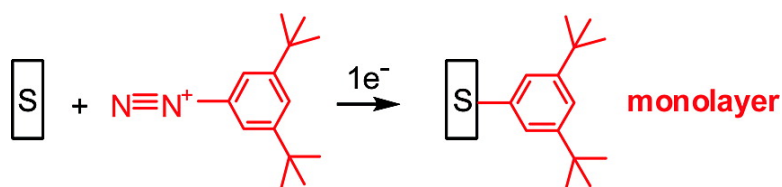


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S = Cu, Au, SiH

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## Sterically Hindered Diazonium Salts for the Grafting of a Monolayer on Metals

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Grafting and electrografting<sup>1</sup> of carbon (including nanotubes and diamond),<sup>2</sup> metals, and metal oxides<sup>3</sup> as well as hydrogenated silicon<sup>4</sup> by diazonium salts provide an easy and efficient way to covalently modify the surface of these materials. Electrografting is achieved by electrochemical reduction,<sup>1–4</sup> while grafting takes place by simple dipping of the material into a solution of the diazonium salt.<sup>5</sup> The process can be run in either aprotic (CH<sub>3</sub>CN) or aqueous media.<sup>6</sup>

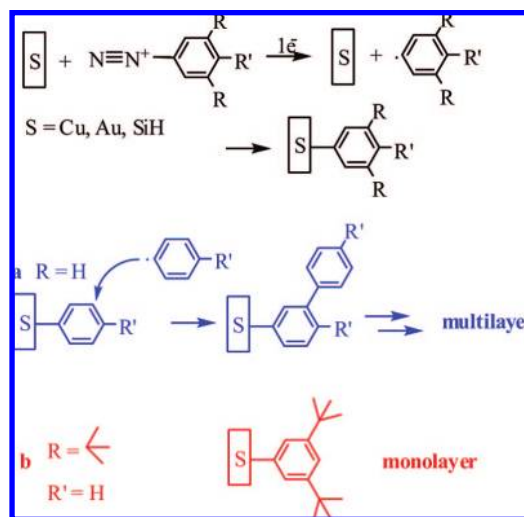
The covalent bond<sup>7</sup> between the substrate and the organic layer originates from the attack of the aryl radical obtained from the reduction of the diazonium salt. The calculated bonding energy ranges from 24 kcal/mol on gold to 70 kcal/mol on Si and up to 105 kcal/mol on carbon.<sup>7</sup>

However, this same radical attacks the first grafted aryl group to give a polyaryl layer with a nanometer to micrometer thickness.<sup>8</sup> As a consequence, this method does not routinely provide monolayers or even very thin layers (1–5 nm) at the difference of self-assembled monolayers (SAMs)<sup>9</sup> on gold. However, as shown by STM, a true, organized monolayer has been obtained on SiH by careful control of the charge used for the electrochemical reduction of the ion.<sup>10</sup> Very thin and homogeneous layers have also been obtained by electrografting 4-nitrophenyl groups on a very flat kind of carbon (pyrolyzed photoresist films, PPF), their thickness measured by AFM was close to a monolayer.<sup>11</sup> On gold, by scanning the potential close to the voltammetric peak and recording the IR spectrum, the authors concluded to the formation of a monolayer.<sup>12</sup> With a different method, the diazonium salt of diaryldisulfides, <sup>+</sup>N<sub>2</sub>Ar–S–S–Ar, has been electrografted providing a "thick" layer; further electrochemical cleavage of the S–S bonds permits one to obtain a layer as thin as 1.3 ± 0.5 nm, that is, very close to a monolayer.<sup>13</sup>

In the present paper, we speculated that it should be possible to prevent the layer from growing by hindering different positions of the diazonium ion. Scheme 1 represents the electrografting of a diazonium salt substituted in the para position by the R' group and in the two meta positions by R. The radical mechanism responsible for the growth of the layer has been established; it involves the attack of an aryl radical on a first grafted phenyl group to give a cyclohexadienyl adduct that is rearomatized by electron exchange with the electrode or another diazonium salt.<sup>8</sup> As a first example of the influence of steric hindrance, we have observed that, if the 2- and 6-positions are occupied by a methyl group, grafting does not occur (positions are numbered by reference to the position of the diazonium ion and therefore of the radical).

As shown in Scheme 1, whatever the diazonium salt, the first grafted phenyl group is sterically protected on the 2- and 6-positions by the surface of the material. Without any substituent on the phenyl

**Scheme 1.** Electrografting of Diazonium Salts and Formation of (a) Multilayer and (b) Monolayer

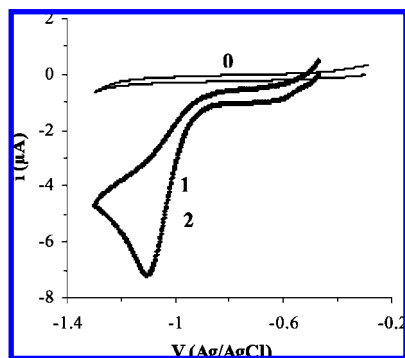


ring, micrometer multilayers are obtained (Scheme 1a with R = R' = H).<sup>8</sup> If one considers a 4-substituted aromatic ring (Scheme 1a), the attack will take place on the 3- and 5-positions. If now the 3- and 5-positions are sterically blocked by bulky groups and the 4-position is free (Scheme 1b), the growth of the layer by attack on the 4-position should be disfavored. Indeed, as we will show here, when using the 3,5-bis-*tert*-butyl benzenediazonium ion (**1**), a layer very close to a monolayer can easily be obtained.

The voltammogram of **1** is very different from that usually observed for other diazonium salts. As shown in many papers,<sup>1</sup> the voltammogram of the typical 4-nitro benzenediazonium ion presents a broad irreversible wave that disappears on the second scan at –0.02 V/SCE in ACN on a carbon electrode. This phenomenon is due to the blocking of the electrode by the 4-nitro polyphenylene layer attached to the electrode. Voltammograms of **1** on a copper electrode are different: they present an irreversible wave ( $E_p = -1.10$  V<sub>Ag/AgCl</sub>, Figure 1) that decreases only slightly upon scanning at low scan rates (Figures S4–6). Similar voltammograms are obtained on gold ( $E_p = -0.83$  V<sub>Ag/AgCl</sub>, Figures S1–3). A broad irreversible wave is observed on n-doped hydrogenated silicon ( $E_p = -1.3$  V<sub>Ag/AgCl</sub>, Figure S7).

The voltammogram of **1** is typical of a product that is reduced on an electrode and undergoes an irreversible chemical reaction. The most likely explanation for the fact that the successive scans do not lead to a complete disappearance of the wave—as for example with the 4-nitro benzenediazonium ion—is that the surface is not blocked and that the layer grows relatively slowly. Nevertheless, such a voltammogram has been previously observed starting from benzenediazonium tetrafluoroborate itself, which gave a quite

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**Figure 1.** Cyclic voltammograms of 3,5-bis-*tert*-butyl benzenediazonium tetrafluoroborate **1**: (1) first scan; (2) second scan in ACN + 0.1 M NBu<sub>4</sub>BF<sub>4</sub> on a copper electrode ( $d = 1$  mm),  $c = 4$  mM (scan rate  $v = 50$  mV s<sup>-1</sup>, reference Ag/AgCl); (0) blank.

conductive thick layer that could be observed with the naked eye.<sup>8</sup> Since this is not the case with **1**, the formation of a very thin layer is likely. In order to confirm this possibility, copper, gold, and n-doped silicon (SiH) surfaces were modified by reduction of **1** under the conditions indicated in Table 1.

**Table 1.** Modification of Surfaces by **1** by Chronoamperometry<sup>a</sup>

substrate	time (s)	$E$ (V <sub>Ag/AgCl</sub> )	layer thickness (nm)
Cu	30	-1.2	1.3, $\sigma = 0.6$
Au	300	-1.4	1.0, $\sigma = 0.3$
SiH	150	-0.5	1.6, $\sigma = 0.1$

<sup>a</sup> [**1**] = 4 mM in ACN + 0.1 M NBu<sub>4</sub>BF<sub>4</sub>.

We examined by IR-ATR spectroscopy the surface of the copper wafer. The spectrum shows the following peaks: 2918 and 2850 cm<sup>-1</sup> in the CH stretching region; 1560 and 1540 cm<sup>-1</sup> in the region of the ring vibrations, and 710 cm<sup>-1</sup> in the region of the CH out of plane. By comparison, **1** absorbs in the same regions at, respectively, 2965, 2955, 2903, and 2867 cm<sup>-1</sup>; 1598, 1525, and 706 cm<sup>-1</sup>. The spectrum on gold is similar.

In addition, the water contact angle of a clean deoxidized copper surface changes from  $37 \pm 3$  to  $73 \pm 3^\circ$  after modification by **1**. This indicates a modification of the copper surface by a thin organic layer.

We measured the thickness of the layer on copper, gold, and n-doped hydrogenated silicon by ellipsometry, and values in the range of 1.0–1.6 nm were found (see Table 1, each value is the mean of three independently prepared samples). One observes that grafting is more efficient on copper and silicon than on gold as lower potentials and shorter times must be used to produce a monolayer, but in every case, the formation of multilayers is slow enough—much slower than with unhindered diazonium salts—so that the conditions that permit one to obtain a layer close to 1 nm are easily determined.

An estimation of the distance between the copper surface and the outer extremity of the organic layer can be obtained from molecular models and from the structure of the grafted layer, as calculated by DFT methods by Jiang et al.<sup>7</sup> who showed that the aromatic rings are tilted 40° to the surface normal on copper. From

these data, one finds that the thickness of the organic layer should be 1.0 nm. This permits one to conclude that a covalently bonded monolayer is formed by reduction of **1** on copper, gold, and silicon (SiH). We also investigated 3,5-trifluoromethyl benzenediazonium tetrafluoroborate and found that the trifluoromethyl groups are not bulky enough to prevent the growth of the layer, which reaches  $16.7 \pm 0.1$  nm on copper under the same conditions as above.

These results indicate that the reaction of the 3,5-bis-*tert*-butylphenyl radical with the first grafted phenyl group is sterically hindered and that the multilayers grow very slowly. For identical electrolysis conditions on the same substrate, a layer of  $16.0 \pm 0.1$  nm is obtained starting from 4-methyl benzene tetrafluoroborate. Most likely, the aryl radicals that are prevented from attacking the bis-*tert*-butylphenyl group react by hydrogen atom abstraction from the solvent.<sup>14</sup> It could be possible that the 3,5-bis-*tert*-butylphenyl radical abstracts hydrogen atoms from the *tert*-butyl groups on the surface, but this reaction should be disadvantaged by comparison with the hydrogen abstraction from the solvent in view of the relative concentrations (of the order of  $10^{-9}$  mol cm<sup>-2</sup> for the organic layer and 19 mol dm<sup>-3</sup> for ACN as the solvent).

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**Supporting Information Available:** Experimental section, cyclic voltammetry on Au, Cu, and SiH, and IR-ATR characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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