

Air-oxidation of Gold Metal in Polybenzimidazole Solution

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Gold(0) has been found to dissolve in polybenzimidazole solution under extremely mild conditions resulting in a polymeric 'gel' with gold(I) and gold(III) cations acting as chain bridging sites.

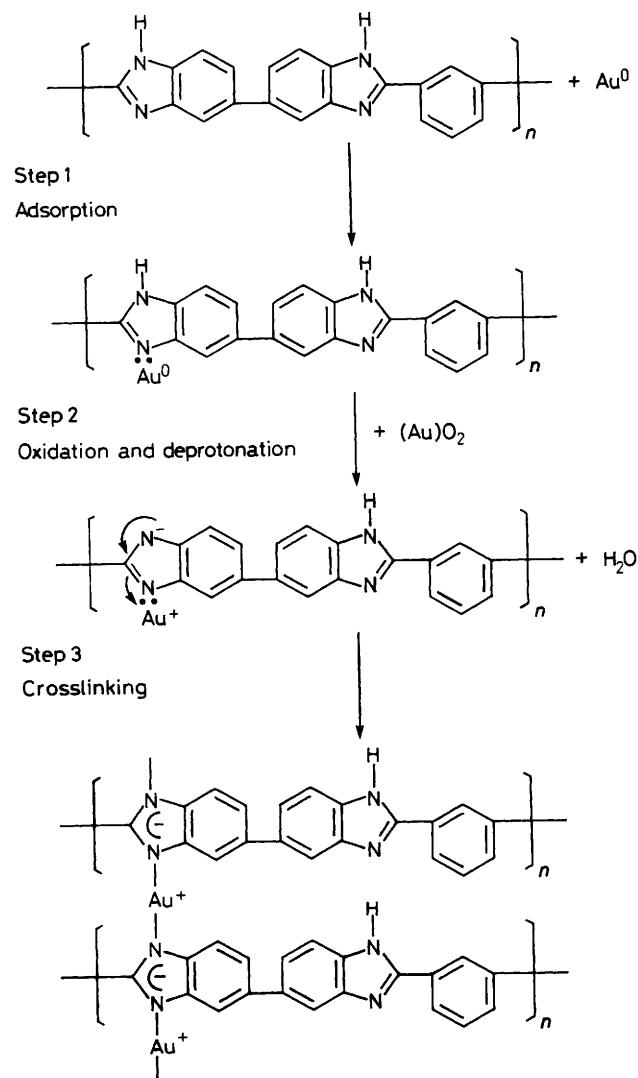
Gold is traditionally known as an inert metal even under severe conditions. We report here an unusual chemical reaction of a gold plate in a neutral, non-corrosive organic solution, consisting of polybenzimidazole (PBIMH) and dimethyl formamide (DMF), during which gold metal is gradually oxidized and dissolved under extremely mild conditions.

A gold plate (99.99%, $2 \times 5 \times 10$ mm) was etched in 10% HNO_3 to remove surface oxides, and repeatedly washed by distilled water. The clean gold plate was then immersed in 5 ml of PBIMH-DMF solution (2% concn.) at room temperature without agitation. This solution was exposed to the air and after one day became a 'gel'. The rigidity of the gel increased gradually with time. After two weeks, the gold plate was

removed from the solution and washed with warm DMF. The gel was dried at 50°C *in vacuo*. X-Ray photoelectron (XPS) and IR spectroscopies were used to characterize the structures of both the gold plate surface and the dried gel residue. In XPS, the C(1s) line (binding energy = 284.5 eV) from residual pump-line oil contamination was used as the internal standard.

Figure 1(b) shows the wide scan XPS spectrum of the gold plate after immersion in the PBIMH solution. The existence of N(1s) and C(1s) bands illustrates the adsorption of PBIMH on the surface of the metal. The O(1s) band is probably due to the adsorption of oxygen on gold. Figure 1(a) was obtained from the dried gel residue. The small bands of Au(4f) and Au(4p) indicate that a small amount of gold had entered the solution. This is quite unusual although the reaction is very slow.

Figure 2(b) shows an XPS photoline in the Au(4f) region of the gold plate after immersion in PBIMH solution. This is essentially the same as the spectrum obtained of the surface after it had been etched with argon ions in the spectrometer for 30 min [Figure 2(c)]. These spectra show two binding energy values: 83.7 eV for Au(4f_{7/2}) and 87.4 eV for Au(4f_{5/2}). These show that the gold metal on the surface is in the zero



Scheme 1

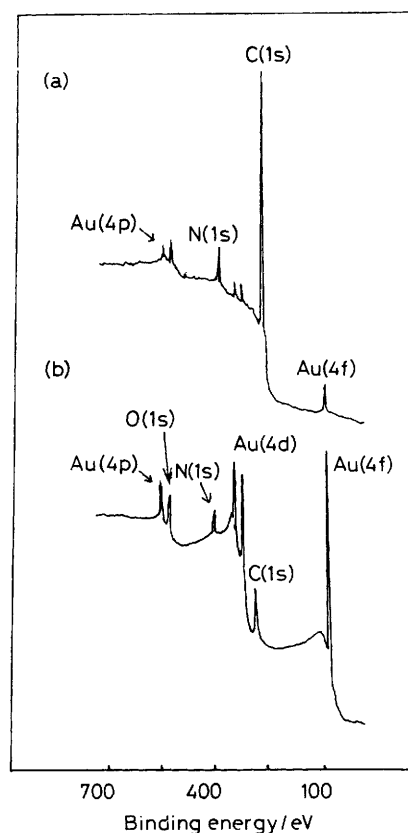


Figure 1. Wide scan XPS spectra. (a), the dried gel residue; (b), the gold plate pre-treated with polybenzimidazole solution.

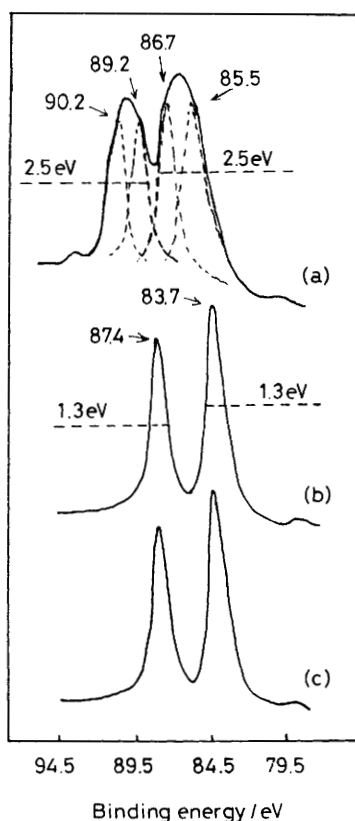


Figure 2. XPS spectra in Au(4f) region. (a), gel residue; (b), plate surface; (c), gold plate after being etched by argon ions for 30 min.

oxidation state.¹ The XPS spectrum of Figure 2(a) taken from the gel residue also shows two Au(4f) bands. However, these bands are quite different from those which appear in the spectrum of the gold plate, both in their binding energies and in band width, indicating that the gold had been oxidized and entered the solution. The peaks for Au(4f) in Figure 1(a) appear to be significantly broader, from 1.3 eV full width at half maximum (FWHM) in the gold plate form to 2.5 eV in the gel residue. Peak deconvolution shows that the photoline of Figure 1(a) consists of Au^I bands at 85.5 and 89.2 eV, and Au^{III} bands at 86.7 and 90.2 eV.¹ The possibility of two experimental artefacts, electrostatic charging of the specimen and change induced broadening, was eliminated since the Au(4f) was referenced to C(1s) = 284.5 eV and the C(1s) spectra of Figure 2(a–c) had similar FWHM (2.9–3.0 eV).

Figure 3(a) shows an XPS spectrum of the gel residue and Figure 3(b) shows the spectrum of the gold plate in the N(1s) region. The binding energy of the N(1s) level of the gold surface is 400.3 eV, which coincides with the value of benzimidazole,¹ indicating that some of the polymer chains were adsorbed on the surface of the gold metal. The analysis of the N(1s) spectrum of Figure 3(a) shows two binding energy values, 400.0 and 398.4 eV. The first value coincides with the benzimidazole linkages of the polymer chain and the second with the benzimidazolate anion resulting from deprotonation.

IR spectroscopic studies provided further information about the structure of the gel residue. PBIMH has strong hydrogen bonding in the solid state and therefore the IR spectrum shows strong and broad absorption in the region

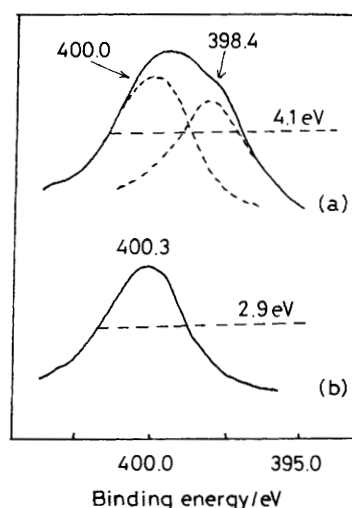


Figure 3. XPS spectra in N(1s) region. (a), gel residue; (b), gold surface.

3600–2400 cm⁻¹. The spectrum recorded from the gel residue shows a relatively weaker and narrower absorption in this region. The reduction in intensity of the N–H stretching band is probably due to the deprotonation of some of the benzimidazole linkages of the polymer chains. Far-IR spectroscopic studies of the gel residue show a new band near 290 cm⁻¹, which could be assigned as Au–N stretching.² XPS and IR studies provided evidence to show that the polymer chains were crosslinked by gold–nitrogen linkages.

The co-ordination of N ligands to metal centres is well known and forms the basis of adhesion to, extraction of, and protection of the metal in industry. However, the above experimental evidence illustrated that PBIMH solution could dissolve and oxidize the gold metal. This is unusual and surprising, as gold metal had been considered to be quite stable to most chemicals, even under severe conditions.

When a pre-dried solvent was used, a minute quantity of water was detected after the reaction. When oxygen was removed from the solution, by bubbling with pre-purified nitrogen, the gold was not oxidized. On the basis of the reaction conditions and the structural properties of the gel residue, we propose the reaction scheme shown in Scheme 1.

The first step in the reaction is the formation of the Au⁰–PBIMH complex by ligation of the pyridine nitrogen of PBIMH to metallic gold. In this complex gold and the imino group are more reactive than when in their pure states. When the solution was exposed to air, gold metal could adsorb oxygen to form undissociated, diatomic oxygen, which shows stronger basic and oxidizing properties.³ The energy barrier for the reaction of these surface species is much lower than in their isolated states. So, under mild conditions gold metal was oxidized, and benzimidazole linkages of PBIMH were deprotonated, resulting in the formation of gold cations and benzimidazolate anions. Molecular motion of the polymer chains brought the gold cation into solution. The two nitrogen atoms in the benzimidazolate anion are not distinguishable, and are equivalent for co-ordination. Each gold cation could co-ordinate with two or more nitrogen ligands. In fact it has been reported that metal azolates are polymeric materials).^{4,5} The PBIMH chains were then crosslinked with Au–N bonds and became insoluble in DMF; this resulted in a gel being formed, with Au^I and Au^{III} cations acting as chain crosslinking sites.

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