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Electrochemical study of ferrocene functionalized colloids; an insight into the surface fractal dimension of TiO_2 and SnO_2 colloids

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Ferrocenes functionalized by a π-conjugated phosphonic acid group have been bound to several metal oxide colloids. Electrochemical studies of such SnO_2 and TiO_2 colloids have been performed in solution as well as for colloids deposited on an electrode. While the results in solution correlate the colloid sizes, the electrochemical response of solid modified electrodes made from such colloids exhibit quite atypical behaviour, which demonstrates the fractal nature of the colloid surface, as well as allowing determination of their fractal dimensions.

Introduction

There has been a large amount of research devoted to the coating of colloids with organic substrates, in order to obtain nanoparticles displaying a specific property of the substrate,[1] such as fluorescence,[2] conductivity[3] (in the case of a conducting polymer), or molecular recognition.[4] Recently, several groups have tried to bind ferrocenes to either nanosize colloids, or dendrimers, either to recognise specific substrates such as phosphate anions,[5] or in order to perform theoretical analysis of electron transfer within the dendrimer core.[6]

As the phosphonic acid group proved to be very efficient to anchor functionalized organic molecules on metal oxides surfaces[7] (such as for the preparation of highly ordered monolayers on ZrO_2 or TiO_2,[7d] or the study of supported bipyridine–[7a] or terpyridine–Ru complexes[7b] on TiO_2), we used this function to covalently bind π-conjugated ferrocenes[8] to SnO_2 and TiO_2 particles (Scheme 1). The grafting of phosphonic acid on metal oxides is known to be irreversible and very stable over a wide range of pH.[7e] Therefore it is possible to study the electrochemistry of such colloids, either dispersed in a suspension, or in the solid phase, which is obtained by evaporation of a drop of the colloidal suspension onto an electrode. We have shown that the electrochemical response of the colloidal suspension allows us to determine the hydrodynamical diameter of the colloids, which correlates well with the diameter of the dried powder.

However, the electrochemical response of the modified electrode that can be obtained from the colloidal suspension is still more informative, since the response strongly depends on the repartition of the electroactive sites at the surface of each colloid grain. When the characteristic transport length of the electrons is much larger than the grain dimension, a classical pseudo-diffusion behaviour is observed. However, when the transport length becomes in the range or smaller than the colloid dimension, an abnormal behaviour, typical of a fractal site repartition is obtained, and the analysis of the curves allows one to determine with a reasonable precision the fractal dimension of the grain surface.

Experimental

All reactions were performed under an argon atmosphere, microanalyses were performed by the central analyses service at CNRS (Vernaison), density measurements were performed with a Micromeritics AccuPyc1330 apparatus and transmission electronic microscopy analyses were performed on a JEOL JEM 2010 apparatus.

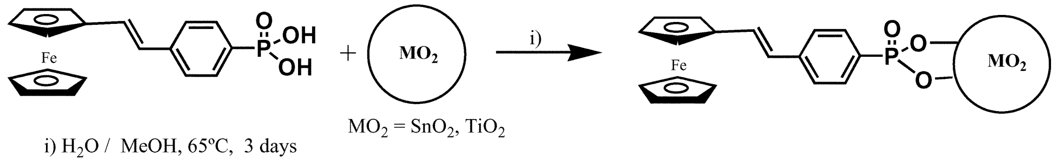
(1) Colloid preparation and characterization

The synthesis of the ferrocene π-conjugated phosphonic acid has been described elsewhere.[8] SnO_2 was purchased from Merck and TiO_2-P25 was supplied by Degussa. These oxides were functionalized in the following way.

The metal oxide (600 mg TiO_2 or 500 mg SnO_2) was suspended in a mixture of methanol (MeOH) (40 mL) and water (10 mL). Phosphonic acid (200 mg, 0.524 mmol for TiO_2; 150 mg, 0.41 mmol for SnO_2) was added and the mixture heated at 65 °C for 3 days under stirring. The suspension was then cooled, filtered on a Millipore membrane (0.45 μm), washed successively with water, MeOH, EtOH, acetone, diethyl ether and dried at RT.

Elemental analyses (%): for grafted TiO_2: Fe 2.2, P 1.5, Ti 48.5; for grafted SnO_2: Fe 1.17, P 0.90, Sn 65.45

The colloids have been characterized by TEM (transmission



Scheme 1 functionalisation of the colloids.

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electron microscopy), elemental analysis, density measurements, ^{31}P NMR and IR. TEM showed that the SnO_2 colloidal particles are about 15–20 nm in size while for TiO_2 the size is 23 nm with a low polydispersity in this case. Density measurements indicated that the density of the functionalized colloids was lower than the unmodified colloids, 6.3 *cf.* 6.9 g cm^{-3} for SnO_2 and 3.5 *cf.* 4 g cm^{-3} for TiO_2.

Solid-state ^{31}P H–P decoupled MAS NMR: for grafted TiO_2: $\delta = 13.6$ ppm; for grafted SnO_2: $\delta = 14.1$ ppm. IR (KBr pellet, ν/cm^{-1}): for grafted TiO_2: 3700–2000; 1631; 1600; 1472; 1402; 1261; 1138; 1050; 1002.

A more precise assignment of the IR data can be given for some bands: 3420–2500, ν(OH); 3050, ν(CH); 2921, ν(CH); 1631, δ(OH); 1472, ν(C=C); 1402, ν(C=C); 1261, ν(P=O); 1138, ν(P–O); 1050, ν(P–O); 1002, δ(Ar–H).

However, it should be noted that the significant TiO_2 absorption often makes it difficult to observe some bands related to the organic species.

2) Electrochemical measurements

Two types of measurements have been performed; in the first series, the colloids were dispersed into a 2 mL solution of either dichloromethane or dimethyl sulfoxide (DMSO), in the presence of 0.1 M tetraethylammonium perchlorate (TEAP).

In the second set of experiments, a drop of a colloidal suspension (*ca.* 15 mg mL^{-1}) of the colloid was allowed to dry on a 1 mm diameter microelectrode (this results in a layer of approximately 10 μm). The modified electrode was then transferred into an electrochemical cell filled with 0.1 M TEAP in acetonitrile, a solvent which leaves the deposit essentially unaffected, before being electrochemically cycled.

The electrochemical apparatus was home-made equipment fitted for fast (up to 2000 V s^{-1}) electrochemistry with an ohmic drop compensation system,[9] and a computerised acquisition system. Since we worked with very small amounts of solution an Ag/AgCl reference was used with a platinum wire as counter electrode.

Results and discussion

1) Study of suspensions of the functionalized colloids

The suspensions of the functionalized colloids are quite stable in DMSO and fairly stable in dichloromethane enabling electrochemical measurements to be performed. Typical voltammograms are displayed in Fig. 1 and show, as expected, small peak currents, indicative of slowly diffusing species. The potential values listed in Table 1 demonstrate that a difference exists between SnO_2 and TiO_2 functionalized colloids. This is not unexpected since the PZC (points of zero charge) of the oxides are different, and therefore the oxides exert a different donor/attracting balance on the bonded ferrocenes, which is expected due to the electronic conjugation between the ferrocene and the phosphate link. The lower the PZC, the more acidic the oxide surface is, and therefore the more electron attracting it should be. The PZC found for the Degussa TiO_2 is 5.75 which is in relatively good accordance with the literature theoretical value of 6.3[10] (experimental data were found to vary importantly with the oxide preparations and treatments); for our SnO_2 no data was available, but literature data suggest a value of 6.6–6.7.[10, 11] This is in agreement with a more attracting power of the TiO_2 surface, which is suggested by the higher redox potential of the ferrocenes grafted on TiO_2 (as well as by the fact that the grafting of the acidic phosphonic groups is more efficient on SnO_2). The grafting of phosphonic acid on metal oxides is known to be irreversible and very stable in a wide range of pH,[7] and was mainly characterized by ^{31}P H–P decoupled MAS solid-state NMR spectroscopy.

Table 1 Potential values for functionalized colloid suspensions

Compound	ν/V s^{-1} (solvent)	E_{pa}/V	E_{pc1}/V	$E_{1/2}$/V
Fc-TiO_2	1 (CH_2Cl_2)	0.37	[a]	[a]
Fc-TiO_2	5 (DMSO)	0.69	0.63	0.66
Fc-SnO_2	1 (CH_2Cl_2)	0.49	0.41	0.45
Fc-SnO_2	5 (DMSO)	0.81	0.47	0.59

[a] The return peak was ill-defined so that no potential determination was possible.

Even at low scan rates, the peak width is about 150 ± 10 mV, showing that there is some heterogeneity in the ferrocene environment on the colloids, leading to a potential dispersion; sometimes a small shoulder is even discernible on the downfall of the reduction peak. Besides, this value varies little with the scan rate, therefore excluding the participation of kinetic effects. This result shows that there are probably several different fixation modes of the ferrocenes on both colloids, involving various numbers of P–O bonds. Indeed different types of P–O bonds are involved in the grafting of phosphonic acids at the surface of metal oxides as evidenced by ^{31}P solid state NMR and IR analyses.[7d,e]

The diffusion coefficients of the colloids have been determined both in DMSO and dichloromethane. The results for both oxides are in the range 10^{-6}–10^{-7} cm^2 s^{-1}, which is in accord with the Stokes–Einstein law.

Table 2 displays the calculated D values for the colloids on the basis of the diameters determined from TEM experiments[12]

Table 2 Experimental and calculated D values for functionalized colloid suspensions

Compound	Solvent	$10^7 D_{theor}/cm^2\ s^{-1}$	$10^7 D_{exptl}/cm^2\ s^{-1}$
Fc-TiO_2	CH_2Cl_2	4.1	5.9
Fc-TiO2	DMSO	1.6	1.5
Fc-SnO_2	CH_2Cl_2	5.2	3.6
Fc-SnO_2	DMSO	2.1	3.4

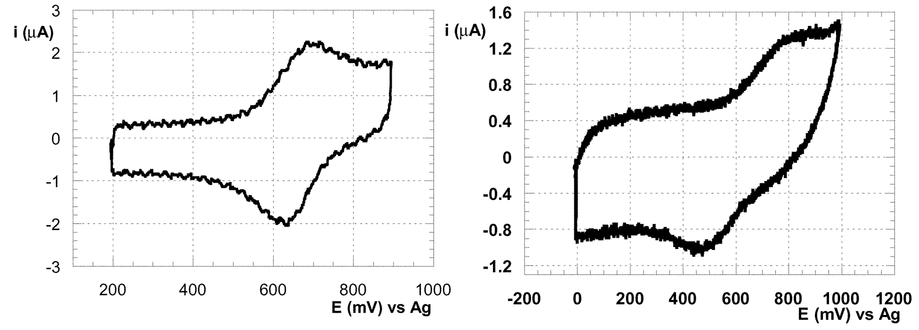


Fig. 1 Cyclic voltammograms of (left) ferrocene-TiO_2 colloid (10 mg in $V = 2$ mL) in DMSO, $\nu = 5$ V s^{-1} and right (ferrocene-SnO_2 (10 mg in $V = 2$ mL) in DMSO, $\nu = 5$ V s^{-1}.

and it is clear that a very good agreement is obtained between the experimental and the deduced values.

(2) Modified electrodes from the colloids

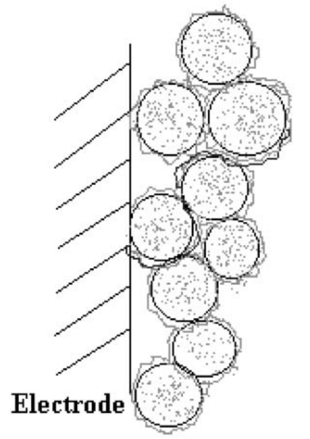
Since in solvents such as DMSO the colloids disperse to form a suspension, it is possible to prepare a modified electrode by depositing a drop of a colloid suspension onto an electrode and allowing it to dry. While the deposit may slowly go back again in solution in dispersing solvents such as DMSO or dichloromethane, on the other hand they are quite stable in less solvating solvents such as acetonitrile. This allows investigation of the behaviour of such modified electrodes, built from colloid stackings, as represented on Scheme 2.

Electrochemical behaviour: classical and 'abnormal' electron diffusion. Cyclic voltammetry experiments have been performed over about five orders of magnitude of scan rate, as well as chronoamperometry over selected time intervals. The voltammograms are displayed in Fig. 2. First, the potentials correlate well with those measured in solution, although the solvents were not the same, indicating only a minor solvent influence on the redox potentials of the functionalized ferrocenes. Similarly, the same broadening of the peak is observed in the modified electrode as might be expected. However, the most striking results come from the analysis of the cyclic voltammetry (CV) currents with the scan rate, or from the time–current relationship deduced from the chronoamperograms.

At very low to low scan rates ($\leqslant 0.1$ V s^{-1}), the CV peak currents correlate well with the square root of the scan rates, as expected for a classical semi-infinite diffusion process. As previously demonstrated, the limiting step is electron pseudo-diffusion, since all electroactive species are immobilised in the modified electrode. In the case of electrodes with homogeneously dispersed redox sites, the electron pseudo-diffusion coefficient D has been related to the concentration of the redox sites C°, the average distance between the sites Δx, and the exchange rate constant in the material k, according to the relation: $D = k\Delta x^2 C^\circ$.[13] From the CV or the chronoamperograms at low scan rate, we can determine the electron pseudo-diffusion coefficient D, which has been calculated as *ca.* 5×10^{-13} and 2×10^{-13} cm^2 s^{-1} for the TiO_2 and the SnO_2 electrodes, respectively. These values are low, but are however in the range of what is expected for modified electrodes with rigid skeletons (*e. g.* conducting polymers,[14] functionalized silica[15] or zirconia).[16] In addition, the dependence of the D values with concentration in the modified electrode, is in accordance to what is expected from the theoretical predictions. In fact, from the density measurements and the elemental analyses (see Experimental section), C° has been measured to be 1.8 times higher in TiO_2 than in SnO_2, which should lead to the same factor between the D values. This correlates approximatively with the experimentally found ratio of 2.5 (the difference may be due to the fact the k value is not the same).

This behaviour actually ceases at higher scan rates (above 0.1 V s^{-1}). The CV currents however correlate well on a log–log scale with the scan rate between 0.1 and 1000 V s^{-1}, but the slope is higher than 0.5 (Fig. 3). Since on the other hand, a thin layer behaviour would have been expected at even lower scan rates, this is indicative of a different process for the charge transfer. In fact, one of us showed recently that such a behaviour could be expected if the electroactive sites were distributed on a fractal geometry, and in addition, that the log(i)–log(v) slope was a monotonous function of the fractal dimension.[17] The chronoamperograms (Fig. 4) display the same features, since instead of the classical Cottrell relation $i \sim t^{-1/2}$, a dependance relation $i \sim 1/t$ is obtained (see Fig. 4), which is quite unusual in electrochemically modified electrodes. All these experiments clearly demonstrate that the electroactive sites are located on a fractal geometry.

One should keep in mind that the thickness of the layer affected by the electrochemical process (for classical diffusion) is $(\pi Dt)^{1/2}$. With D values in the range of 10^{-12}–10^{-13}, this shows that the diffusion layer becomes smaller than the colloid diameter at scan rates above about 0.1 V s^{-1} (a scan rate of 0.1 V s^{-1} corresponds to a characteristic measure time τ of



Scheme 2 Schematic representation of the modified electrode, with an example of a percolation path (among many others) for the electrons.

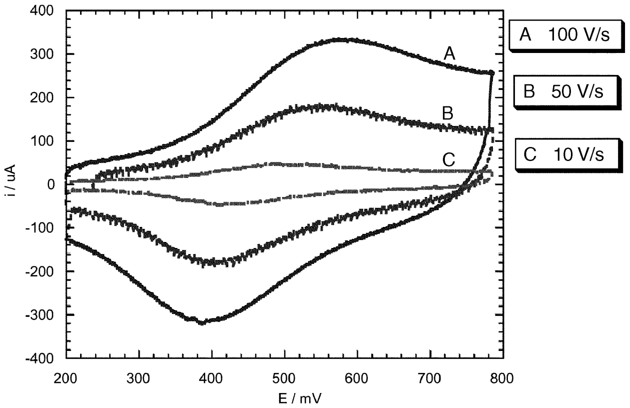


Fig. 2 CVs of SnO_2 modified electrode in acetonitrile at various scan rates.

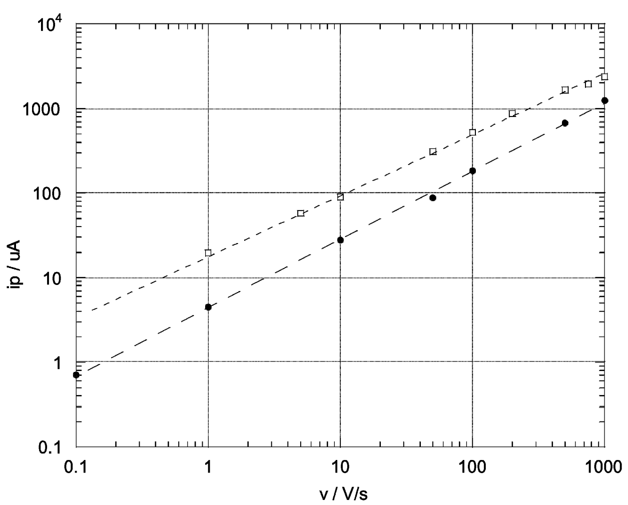


Fig. 3 Plot of anodic peak current *vs.* scan rate (in log–log units) for TiO_2 modified electrode (□) and SnO_2 modified electrode (●), in acetonitrile. The slopes of the interpolated straight lines are 0.71 and 0.79, respectively.

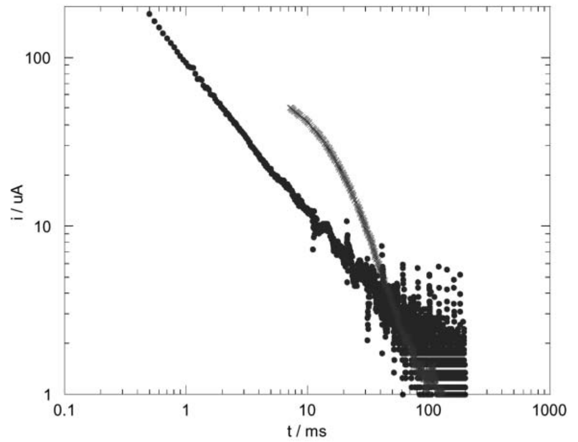


Fig. 4 Chronoamperograms (in log–log units) for TiO_2 modified electrode (●) and SnO_2 modified electrode (×) in acetonitrile.

about 2 s, and in turn to a diffusion layer of $(\pi D\tau)^{1/2} \sim 20$ nm for TiO_2 and 10 nm for SnO_2 which is precisely in the range of the colloid grain size). On the other hand, the limit of the 'classical' diffusion domain is found precisely around the scan rate of about 0.1 V s^{-1}. Thus we have confirmation that the change in regime between classical and 'abnormal' electron pseudo-diffusion occurs exactly at the grain layer boundary, which may also be viewed as the long range cut-off length of the fractal behaviour (Scheme 2).

'Abnormal' diffusion; determination of the fractal dimension. According to our previous work,[17] both chronoamperometry and cyclic voltammetry experiments would be suitable to determine the fractal dimension d_f of a volumic modified electrode. However, chronoamperometry is preferable for two reasons: (1) the variation of the slope of the log(i)–log(v) curves, although monotonous with d_f , is weak, so that the determination of d_f is not precise. (2) In addition, when d_f gets close to 3, the expected 0.5 limit is not reached, indicating that the determination of fractality is maybe no longer possible by this method in this d_f range.

On the other hand, chronoamperometry is a much more sensitive technique, since the log(i)–log(t) curves exhibit a sharp dependence, leading to a relatively accurate determination of d_f. Chronoamperograms at short times are shown in Fig. 4; the respective slopes extracted from the chronoamperograms at short times are -1.00 for the TiO_2 electrode and -0.64 for the SnO_2 electrode; these correspond to fractal dimensions of 2.5 and 2.9, respectively.

It should be noted that the fractal dimension that is actually measured is the *surface fractal dimension* (see Scheme 2), since the ferrocene groups are adsorbed on the surface, and therefore the pathways for the site-to-site electron pseudo-diffusion necessarily follow the grain surfaces. The fractal dimension values of several oxide surfaces have been determined by Avnir *et al.*,[18] and also by other groups,[19] mainly on the basis of adsorption studies. Our measurements may be compared to adsorption measurements, except that in our case, the functionalized ferrocene group itself acts as the probe.

One can check that the two oxides exhibit different fractal dimensions; in particular, the tin oxide particles have a surface dimension close to 3, which shows that they are extremely highly textured. In fact, the ferrocene distribution in such a fractal surface tends towards isotropic behavior. On the other hand, the titanium oxide appears much less textured since it exhibits a much lower surface dimension.

The cyclic voltammetry measurements correlate well with the chronoamperometry measurements in the case of SnO_2 since a value for d_f of 2.8 can be deduced from the i = f(v) bilogarithmic plots. However, this is not so for TiO_2, where the CV data lie out of range for the calculation of d_f, although it is difficult to rationalize this observation.

Conclusion

We have shown in this work that ferrocene anchoring to metal oxide colloids *via* phosphate groups lead to very stable functionalized nanoparticles, which in turn allow the preparation of very stable modified electrodes. In addition, the study of the charge transfer in such electrodes was not found to follow a classical behaviour, which is indicative of the fractal character of the colloid surface. More detailed analysis of the electrochemical data allow an estimation of the fractal dimension of these surfaces.

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