diffraction (XRD) measurements at room temperature. However, the nanometric scale of the deposits made it difficult to identify the as-produced material correctly. To precisely determine the structure/texture of the copper/palladium interface, investigations were made using high-resolution transmission electron microscopy (HRTEM). Commercially available copper grids for electron microscopy were used as the substrate to study the Cu/Pd interface. Three samples were prepared for TEM investigation by dipping a copper grid into a fresh acidic solution of $\text{Pd}(\text{Y}^n)_{2/n}$. Electron-transparent specimens were obtained. The TEM and HRTEM imaging were performed using a FEI Tecnai F20 S-TWIN

microscope. The elemental composition was also determined by energy dispersive spectroscopy (EDS) at nanometre resolution. The diffraction patterns were obtained using the selected area electron diffraction (SAED) mode or by Fourier transform of the HRTEM imaging.

Electrochemical Procedures: Salts and Solvents

In all the electrochemical experiments, tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) was used as the supporting salt at a fixed concentration of 0.1 M. Its purity (at least 98%, Aldrich) was considered suitable for the experiments; there was no further purification. The dimethylformamide (DMF) solvent (SDS, France) was typically employed without drying. However, if ultra-dry solutions were required, DMF stored over activated alumina was used. Alumina activation was by heating at 340°C under vacuum overnight. Alumina could be added into the electrode cell if necessary, and this *in situ* drying technique gave a moisture level well below 100 ppm. It is worth mentioning that the procedures given below do not require extremely dry solutions. If one wishes to reach potentials as low as -2 V *vs.* SCE, the solution could be dried more efficiently to avoid hydrogen evolution *via* the reduction of residual water, thereby increasing the electrical yield of the overall organic cleavage. The organic halides (RX) used in the present work were purchased from Aldrich (minimum purity 95%) and used as supplied.

All electrochemical experiments were performed under an inert atmosphere (dry argon) using a three-electrode cell with a glass separator, as described elsewhere (8). Potential values given in this study are quoted *versus* SCE. The electrodes used here had an apparent surface area of $S = 0.8 \text{ mm}^2$, except for those using copper as a substrate ($S = 1.6$ or 3.2 mm^2). Glassy carbon, pure palladium disc and copper electrodes were always carefully polished with silicon carbide paper (Struer) or with Norton polishing paper (grades 02 and 03). Before use, the conventional working electrodes were rinsed twice with water, then alcohol and finally acetone before drying with a hot air

flow. Palladised electrodes (including those used for comparison purposes) were prepared by a galvanostatic deposit of Pd from a palladium chloride solution onto several types of metallic substrates (platinum, gold or palladium). The plating bath contained 10 g l^{-1} of PdCl₂ (Alfa Aesar) in aqueous 0.1 N HCl. In the present experiments, the charge density for galvanostatic deposition was 4 mC mm^{-2} throughout, with current densities of the order of a few hundreds of $\mu\text{A cm}^{-2}$.

Coulometry and Electrolyses

Coulometric experiments and electrolyses of organic chlorides, bromides and iodides were carried out using three-electrode cells allowing a total catholyte volume of about 5 to 10 cm^3 . The anodic compartment was separated by a fritted glass of weak porosity. Substrate volume was about 0.1 mM. In order to avoid disturbance resulting from the possible presence of copper oxide, which could depend on the history of the copper substrate, the solution was always pre-electrolysed before adding the RX compound to the cell. Owing to the high reactivity of the Cu/Pd interface towards impurities (in particular dioxygen), there was efficient argon bubbling in all cases, ensuring a good reproducibility of results, especially in voltammetry.

Results

Characterisation of the Palladised Copper Interface

A complete TEM study was performed on all the samples in order to determine the texture, the structure and the precise composition of the palladium-based layer. The bright field image (Figure 1(a)) shows a dendritic-like growth of the layer (particle size < 50 nm) obtained with the palladium sulfate solution. The HRTEM image of one part of the bright field image represents one of the 12 nm nanoparticles of which the dendrite was composed. The morphology and dimensions (around 10–15 nm) of these particles are homogeneous, and each is well crystallised. For the two other samples, prepared with palladium chloride and palladium nitrate solutions, the growth of the Pd-based layer is not dendritic (Figures 1(b) and

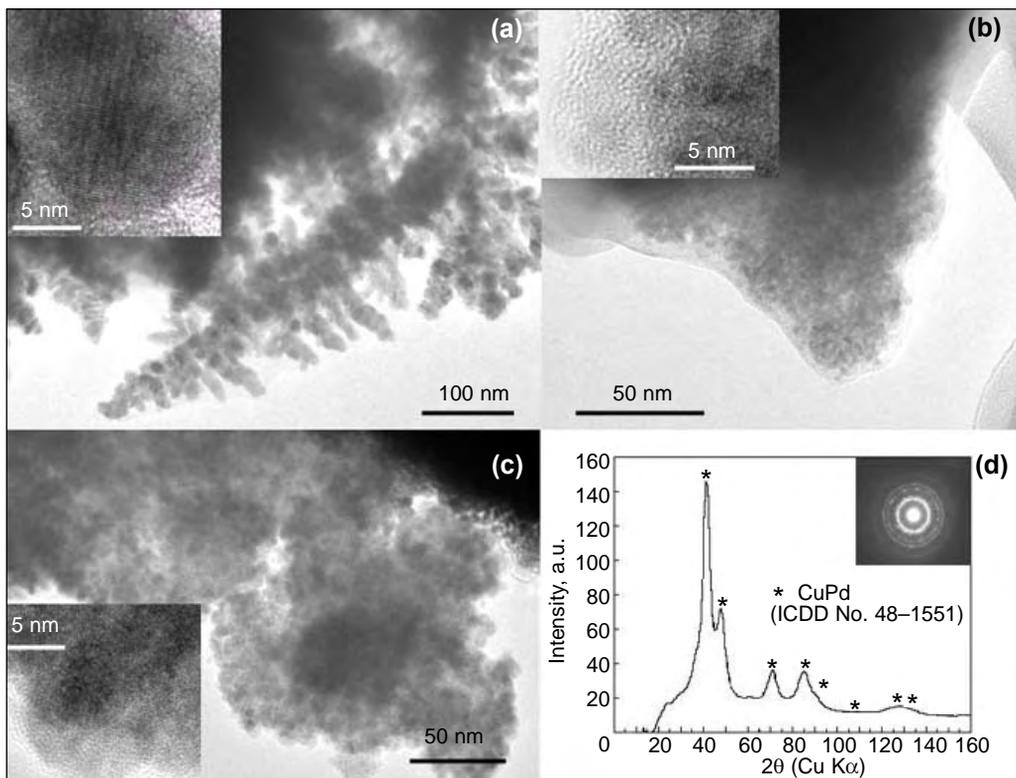


Fig. 1 Bright field images of the palladium-based layer obtained with the solution of: (a) palladium sulfate; (b) palladium chloride; and (c) palladium nitrate, (insets: HRTEM images of CuPd nanoparticles composing these layers); (d) common SAED pattern of these three layers combined with a graph similar to an X-ray diffraction pattern which enables characterisation of the disordered CuPd alloy

1(c), respectively). However, the layer is always composed by the juxtaposition of nanoparticles, the size of which is closely dependent on the precursors and varies from 3 to 5 nm (Figure 1(b)) and from 5 to 8 nm (Figure 1(c)). All these nanoparticles are well crystallised. The SAED patterns obtained from these three samples are identical, as shown in Figure 1(d). They are composed of diffraction circles due to randomly oriented nanoparticles. Thanks to the 'ProcessDiffraction' software, a line profile of the electron diffraction pattern may be plotted, similarly to the X-ray diffraction pattern (Figure 1(d)). Hence it was determined that the layer can be related to the CuPd disordered alloy (ICDD card No. 48-1551, space group: $Fm\bar{3}m$). The nature and crystallographic properties of this layer are presented and developed in the Discussion section of this article. The EDS analysis of these layers (not given here) systematically indicates a Cu:Pd ratio

near to unity, corroborating the CuPd alloy formation. It was concluded that, for all samples, the Pd-based modified electrodes consisted of a thin layer of the stoichiometric CuPd alloy. Additionally, as mentioned in a previous paper (17), it is worth noting that, when using palladium chloride as the salt in solution, the sparingly soluble compound copper(I) chloride (CuCl) may also be incorporated into the surface electrode layer, in which case Cu(I) is stabilised by the excess chloride as a transient in the redox process.

Primary Alkyl Iodides

When using Cu-Pd electrodes, and in particular those obtained with palladium sulfate and nitrate solutions, the results regarding the electrochemical reduction of primary alkyl halides differ from those already described for conventional solid electrodes. Several alkyl iodides such as 1-iodobutane, 1-iodohexane, 1-iodooctane and 1-iodohexadecane

were tested (see Figure 2). 1-Iodobutane was found to exhibit a strong activation phenomenon at any Cu-Pd electrode. This activation is quantifiable as a positive shift in potential with respect to results obtained at a GCE, which is supposed to be the ideal type of electrode with zero activity towards alkyl halide molecules. Thus under standard conditions, the half-peak potential of iodobutane ($E_{p/2} = -1.93$ V *vs.* SCE) has been unambiguously assigned to the classical two-electron reaction step, which is regarded as unchanged by the nature of the interface. By contrast, using a Cu-Pd electrode prepared from a PdSO₄ solution yields a cathodic step that is strongly shifted in potential, and of much smaller limiting current ($E_{p/2} = -1.44$ V). This electrochemical process is diffusion-controlled, but strongly irreversible. The transfer coefficient estimated from half-peak width measurements was found to be smaller than 0.2. The catalytic efficiency of the Cu/Pd interface was also compared with those of palladised interfaces such as smooth platinum and polished palladium.

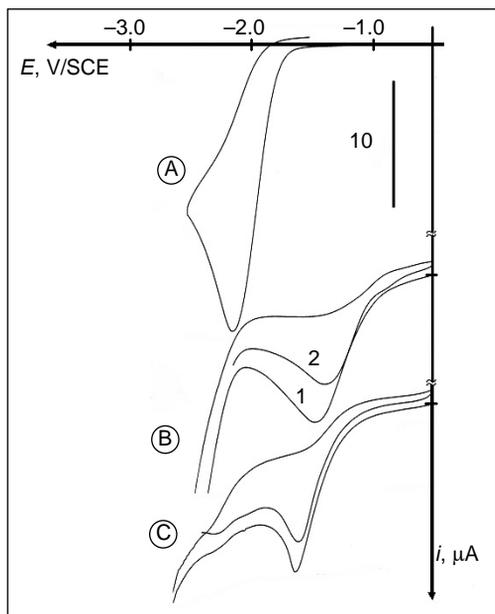


Fig. 2 Voltammetry of 1-iodohexane (concentration: 9 mM) in 0.1 M TBABF₄ using DMF as solvent, recorded at different microelectrodes. Scan rate: 100 mV s⁻¹
 (A) Response at a GCE ($S = 0.8$ mm²)
 (B) Response at a palladised platinum electrode ($S = 0.8$ mm²)
 (C) Response at a Cu-Pd modified electrode prepared from a palladium sulfate solution ($S = 1.6$ mm²)

As already reported (18) palladised surfaces such as those of Pt/Pd electrodes led to a higher potential shift ($E_{p/2} = -1.36$ V) as compared with that of a GCE. As a general trend, all types of palladised surfaces exhibit highly significant potential shifts with alkyl iodides. Peak currents are halved when using Cu-Pd electrodes, suggesting that the overall electrochemical process has become a one-electron reaction. Coulometric measurements verified this proposal satisfactorily with all the primary alkyl iodides tested. It is worth noting that smooth copper also exhibits a one-electron step with butyl iodide, but located at more negative potentials, typically -1.82 V *vs.* SCE. Therefore the sole participation of the copper substrate in the overall activation process is vanishingly unlikely.

Whatever the formation mode, the one-electron reduction process at Cu-Pd surfaces could be verified by microcoulometric measurements on millimolar amounts of reactant. At low reduction potentials ($E_r < -1.2$ V *vs.* SCE) the measured charge values are consistently very close to 1 F mol⁻¹. Since nitrones (classically used as spin markers) do not disturb electrochemical reduction reactions of alkyl iodides, complementary investigations were performed with *N-tert*-butyl- α -phenylnitron (PBN). In all cases, a distinct one-electron process was observed, whereas the formation of paramagnetic nitroxides was demonstrated. Under these conditions, 1-iodobutane produces a six-line ESR signal with the coupling constants $a_H = 3.16$ G and $a_N = 14.9$ G. This remains in good agreement with previous results obtained at regular palladised surfaces (18).

Alkyl Bromides

A large suite of long-chain primary alkyl bromides were reduced at different solid electrodes and their voltammetric data were compared. Almost all of this range exhibited a two-electron irreversible step at a GCE at quite strongly reducing potentials (i.e. $E_{p/2} < -2.5$ V *vs.* SCE). Smooth palladium electrodes also yielded a main reduction step that occurs at very negative potentials (within a comparable potential range < -2.4 V) since the electrolyte was thoroughly dried by adding activated alumina *in situ*. The reduction of

short-chain alkyl bromides at palladised electrodes may be effective at much less negative potentials than -2 V, but currents are generally small. However, these voltammetric steps exhibited a kinetically controlled character, and appeared to vanish completely upon repeated scans with increasing alkyl chain length. At a smooth copper interface, a reduction step was generally observed beyond -1.8 V, together with the possible occurrence of an adsorption-like step attributable to the reduction of copper oxide at moderate potentials. By contrast, Cu-Pd modified electrodes yielded surprising results: much larger reduction steps for alkyl bromides were consistently observable at much higher potentials than -2.0 V (see Figure 3 for the case of 1-bromodecane). The step obtained from the second scan is generally S-shaped, with the overall current indicating a process close to a one-electron transfer. The nature of the step strongly suggests a kind of self-inhibition, probably due to the adsorption at the electrode surface of the free radical produced.

Voltammetric experiments have shown that the shape of the reduction step is strongly sensitive to impurities in the solution. Thus, with traces of dioxygen, there is no pre-peak and the main step is clearly shifted. The second scan of an 'impurity-free' solution also exhibits such a potential shift,

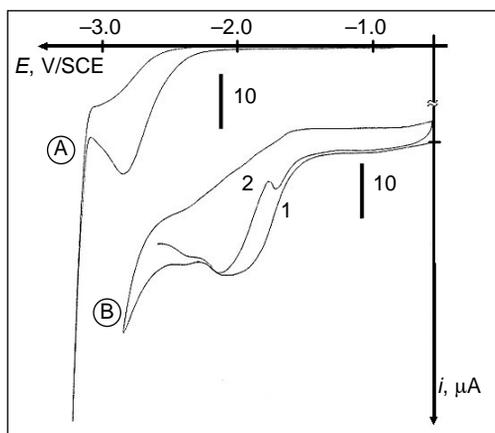


Fig. 3 Voltammetry of 1-bromodecane (concentration: 9 mM) in 0.1 M TBABF₄ using DMF as solvent, recorded at different microelectrodes. Scan rate: 100 mV s⁻¹
(A) Response at a GCE ($S = 0.8$ mm²)
(B) Response at a Cu-Pd modified electrode prepared from a palladium chloride solution ($S = 1.6$ mm²). First two sweeps

probably underlining that the catalysis is slowed down by the decay of the free active surface. The activated surface can only be regenerated by rinsing the electrode according to the procedure described above. However, a pre-peak of variable height is obtained with a freshly produced microelectrode, depending on the nature and the concentration of the alkyl bromides (see Figure 4 in the case of 1-bromohexadecane). The total height of the overall cathodic step is a linear function of alkyl bromide concentration. With R = *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-octyl and *n*-decyl, the total current of the reduction step (found to be diffusion-controlled throughout) is roughly half of the current observed at a GCE. This observation argues in favour of a one-electron reduction. Within the scanned potential range (i.e. $-2.5 \leq E \leq -0.5$ V vs. SCE), there is no appearance of a second step attributable to the reduction of the free radical release by the alkyl halide reduction. Moreover, it has been verified that there is no evidence of a partial reduction of the alkyl halide onto a pure copper cathode at potentials above -2 V.

In order to produce cheap and strongly activated electrodes, we attempted to build a Cu/Pd interface onto a GCE. Copper was

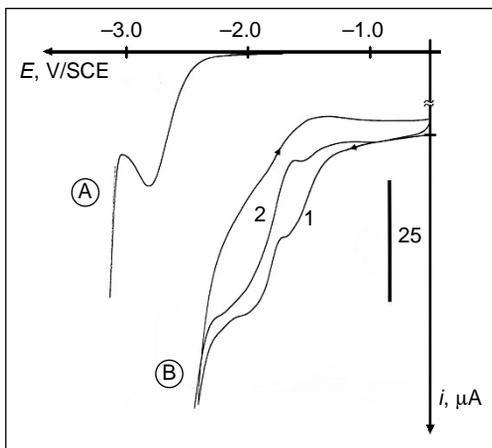


Fig. 4 Voltammetry of 1-bromohexadecane (concentration: 9 mM) in 0.1 M TBABF₄ using DMF as solvent, recorded at different microelectrodes. Scan rate: 100 mV s⁻¹
(A) Response at a GCE ($S = 0.8$ mm²)
(B) Response at a Cu-Pd modified electrode prepared from a palladium sulfate solution ($S = 1.6$ mm²). First two sweeps

galvanostatically deposited from a copper nitrate solution prepared by dissolving 0.1 g of the salt in 100 cm³ of 0.1 N HNO₃. The charge density was limited to 5 × 10⁻³ C mm⁻² and the current was fixed at 0.5 mA. After obtaining the copper deposit, (estimated average thickness ≈ 0.2 μm), the electrode was briefly dipped into a palladium sulfate solution. The glassy carbon surface emerged shiny. Results from use of the interface as a voltammetric electrode were interesting, since the degree of activation appeared extremely favourable. The 'pre-peak' turned out to be the main peak (see Figure 5, curve (C)). If the main reduction step decays during repetitive sweeps, a brief pause at 0 V may regenerate most of the original current. It is likely that a finely divided deposit of the alloy Cu-Pd can be superimposed on the thin copper deposit, producing quite a large activated surface. This procedure has so far only been achieved with a glassy carbon support.

Our observations suggest that using Cu-Pd electrodes at much less negative potentials than those

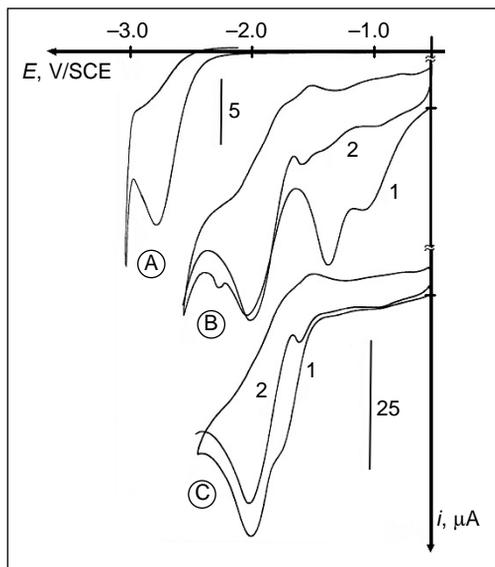
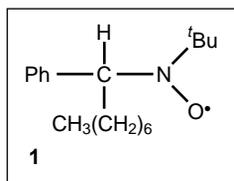


Fig. 5 Voltammetry of 1-bromodecane (concentration: 9 mM) in 0.1 M TBABF₄ using DMF as solvent, recorded at different microelectrodes. Scan rate: 100 mV s⁻¹
 (A) Response at a GCE ($S = 0.8 \text{ mm}^2$)
 (B) Response at a freshly made CuPd cathode prepared from a palladium chloride solution ($S = 3.2 \text{ mm}^2$). First two sweeps
 (C) Response at a GCE first covered by a galvanostatic deposit of copper ($S = 0.8 \text{ mm}^2$) and then treated by palladium sulfate solution. First two steps

already reported with conventional electrode materials leads, at least with alkyl bromides, to one-electron processes. To verify this hypothesis, an extended series of coulometric experiments was carried out on a large suite of primary alkyl halides. Cu-Pd electrodes (visible as a bright metallic deposit) formed from palladium sulfate or nitrate solutions could be reused for a large number of experiments without any apparent deterioration in efficiency. This was not the case with electrodes produced from palladium chloride, which turned blue over time, probably due to the oxidation of residual cuprous ions inside the layer. It was found for all alkyl bromides in the series that the Cu-Pd electrode then consistently produced a one-electron process. Finally, the analysis by gas chromatography/mass spectrometry (GC/MS) of the R-Br electrolysis products showed that R-R dimers and/or mixtures of R(H)/R(-H) in equal amounts were obtained with R = C₈, C₁₀ and C₁₂.

The formation of free alkyl radicals in the cleavage of primary alkyl bromides at Cu-Pd cathodes is strongly corroborated by the spin marker technique. 10–20 mg of the alkyl halide, dissolved in 5 cm³ of DMF, was reduced in the presence of a threefold excess of *N-tert-butyl-α-phenylnitron* (PBN) (electrolysis current = 10–15 mA). By way of example, the reduction current for 1-bromoheptane at -1.5 V on a Cu-Pd electrode vanished completely at 1 F mol⁻¹. ESR analysis of the electrolyte in the absence of dioxygen disclosed a strong paramagnetic signal, fully attributable to the trapping of the *n*-heptyl radical. The nitroxide radical obtained (see Structure 1) displayed a six-ray spectrum with coupling constants $a_N = 14.379 \text{ G}$ and $a_H = 2.614 \text{ G}$.



6-Bromo-1-hexene, which is known to afford a cyclisable free radical, usable as a 'radical clock', gives very similar results. Thus the reduction at a GCE shows $E_{p/2} = -2.34 \text{ V}$, whereas the use of a

Cu-Pd working electrode (still prepared with PdSO₄) produces a spectacular shift to $E_{p/2} = -1.40$ V. As shown in Figure 6(a), the presence of nitrene at the reduction led to two paramagnetic transients, with the formation of two parent nitroxides. It is presently premature to assign these two nitroxides to the trapping of the uncyclised and cyclised *n*-hexenyl radical.

Finally, fixed potential electrolyses on alkyl bromides (all exhibiting one-electron processes) led to mixtures of R-R, RH and R(-H). The ratio RH:R(-H) was equal to 1, as shown by GC/MS experiments with C₈, C₁₀ and C₁₂ bromides.

n-Alkyl Chlorides

It was found possible to reduce 1-chloroalkanes at Cu-Pd cathodes. An appreciable potential shift was also observed. However, in all cases, half-peak potentials were still located at very negative

potentials ($E < -2.5$ V *vs.* SCE). This precludes obtaining one-electron reduction processes similar to those observed with alkyl bromides and iodides.

Discussion

In order to characterise the electrochemical efficiency of our as-prepared electrodes, whatever the palladium precursor used, the primary objective was to unambiguously identify the structure of the deposited layer. Electron diffraction was an appropriate technique here, since the nanometric scale of the metallic particles made valid identification difficult when using a conventional XRD analysis. For all deposits, the electron diffraction line profile enabled identification of the deposited layer as a disordered CuPd alloy, thanks to a perfect match with the diffraction data given by Nekrasov (19) and more specifically by Zhu *et al.* (20). The latter performed a thorough study of clusters of

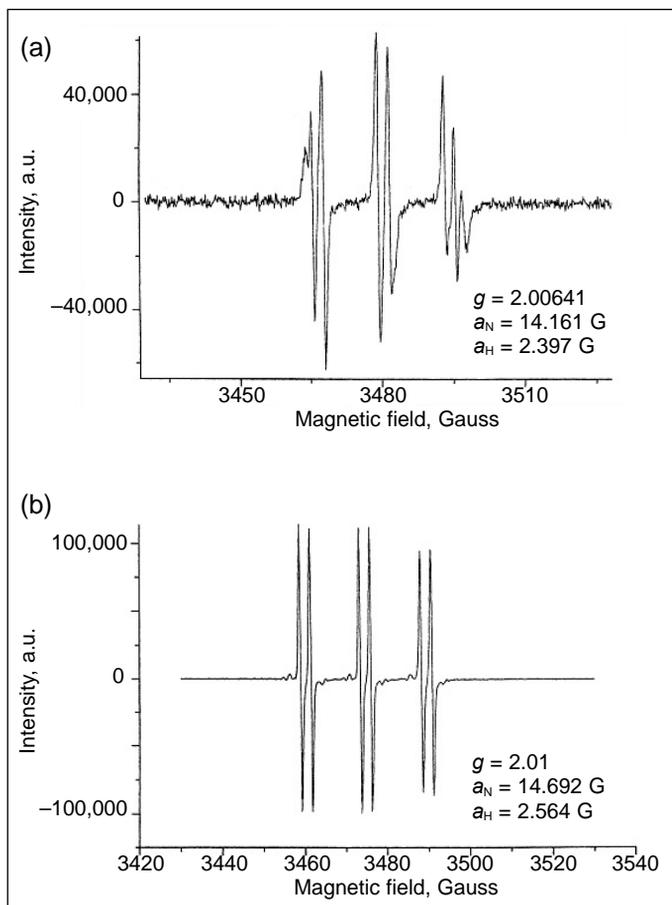


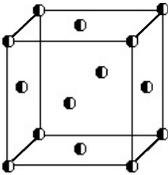
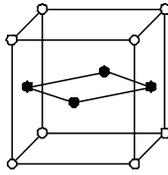
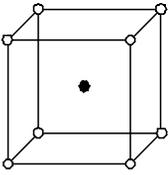
Fig. 6 ESR signals obtained from: (a) 6-bromo-1-hexene and (b) phenyl iodide when reduced in 0.1 M TBABF₄ using DMF and with dissolved TBN (threefold excess). In both cases, reductions were completed after a total consumption of 1 F mol⁻¹ based on the halide amount

disordered CuPd (i.e. nanoparticles) *via* a theoretical approach using the bond order simulation (BOS) model for metals and the corrected effect medium (CEM) theory. The simulation model of Zhu *et al.* predicts diffraction patterns and relative peak intensities, which are in good agreement with the reported experimental data.

Having demonstrated the formation of the disordered CuPd phase *via* TEM investigations, data regarding the Cu-Pd system must be considered, since the disordered structure is not expected at room temperature. Thermodynamically speaking, below the solidus, the Cu-Pd system is first characterised by a continuous solid solution showing a face-centred cubic (f.c.c.) structure (21) with a lattice spacing ranging from 3.615 Å (pure copper) to 3.892 Å (pure palladium) (22). At the 50:50 atomic composition, the disordered CuPd $A1$ -type alloy (solid solution) has a cell constant close to 3.77 Å (22), and is formed of copper and palladium that randomly occupy, with 50% probability, each site of the f.c.c. structure (Table I). As the temperature decreases ($T < 600^\circ\text{C}$), ordering of Cu and Pd atoms is energetically favoured (23–25) and the cubic CuPd alloy adopts the b.c.c.-based structure (CsCl-type). This phase, which is also referred to as $B2$ or CuPd (β), shows an alternation of (001) planes of Cu and Pd (Table I). It is worth noting that the f.c.c.-based $L1_0$ ordered superstructure (CuAu-type) with alternating

(001) planes of Cu atoms and (001) planes of Pd atoms does not exist (Table I). The competition between the $B2$ and $L1_0$ ordered phases of CuPd resolves in favour of the former, thanks to a substantially lower energy of formation (for more details see (25)). Moreover, the high stability of the $B2$ -type structure is substantiated empirically by the recent discovery of the corresponding mineral (skaergaardite) (26). Consequently, under our experimental conditions, the layer growth must be kinetically controlled, since it leads to the $A1$ -type alloy, a metastable phase at room temperature.

A noteworthy result of this study is that we succeeded in synthesising very straightforwardly nanoparticles of the disordered CuPd alloy by immersing a copper substrate (grid, sheet, Cu electrodeposit) into a fresh acidic solution of a palladium salt. Other methods known to date are very much more complicated, usually involving polyvinylpyrrolidone (PVP) as stabiliser to obtain nanoparticles. Esumi's method (27) (or adaptations) yields this alloy at nanometric scale by thermal decomposition of mixtures of copper and palladium precursors in high-boiling organic solvents (20, 27–29) or by condensing Pd and Cu atoms at 350°C under ultra-high vacuum (30, 31). Interestingly, CuPd alloys also show potential as gas-phase catalysts in enhancing the selectivity of hydrogenation of dienes (32) and the reduction of NO by CO (30, 33, 34).

Phase formula	CuPd	"CuPd(α)"*	CuPd(β)
Pearson symbol	$cF4$	$tP4$	$cP2$
Space group	$Fm\bar{3}m$	$P4/mmm$	$Pm\bar{3}m$
Strukturbericht designation	$A1$	$L1_0$	$B2$
Crystal structure			

● Pd
○ Cu
◐ Cu or Pd

*Note the $L1_0$ structure is given only for comparison since "CuPd(α)" phase does not exist for energetic reasons

Conclusion

It may be concluded that a simple redox displacement reaction between Cu^0 and Pd^{2+} , operating in acidic solution at room temperature offers a route to a thin and very stable layer, characterised as a well crystallised nanometric CuPd alloy. The displacement is simply achieved in the presence of Pd(II)-based salts such as sulfate, nitrate and chloride. However, a pure CuPd alloy is formed only with palladium sulfate and nitrate. Electrochemical data obtained from the reduction of a large series of organic halides (mainly iodides and bromides) showed that the use of such alloys as cathode materials very strongly activates the cleavage of the carbon-halide bond, sometimes displaying a +1 V shift in potential. There were no strong passivating phenomena during the electrolyses, even though a moderate decay of the cathodic current could be observed after a few minutes. The deposit was shown to act as a porous material, and its structure may change dramatically with time; this corroborates the assumption that palladium reacts with alkyl halides (Figure 7 depicts the modification in morphology of the Cu-Pd layer during the reduction of alkyl bromides).

We have already mentioned (18) the use of palladium deposits as modifier of the cathode surface (for example deposits onto platinum or glassy carbon). The mode of action of palladium probably stems from the finely divided nature of the deposits (nanosized particles). Hitherto it was believed that electrolytic deposition (from Pd^{2+} in acidic solutions) was a prerequisite for electrocatalytic activity (here quantified mainly in terms of a shift of the main voltammetric step toward much less negative potentials).

The mode of catalysis is not yet fully determined, but it is conceivable as the insertion of palladium into the carbon-halide bond, giving a strongly adsorbed chain species such as C-Pd-X . Such an insertion may corroborate the catalytic hypothesis, given the constant regeneration of the copper-palladium alloy (see Scheme I), promoted by the strong electronic interaction between Pd and Cu upon alloying with a specific feature (33, 34).

In the process proposed here, the rates of adsorption and insertion of palladium into the

C-halogen bond would be rapid compared with diffusion of the electroactive species. As stressed above, catalysis by the Cu-Pd surface is of very great interest for C-Br bond cleavage reactions. The C-I cleavage reaction is also facilitated, but results are quite similar to those already observed with palladised surfaces. Very often (but not invariably), the potential shift is so large that the cathodic reaction is fundamentally changed, and turns out to be mono-electronic. The method may therefore be seen as an efficient source of free radicals (with a possible coupling reaction outside the cathodic layer) more or less strongly adsorbed at the interface. These results are in full agreement with previous estimates by Lund *et al.* (35–37) concerning the standard potentials corresponding to the reduction of a large number of free alkyl radicals in DMF between -1.39 and -1.72 V *vs.* SCE, under very similar experimental conditions.

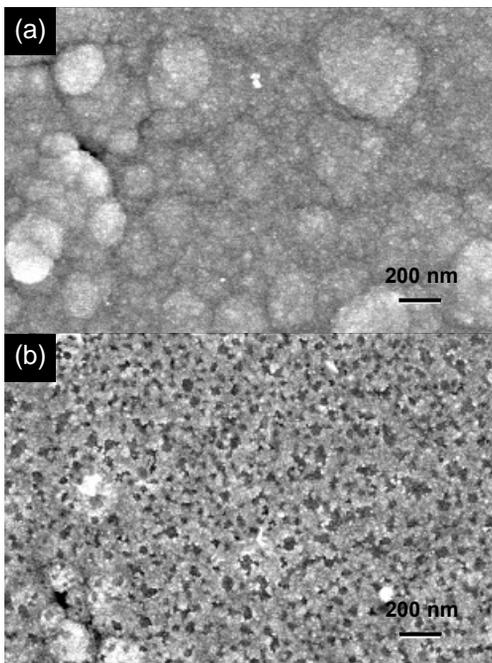
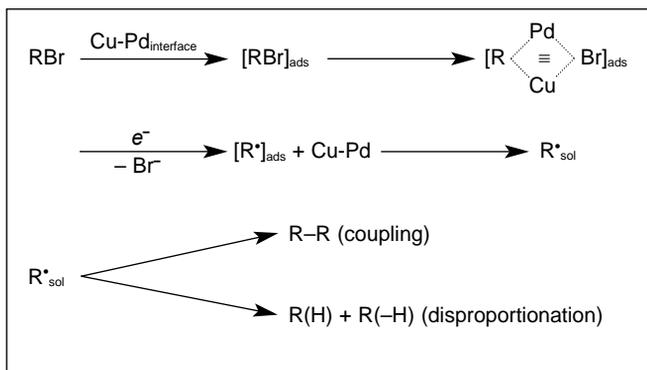


Fig. 7 SEM images of the Cu-Pd layer before and after reduction of 1-bromodecane (concentration 2×10^{-2} M). The metal layer (shown in (a)) has been obtained after a dipping of a copper sheet into PdSO_4 (see Experimental section) for 2 minutes. The structural change (b) of the layer (consecutive to the catalytic reduction of the RBr compound) was obtained by electrolysis at -1.9 V *vs.* SCE after 2 C cm^{-2} have passed through the cell. Average current density: 0.5 mA cm^{-2}



Scheme 1
ads = adsorbed; sol = solution;
 \equiv represents that an interaction exists
 between Cu and Pd atoms in the solid
 state

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