



IR spectroscopy of a Pd–carbonyl surface compound

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Abstract

Pd is deposited onto a model alumina surface in the presence of a CO atmosphere of 3×10^{-6} mbar at liquid nitrogen temperatures. According to the IR spectra the palladium carbonyl compound formed contains weakly bound terminal and more strongly bound bridging CO molecules, the spectra being similar to the IR spectra of colloidal metal particles in solution and the IR spectra of CO adsorbed on small deposited Pd particles. In line with thermal desorption studies of the stability of the compound, the IR spectra reveal the transition from the compound to a situation where CO is adsorbed on larger compact metal aggregates upon heating to room temperature. © 1997 Elsevier Science B.V.

1. Introduction

Chemical vapour deposition of transition metal cluster compounds with well defined stoichiometries is used to prepare supported dispersed metal catalysts [1,2]. By decomposition of the compound the “naked” metal aggregates are formed on the support. The idea here is to use an aggregate precursor which avoids the mass selection of metal clusters in the gas phase before deposition [3], and thus produce a narrow size distribution of deposited particles. However, rather narrow size distributions of aggregates may also be prepared by nucleation and growth via metal vapour deposition if the metal vapour flux to the surface, as well as the surface temperature, are carefully controlled [4–7]. Often metal deposition is carried out under ultrahigh vacuum (UHV) conditions. However, it has been shown that the presence of a gas atmosphere may drastically change the

properties of the deposited particles [8–10]. In fact, recently published thermal desorption and photoelectron spectra of Pd deposited onto alumina in presence of a CO gas atmosphere indicated the formation of a palladium-carbonyl surface compound [10,11], which decomposes at approximately 190 K. Its formation appears to be surprising because stable binary stoichiometric polynuclear Pd–carbonyl compounds are not known. Such compounds have only been observed in zeolites [12–14]. In order to characterise the Pd–carbonyl system in more detail it appeared to be necessary to perform IR measurements which may be compared with the IR spectra of reference compounds [15], and also with the IR spectra of dispersed metal particles in contact with adsorbed CO [16–19]. Such measurements are reported in the present Letter. The spectra of the compound are compared with those of colloidal metal particles in solution [20] and with spectra taken of CO adsorbed on Pd particles which have been deposited on the same support under UHV conditions [21].

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2. Experimental

The experiments have been carried out in an ultrahigh vacuum system with a base pressure of 3×10^{-10} Torr [22]. The system contains a preparation chamber where the order of the surface can be checked by LEED and its chemical constitution by Auger electron spectroscopy. The IR light is generated by a globar and after passing a Mattson type (RS1) interferometer focused onto the sample. The interferometer is mounted in a home-made chamber which is evacuated to 10^{-3} Torr. The light passes through viton-O-ring sealed KBr-windows before and after reflection from the sample surface. It is detected with a liquid nitrogen cooled MCT detector placed in a detector chamber which is flushed with dry nitrogen. All spectra were recorded with a spectral resolution of 2 cm^{-1} accumulating 500 scans for each spectrum. At another sample position electron energy loss spectra may be recorded by a Leybold Heraeus ELS 22.

The aluminium oxide film has been prepared by oxidation of a cleaned NiAl(110) single crystal alloy surface according to well-known recipes [23,24]. The reflectivity of the well-ordered thin oxide film is still very high due to the metal support. Pd has been evaporated from a rod via electron bombardment and the deposited amount controlled by a quartz balance.

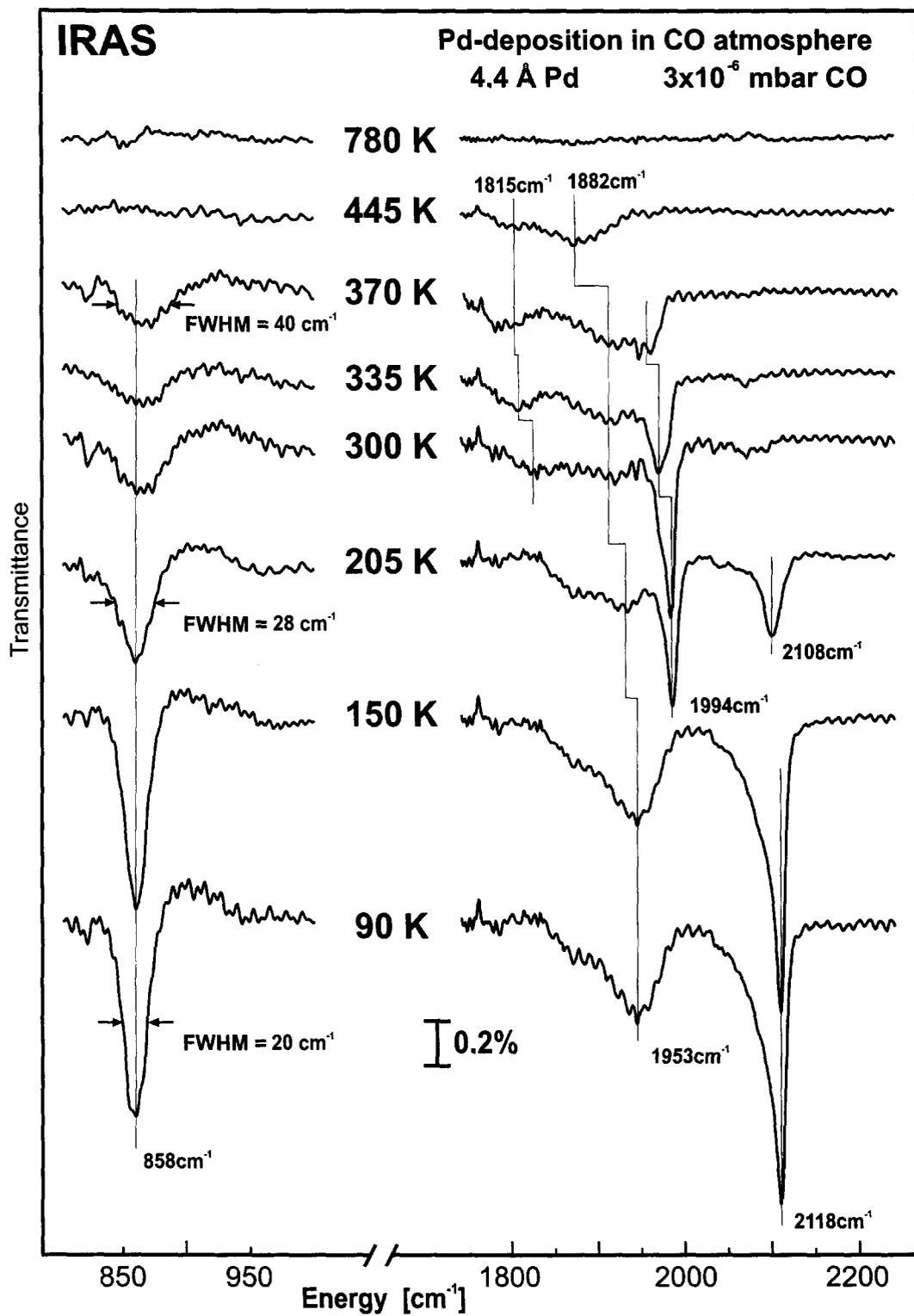
3. Results and discussion

Fig. 1 shows a set of IR spectra taken after deposition of the equivalent of 4.4 \AA Pd, as determined by a quartz balance, in the presence of a CO atmosphere of 3×10^{-6} mbar pressure. The substrate, which is a thin, well-ordered alumina film grown on a NiAl(110) single crystal surface according to well-known recipes [23,24], has been cooled to 90 K during deposition. The panel on the right hand side of Fig. 1 shows the region of CO stretching frequencies, the left hand side panel shows the region of the alumina phonon band. The position of the alumina Fuchs–Kliwewer phonon is known from

earlier electron energy loss studies [23] and the observed frequency in the present Letter is in full agreement with those data [23].

We start the discussion by considering the IR spectrum taken directly after deposition at 90 K which is shown at the bottom of Fig. 1. In the region of CO stretching frequencies there is a narrower band at 2118 cm^{-1} and a broad band with maximum absorbance at 1953 cm^{-1} . As mentioned above, the band at 858 cm^{-1} is due to the alumina phonon [23]. To assign the CO stretching region, in Fig. 2b we have plotted this particular spectrum from Fig. 1 in comparison with a spectrum taken after the same amount of Pd has been deposited in UHV onto the same substrate and then exposed to saturation with a dosage of 20 L CO (Fig. 2a). The relative intensity ratios of the two bands are almost identical. The strong narrower bands are located at very similar frequencies, i.e. 2118 cm^{-1} and 2113 cm^{-1} . The broader bands are shifted with respect to each other in the sense that the systems where Pd was deposited and later exposed, exhibit a broad but a little more structured band at higher frequencies with a sharper maximum at 1985 cm^{-1} and a shoulder near 1930 cm^{-1} [21]. In the case of UHV grown Pd aggregates exposed to CO we have earlier proposed an assignment which we now transfer to the present case: the band near 2100 cm^{-1} is due to weakly bound CO terminally bound to Pd atoms. The band below 2000 cm^{-1} has been assigned to bridge bonded CO with contributions of two subbands: bridge bonded CO on defect rich terraces (lower frequencies) and on the edges of the aggregates (higher frequency). Therefore we believe that the band at 2118 cm^{-1} originates from linearly bound CO and the lower frequency band from bridge bonded CO. The reason for the absence of the absorption band at 1985 cm^{-1} observed for the vacuum deposited Pd aggregates is the almost complete absence of extended edges in case of the aggregates deposited in the presence of a CO atmosphere. If we estimate the relative amount of bridging to terminal CO we find a ratio of about 1:1. In the lower part of Fig. 2 we compare the spectrum of the Pd–carbonyl compound with the

Fig. 1. IR spectra for 4.4 \AA Pd (average thickness) deposited at 90 K in presence of a CO atmosphere of 3×10^{-6} mbar pressure and subsequent annealing to the indicated temperatures. All spectra were recorded after cooling the sample down to 90 K again.



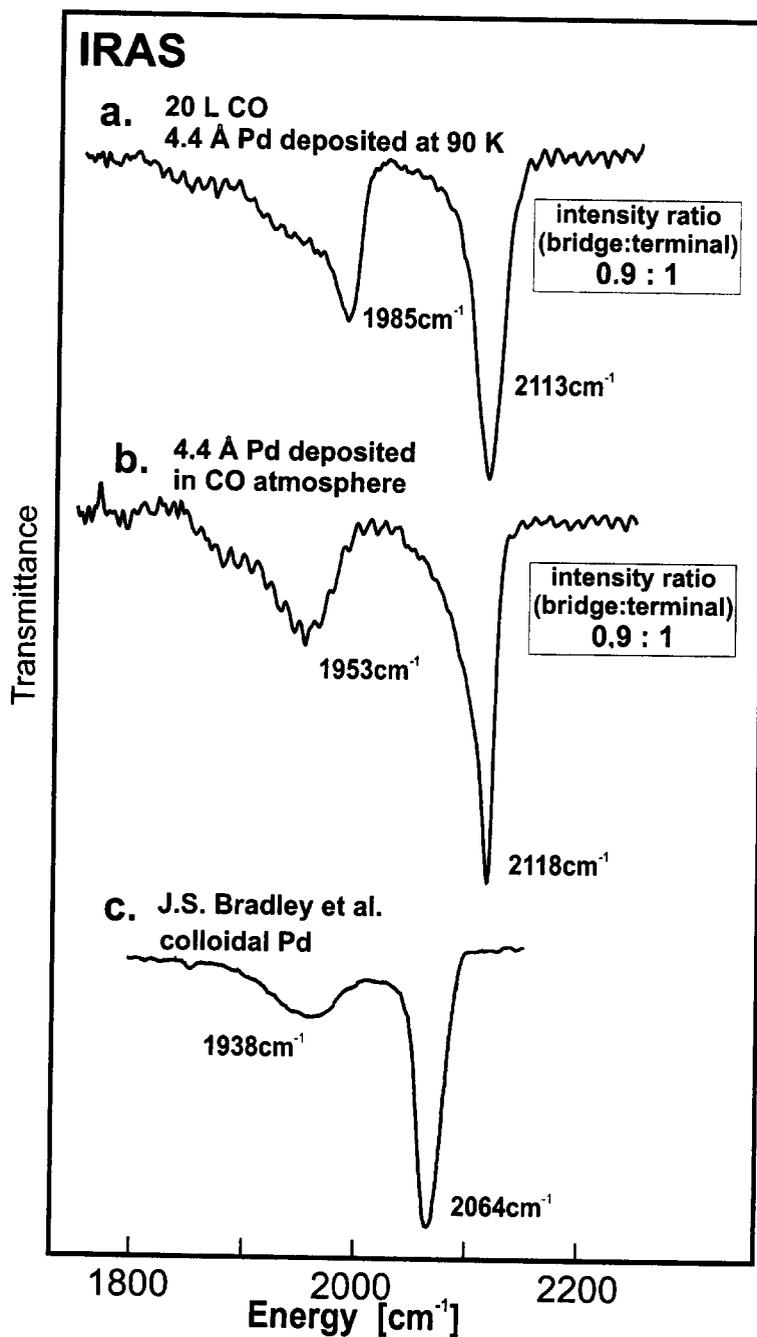


Fig. 2. (a) Spectrum for 4.4 Å Pd (average thickness, 300 atoms per particle) deposited at 90 K under UHV conditions and a dosage of 20 l CO at 90 K. (b) Spectrum for 4.4 Å Pd (average thickness) deposited at 90 K in presence of a CO atmosphere of 3×10^{-6} mbar pressure (taken from Fig. 1). (c) Spectrum of CO on colloidal Pd in solution taken from Ref. [20]

corresponding spectrum of colloidal Pd in solution (Fig. 2c). Clearly, the behaviour of the spectrum of the colloidal CO covered Pd particles is similar but

the peak assigned to terminal CO is shifted to lower frequency in the case of the colloidal Pd [20]. This, however, is not too surprising because the terminally

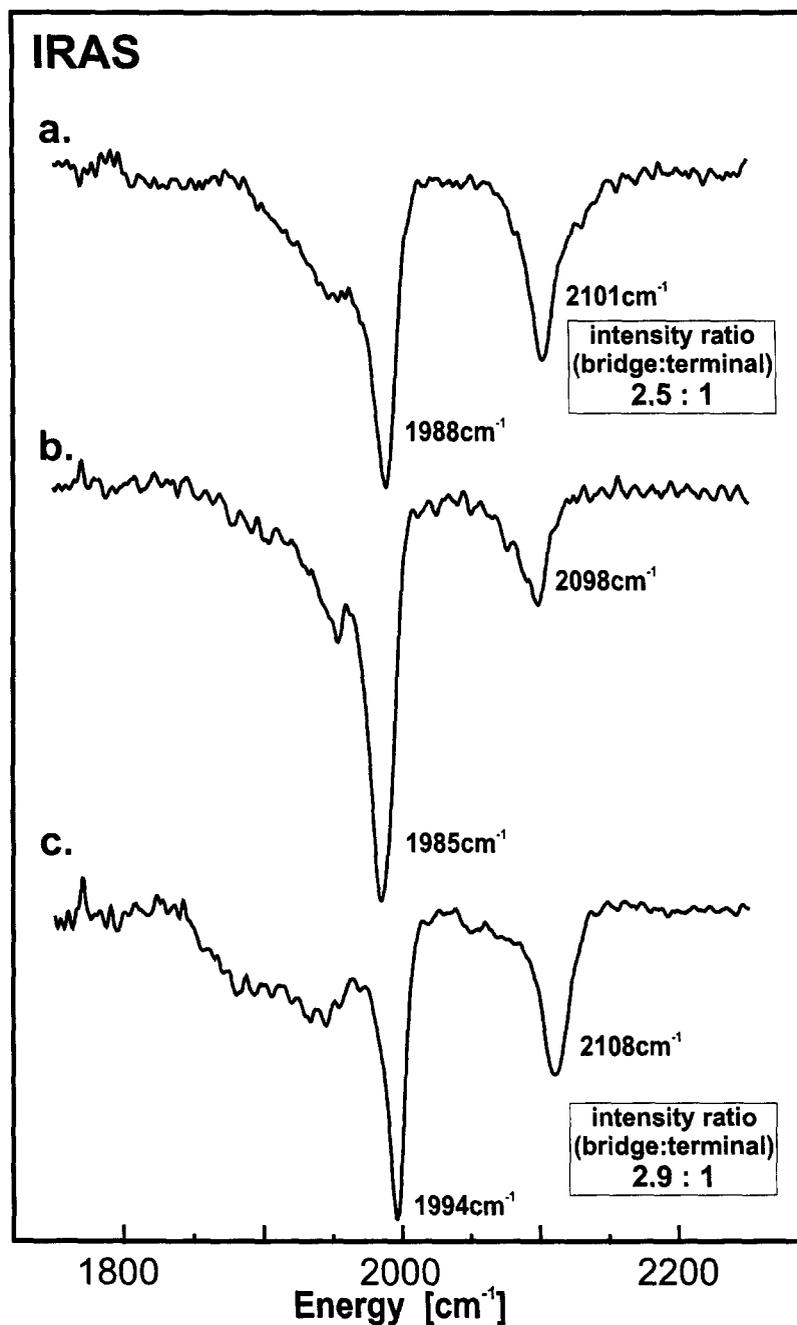


Fig. 3. (a) Spectrum for 4.4 Å Pd (average thickness, 4500 atoms per particle) deposited at 300 K under UHV conditions and a dosage of 20 l CO at 90 K. (b) Same preparation as in Fig. 3a after annealing to 205 K. (c) Spectrum for 4.4 Å Pd (average thickness) deposited at 90 K in presence of a CO atmosphere of 3×10^{-6} mbar pressure (taken from Fig. 1)

bound CO molecules reach far out into solution and experience a solvent shift, while the bridge bonded CO molecules which are closer to the metal particle do not seem to be shifted as strongly. Therefore, the above given assignment of the CO stretching frequencies is reasonable. We can now return to Fig. 1 and the changes that occur when the Pd–carbonyl is heated above 90 K. At 150 K the compound is still stable and the spectrum has not changed. However, only slightly above the decomposition temperature (at 205 K) the IR spectrum is completely altered. Fig. 3 compares the spectrum taken at 205 K (from Fig. 1) with those IR spectra recorded for CO adsorbed on Pd, UHV deposited at 300 K and then exposed to CO saturation coverage at 90 K, as well as with the same preparation after heating to 205 K. Firstly, we note that at this temperature the amount of adsorbed CO has considerably decreased as compared with 90 K (Fig. 1). This is expected from the earlier reported thermal desorption spectra [10,11]. Also, the relative ratio of bridge bonded CO with respect to linearly bound CO has increased. Such a situation is similar but not identical to what is observed for post exposed vacuum deposited Pd (Fig. 3a). Obviously, there is a component in the shoulder that extends towards 1850 cm^{-1} . In this frequency range we do observe bands for large aggregates and low CO coverage [21]. In connection with the formation of larger metal aggregates it is interesting to check the appearance of the alumina phonon in Fig.

1. Clearly, the phonon band is damped and its width increases as the aggregate size increases. This is caused by the creation of larger Pd aggregates which are formed when the Pd carbonyl compound decomposes and the CO coverage decreases. The larger metallic aggregates screen the excitation of the Fuchs–Kliwer phonon as has been observed in other systems [25–29]. We attribute the larger width to the faster decay of the phonon of the alumina substrate through coupling to electron hole pairs in the metallic aggregates. This effect becomes more and more pronounced as the surface temperature is increased and more CO desorbs from the surface. We note, however, that the spectra have been recorded after the sample has been brought back to 90 K. While the phonon energy remains unchanged, its width increases due to the creation of larger metallic aggregates and the above phonon–electron hole pair coupling. Simultaneously, its intensity decreases until above 400 K it cannot be distinguished from the background because the metallic overlayer leads to a complete screening of the phonon. The CO stretching vibrations at this temperature exhibit frequencies and intensities that have been observed previously for large Pd deposits at high temperatures [21]. Inspection of Fig. 3 again shows, however, that the bands observed for deposits prepared at 300 K and then heated to a higher temperature (Fig. 3b) are still narrower than in the present case. This indicates that the shape of the Pd particles formed by decomposi-

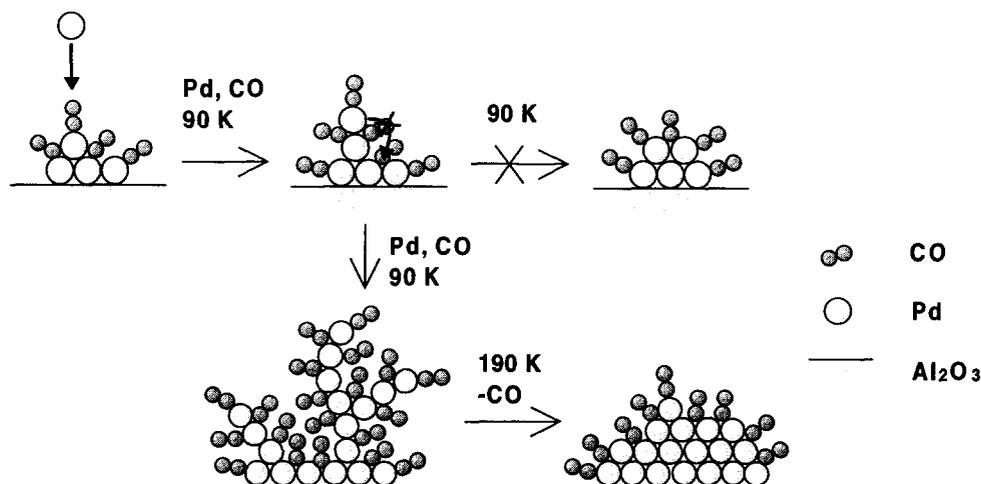


Fig. 4. Schematic representation of a possible growth model for Pd deposition in a CO atmosphere.

tion of the Pd carbonyl are still controlled by the kinetics of the processes involved. The picture evolving which describes the processes involved is fully compatible with the one reported in Refs. [10,11]. It is, again, summarised in Fig. 4: at low temperature, diffusion of the impinging metal atoms to sites where the number of metallic neighbours is maximised is hindered due to the presence of the rather dense adsorbate coverage. Therefore the formation of compact metallic nuclei is unfavourable and strongly branched CO saturated Pd carbonyl-like aggregates form. Only at higher temperatures when the CO coverage is lowered via desorption does the formation of larger aggregates set in.

4. Summary and conclusion

The presented IR data recorded for Pd deposited in a CO ambient atmosphere onto an alumina model substrate, corroborate the previously proposed formation of a binary Pd carbonyl surface compound [10,11]. The compound contains terminally and bridge bonded CO with an intensity ratio of about 1:1 indicating that per Pd atom there may be a terminal and a bridging CO molecule which would be consistent with the previous XPS results from which a Pd/CO ratio of about 1:2 has been deduced. The compound is known to decompose at 190 K and at this temperature we find a change in the infrared spectra which is consistent with the formation of larger metal aggregates onto which CO is chemisorbed [21]. The spectra reveal that the shape of the aggregates as documented by the behaviour of the spectra is still determined by the kinetics of the formation process.

It is interesting to note that the high resolution of the IRAS experiment allows to observe the change in phonon linewidth of the alumina substrate which might be due to coupling of the phonons to electron hole pairs in the metal aggregate. The phonon intensity is attenuated due to screening by the presence of the metal aggregates.

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