SERS study of polymer on metals: 5. Chemisorption and reactions of acrylonitrile and poly(acrylonitrile)

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Surface enhanced Raman scattering (SERS) studies of chemisorption of acrylonitrile and poly(acrylonitrile) on Ag are presented. The SERS spectra obtained at room temperature with low laser power irradiation are markedly different from normal Raman spectra of neat acrylonitrile and poly(acrylonitrile). This is ascribed to surface reactions after adsorption. Under high laser power irradiation, the SERS spectra show graphitic formation. When the temperature is raised, graphitization of poly(acrylonitrile) on the Ag surface is nearly complete. The reaction mechanisms consistent with the spectral results are proposed.

(Keywords: surface enhanced Raman scattering; silver; acrylonitrile)

INTRODUCTION

In previous work, we used surface enhanced Raman scattering (SERS) to study the chemisorption of poly(vinyl pyridine) and polybenzimidazole on metals[1,2]. Here, we present SERS studies of surface reactions of acrylonitrile (AN) and poly(acrylonitrile) (PAN) on Ag. An early communication has briefly reported our preliminary SERS study of PAN on Ag[3]. We still feel it important to understand the interaction of cyanide (and more complex CN-containing molecules) with metal surfaces from both theoretical (cyanide being a member of isoelectronic CN^-, CO, NO^+ series) and practical (catalytic) points of view. However, only recently have detailed studies of CN surface chemistry appeared[4]. High resolution electron energy loss spectroscopy (HREELS) studies of a variety of CN-containing compounds on the Pd(111), Pd(100) and Cu(111) surfaces indicate that adsorption takes place with the CN group orientated parallel to the surface.

The interaction of acetonitrile (ACN) with Pt, Ru, Ni, Ag and Cu single crystal surfaces has been studied to date mainly with temperature-programmed thermal desorption (TDS) and HREELS[5–13]. On transition metal surfaces, the formation of the rehybridized η^2 (C,N) species is usually observed for ACN, while on noble metal surfaces a weak N-end bonding takes place. Benzonitrile interacts strongly with the Au(100) surface, having the molecular plane parallel to the surface[14]. Studies of AN surface chemistry are scarce. To the best of our knowledge, only the *FT*i.r. data for the Cu/SiO_2 surface have been reported[15]. The C≡N stretching vibration of AN adsorbed on Cu/SiO_2 was appreciably shifted to lower frequency regions in comparison with that in the liquid state, suggestive of a π-component coordination of cyano group in AN with the Cu surface site. In addition, AN electrosorption on a polycrystalline Au electrode in 1 M H_2SO_4 solution has been briefly examined by SERS[16] where, at the positively charged electrode, the majority of the molecules are found to be N-end bonded normal to the electrode surface (SERS figures not shown in ref. 16). On the other hand, far fewer studies of CN-containing polymers on metal surfaces have been published. Dilute PAN solution was found to undergo gelation after interaction with Cu[17]. This is due to the conversion of some nitrile groups into carboxyl groups in the presence of Cu.

A major application of vibrational spectroscopies at metal surfaces is to gain information on the nature of adsorbate–surface interactions and surface reactions from differences in the form of the spectra, especially frequencies and bandshapes for species in bulk and interfacial environments. SERS is a potentially valuable technique for such application. Although limited to polycrystalline, mildly roughened surfaces (most prominently Ag, Cu and Au), absolute spectra can be obtained rapidly with high resolution ($\sim 1\ cm^{-1}$) over wide frequency ranges, enabling a variety of vibrational bands associated with internal and adsorbate–surface modes to be readily detected. A few SERS studies on surface chemical reactions have been done[18–21]. We have been exploring the application of SERS as a structural probe of reactive adsorbates on metal surfaces and at the polymer–metal interface. Our hope was that the detailed scrutiny of the AN and PAN/metal systems would provide further insight into the reactivity in surface chemistry. Our interest in this particular system derives from the fact that AN is a very important and easily polymerizable monomer. It offers a large variety of AN-containing copolymers. However, lack of pertinent structural information has so far hindered progress in polymer–metal interfacial studies and has prompted us to undertake this study.

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EXPERIMENTAL

Preparation of SERS-active substrates by the HNO_3 roughening method has been described in detail elsewhere[22,23]. This kind of SERS substrate is quite thermally stable and gives Raman signals from a region of only a few monolayers. Except for a flat continuum background, which rises to $250 cm^{-1}$, no Raman signals can be detected in the spectral region below $4000 cm^{-1}$ for a roughened blank foil. X-ray photoelectron spectra (X.p.s.) showed no evidence for the existence of Ag^+ on the thoroughly rinsed Ag substrate[24]. The Raman excitation was provided by a Kr^+ laser operated at 647.1 nm, the scattered light being collected by a SPEX model 1403 scanning double monochromator.

AN was obtained as reagent grade from Shanghai Chemical Co. and was redistilled under nitrogen atmosphere before use. AN (0.1 g) was placed in a glass cuvette and uniformly spread on the bottom. A roughened silver foil was hung 0.5 cm above the AN and the SERS spectra of the chemisorption of evaporated AN onto silver foil were recorded after 1 h. PAN was prepared by the method described in ref. 17. PAN solution (in dimethylformamide) was spread on $1 cm^2$ Ag foil and then put into a container to evaporate the solvent, either slowly in 24 h or quickly in 2 h by adjusting the vapour pressure of the solvent. SERS spectra recorded from samples prepared by different methods were compared.

RESULTS AND DISCUSSION

Adsorption and surface reaction of AN and PAN on Ag

The SERS spectrum of AN on Ag and its normal Raman spectrum in the liquid state are given in *Figures 1A* and *B*, respectively. In order to analyse the surface Raman data, it is necessary first to understand the spectral feature of *Figure 1B*. According to the work of Halverson *et al.*[25] on vibrational analysis, AN exhibits a strong C=C stretching band at $1608 cm^{-1}$, and a C≡N stretching band at $2228 cm^{-1}$. Other characteristic vibrational modes appear at 1412, 1288, 1094, 970 and $568 cm^{-1}$, which are attributed to CH_2 deformation, C–H rocking, CH_2 rocking, $H_2C{=}C$ wagging and C=C–C bending, respectively.

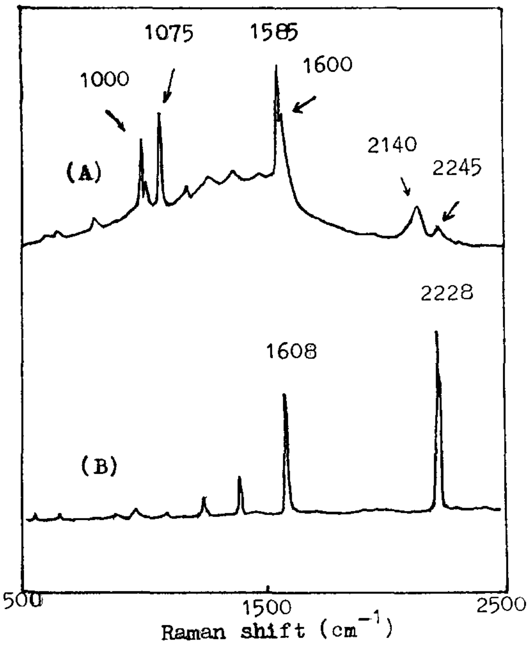


Figure 1 (A) SER spectrum of AN on Ag. The laser power at the sample surface was about 10 mW. (B) Normal Raman spectrum of AN in the liquid state

There are two interesting features in the SERS spectrum (*Figure 1A*) which are not observed in the normal vibrational Raman spectrum of AN. The first is the appearance of two strong SERS bands at 1000 and $1075 cm^{-1}$, and one strong band at $1585 cm^{-1}$ with a shoulder at $1600 cm^{-1}$. This marked difference between *Figures 1A* and *B* suggests that a surface reaction of AN has occurred upon adsorption. The position of these bands is a reminder that aromatic compounds usually exhibit strong vibrational bands in the region near 1600 and $1075 cm^{-1}$, the former being attributed to the ring stretching and the latter to the ring C–H in-plane deformation vibration; a ring breathing band can be observed[26] at $1000 cm^{-1}$. The other feature in *Figure 1A* is the appearance of two weak and broad bands at 2140 and $2245 cm^{-1}$, in the C≡N stretching frequency region. The former (CN) band red-shifted by $88 cm^{-1}$ from its corresponding value in the liquid state, and its bandwidth increased considerably upon adsorption. The $2245 cm^{-1}$ band in *Figure 1A* is blue-shifted by $17 cm^{-1}$ compared with the $2228 cm^{-1}$ band in *Figure 1B*.

From the studies of the metal–nitrile complexes and nitriles adsorbed on metal surfaces using electron energy loss spectroscopy (EELS), X.p.s., ultraviolet photoelectron spectroscopy and other techniques, it has been accepted that the linear coordination (σ-bonding) through the nitrogen lone pair electrons results in an increase in the C≡N stretching frequency from that of the free molecules. On the other hand, coordination through the C≡N π system is known to result in a decrease in the C≡N stretching frequency. Also, additional vibrational relaxation caused by interaction between the metal and the C≡N group is responsible for the increase of the bandwidth[27–29]. From *Figure 1A* it seems that both types of C≡N geometry on Ag surface are observed. In general, the appearance of more than one peak assignable to the same vibrational mode may arise from various causes. First of all, appearance of new peaks in a SERS spectrum can arise from the reduction of the symmetry of a free molecule due to the presence of surface[30]. Hence, a mode that is inactive in the normal Raman spectrum may become active in the SERS spectrum. Lifting of degeneracy for a multiply degenerate vibration may also occur. These possibilities are safely eliminated in the present case, however, if AN exists as an unreacted form on Ag surface, because the C≡N stretching mode is neither degenerate nor inactive in the normal Raman spectrum. The second cause for the appearance of multiple peaks is the presence of more than one conformation, with respect to the surface, of the vibrating moiety attached to the metal-bound atoms. In this case, the multiple peaks originating from the bound atom or group are usually red-shifted or blue-shifted altogether, contrary to the present case. Multiple peaks may also arise from adsorption on more than one type of crystal plane or on adsorption sites with different coordination numbers. Patterson and Weaver[31] studied the adsorption of ethylene on gold by SERS, where splitting of $10 cm^{-1}$ was observed for the peaks associated with the C=C stretching and the CH_2 bending vibrations. Such a spectral feature was ascribed to adsorption at two energetically different metal binding sites. In general, a splitting associated with different crystal planes[32] is far less than the peak separation (105 $\mathrm{cm^{-1}}$) observed for the ν(CN) bands in the present case.

The appearance of two ν(CN) peaks in *Figure 1A* therefore appears to arise from two surface species on Ag. The 2245 $\mathrm{cm^{-1}}$ band arises from the adsorption of unreacted AN via the nitrogen lone pair electrons, while the peak at 2140 $\mathrm{cm^{-1}}$ is attributed to a surface reaction product due to weakening of $\mathrm{C{=}C}$ double bond and $\mathrm{C{\equiv}N}$ triple bond after adsorption, which will be further discussed below. In the latter case, the $\mathrm{C{\equiv}N}$ bond may lie rather flat on the surface. Surface reaction of AN also accounts for the spectral changes in the region below 1600 $\mathrm{cm^{-1}}$. It seems that aromatization of AN is involved in the surface reaction, though the product is still unknown at present. Chun *et al.*[33,34] have shown that adsorption and surface reaction of cinnamonitrile (one H atom of AN molecule substituted by a phenyl ring) would lead to the appearance of a blue shift of 14 $\mathrm{cm^{-1}}$ for CN stretching mode. Similar observations have been made in the SERS studies of benzonitrile on Ag and Au[35]. Chun *et al.*[33] proposed that a nitrile adsorbs through the nitrogen lone pair electrons (end-on type) when the CN group is part of a conjugation system, whilst coordination through the CN π system is favoured when the group is not conjugated with the neighbouring unsaturated moiety.

A facile surface reaction on Ag was also observed for PAN. *Figure 2A* is a SERS spectrum of PAN obtained by slow evaporation of the solvent residue in the sample. The laser power at the sample surface was only 10 mW. A dramatic difference is found between *Figure 2A* and the normal Raman spectrum of a bulk film measured under the same experimental condition (*Figure 2C*). The two strong Raman bands at 2245 and 1455 $\mathrm{cm^{-1}}$ in *Figure 2C* can be attributed to the stretching vibration of the $\mathrm{C{\equiv}N}$ side groups and the deformation vibration of the backbone $\mathrm{CH_2}$ groups, respectively. In *Figure 2A*, the $\mathrm{C{\equiv}N}$ stretching was very weak, and the presence of 1600, 1575, 1075 and 1000 $\mathrm{cm^{-1}}$ in *Figure 2A* indicates that PAN has undergone structural changes on adsorption. The SERS spectrum is also typical of aromatic ring vibrations. It is well known that at a relatively high temperature ($\sim$300°C), PAN can undergo cyclization through the cyano groups along the chains, yielding a double-coupled conjugated ladder polymer[36]. Further heating to about 1000°C will ultimately lead to a graphite structure. Recently, investigations by *FT*i.r. reflection–absorption spectroscopy showed that the cyclic structure could be formed readily after pyrolysis on Ni, Al and Cu surfaces at temperatures 100–200°C lower than for bulk PAN[37,38]. We propose that PAN can undergo cyclization at room temperature upon adsorption on Ag. Thus, the bands at 1600 and 1580 $\mathrm{cm^{-1}}$ in *Figure 2A* can be assigned to $-(\mathrm{C{=}C})-_n$ or $-(\mathrm{C{=}N})-_n$ conjugation ring stretching vibrations. Similar band positions have been observed by i.r. studies of thermal cyclization of PAN[37–39]. The fact that the chemisorbed PAN monolayer adjacent to the metal surface has been turned into a fused ring structure also accords with the great reduction of the $\mathrm{C{\equiv}N}$ band near 2245 $\mathrm{cm^{-1}}$. The bands at 1075 and 1000 $\mathrm{cm^{-1}}$ can be ascribed to in-plane ring C–H deformation and ring breathing frequencies, respectively. Because of their strong intensity, it is reasonable to propose that the aromatic ring structure is raised up to the metal surface via its N atoms if the electromagnetic theory on the SERS selection rule is applied.

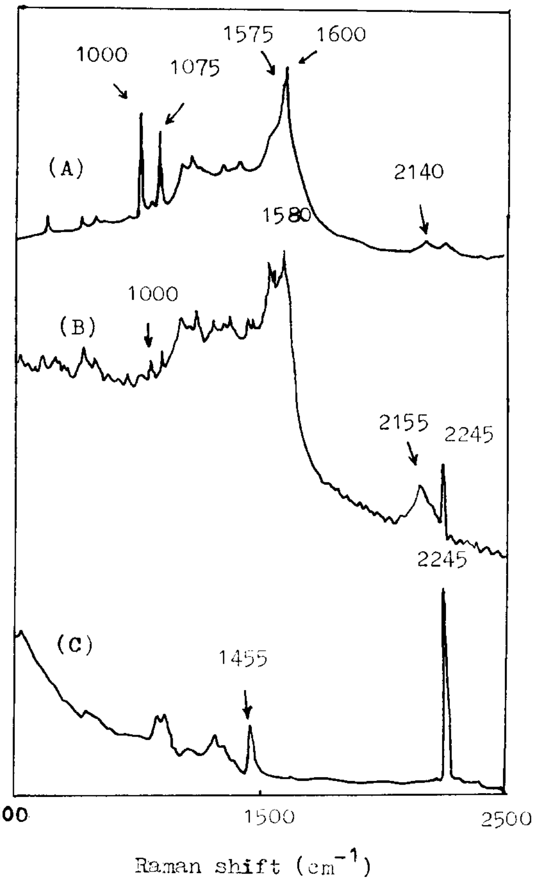


Figure 2 (A) SERS spectrum of PAN on Ag prepared by slow evaporation of the solvent. The laser power at the sample surface was about 10 mW. (B) SERS spectrum of PAN on Ag prepared by fast evaporation of the solvent. (C) Normal Raman spectrum of PAN film

Figure 2B shows the SERS spectrum of PAN adsorbed on Ag prepared by fast evaporation of the solvent under vacuum at room temperature. The enhancement factor is reduced by some degree and the signal-to-noise ratio is poorer than that in *Figure 2A*. Fast evaporation made the formerly solvated polymer chains crash down on the surface and pile up on one another randomly. The side groups had insufficient time to move onto the surface and arrange themselves through molecular motion, and the polymer has a more random orientation on the Ag surface, yielding only partial cyclization of the first monolayer. The band at 2245 $\mathrm{cm^{-1}}$ in *Figure 2B*, having the same position and bandwidth as that in *Figure 2C*, can be assigned to freely dangling (uncomplexed) CN groups in the first couple of PAN monolayers. A broad band centred at 2155 $\mathrm{cm^{-1}}$ is also attributed to the $\mathrm{C{\equiv}N}$ stretching mode. The substantial red shift ($\sim$90 $\mathrm{cm^{-1}}$) and band broadening upon adsorption indicate the direct interaction (side-on coordination) between the cyano groups and the silver surface atoms. Here, the presence of side-on coordination of CN groups of PAN on Ag corroborates Chun's proposal that this fashion is favoured when the CN group is not conjugated with an unsaturated group. A similar phenomenon has been observed in the case of aliphatic dinitriles adsorbed on Cu surfaces in SERS studies[40,41]. Therefore, the 2155 $\mathrm{cm^{-1}}$ band implies that the coordination of Ag surface atoms to the cyano groups brings about back donation of electrons from the metal to the C≡N antibonding orbitals, therefore reducing the C≡N triple bond order. Such a favourable adsorption configuration on the roughened surfaces weakened the C≡N triple bond and facilitated the adsorption-induced cylization at room temperature.

SERS of AN and PAN obtained under different conditions

Figure 3A is a SERS spectrum of PAN obtained by fast evaporation of the solvent residue in vacuum, but the laser power at the sample surface was raised to 50 mW. Increasing the power brings about two strong and broad bands at 1352 and 1580 cm^{-1}. This is due to carbonization of the surface species. AN exhibits a similar phenomenon (see *Figure 3B*). Several other investigators have studied a pair of strong, broad bands in the region between 1200 and 1600 cm^{-1} in SERS spectra of graphitic carbon. Tsang *et al.*[42] studied SERS from benzoic acid and carbon using silver overlayers. SERS spectra of both compounds were characterized by a strong broad band near 1350 cm^{-1} and a weaker band near 1590 cm^{-1}, indicating the formation of graphitic carbon. Graphitic formation was eliminated in SERS experiments on benzoic acid if laser power densities of less than 0.5 W cm^{-2} were used or if the samples were held at liquid helium temperature while the spectra were obtained. Roth and Boerio[43] investigated SERS from poly(4-vinylpyridine) adsorbed onto silver island films. It was observed that the SERS spectra of this polymer at high laser powers showed broad bands near 1383 and 1585 cm^{-1}. However, formation of these bands was prevented by coating the SERS samples with a thin film of another polymer. In another experiment, Venkatachalam *et al.*[44] found that polystyrene films that were only a few nanometres in thickness degraded rapidly during laser irradiation to form graphite-like species on silver island films. The intensity of the two broad bands between 1200 and 1600 cm^{-1} in SERS spectra of polystyrene was proportional to the power. No degradation was observed while normal Raman spectra of neat polystyrene were obtained. They proposed that the graphitization was induced by laser heating of the substrate and was catalysed by silver. These results are consistent with our observations of AN and PAN on HNO$_3$-etched Ag surfaces. The strong bands at 964 cm^{-1} in *Figures 3A* and *B* may be attributed to a degradation intermediate species.

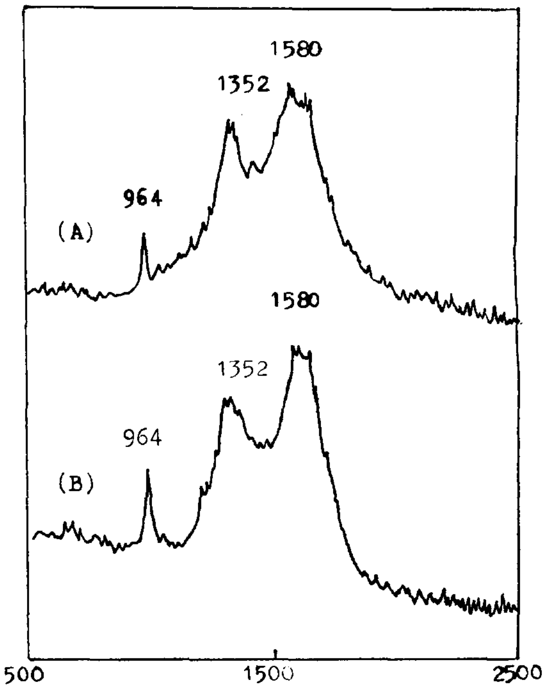


Figure 3 (A) SERS spectrum of PAN on Ag. (B) SERS spectrum of AN on Ag. Both spectra were measured under a laser power of about 50 mW at the surface

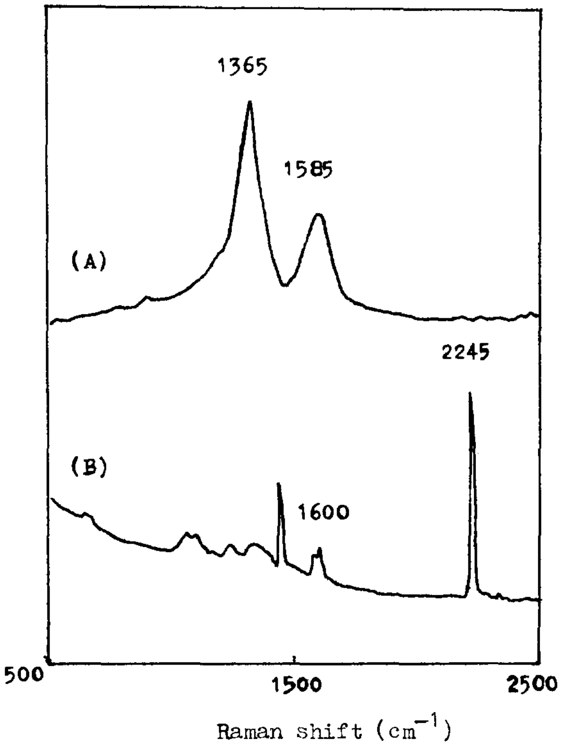


Figure 4 (A) SERS spectrum of PAN on Ag prepared by slow evaporation and heating at 170°C in vacuum for 8 h. (B) Normal Raman spectrum of PAN film prepared by heating at 200°C in vacuum for 8 h. Both spectra were measured under a laser power of about 10 mW at the sample surface

Figure 4A displays a SERS spectrum of the adsorbed polymer sample on Ag after heating at 170°C in vacuum for 8 h. The laser power at the sample surface was only 10 mW. The particularly simple character of the spectrum reveals that PAN on rough Ag surface has been further converted to a graphite-like structure upon heating. This spectrum is identical to the reported SERS spectra obtained by evaporating silver on carbon fibre or graphite fibre[45] as well as the ordinary Raman spectra of graphite or PAN-based graphite fibre[46,47]. In contrast, a bulk PAN film underwent only partial cyclization even if it had been treated at 200°C (*Figure 4B*). The absence of the 964 cm^{-1} band in *Figure 4A*, which is present in *Figure 3A*, indicates that graphitization is nearly complete in the interfacial region of the PAN–Ag system. In other words, heating is favourable for surface graphitization of PAN.

Reaction mechanisms

In order to gain further insight into the reactivity of AN on Ag surface, we have performed quantum chemical calculations to find out how weak the C=C and C≡N bonds in AN are after adsorption. The extended

Hückel tight binding band approach was adopted. (Calculations were performed using NEWBAND3, a program developed at Cornell University[48-50].) Though approximate in nature, this type of calculation can give much chemical insight and has recently been applied to various systems that model the metal, metal oxide, surface or interface. Since no experimental data on the adsorption configuration of AN on Ag can be found in the literature, we considered the geometry by choosing four adsorption models: (a) the AN molecule lying down with the C=C bond across an Ag atom; (b) AN lying down with the C≡N bond across an Ag atom; (c) AN lying down with the N atom on top adsorbed on an Ag atom; (d) the AN molecule erect with the N atom on top adsorbed on an Ag atom and the N≡C–C bond perpendicular to the Ag surface. In all cases, the Ag surface was modelled by a monolayer slab of (111) plane. The magnitude of bond strength in the adsorbate molecule could be gauged by looking at the overlap populations (see *Table 1*). We saw the lowest unoccupied molecular orbital (LUMO) and LUMO^{+1} (π^*) of AN occupied. As a consequence, the C=C and C≡N bond overlap populations are reduced in the four alternative geometries. In other words, adsorption-induced interaction on the Ag surface led to the transfer of electrons into antibonding levels of the adsorbate and, at the same time, the weakening of bonding in the adsorbate. This activating effect provides the possibility for the facile reaction of AN on Ag.

Due to the similarity between *Figures 1A* and *2A*, it is reasonable to propose that the surface reaction of AN may be a spontaneous polymerization, yielding PAN, and then partially cyclized PAN on Ag. In PAN, the C≡N group is no longer conjugated to the unsaturated C=C bond. Thus, side-on coordination of the C≡N group to the Ag atom may lead to the appearance of the 2140 cm^{-1} band in *Figure 1A*, while partial cyclization (aromatization) of the chain segments may lead to the presence of ring bands at 1585, 1000 cm^{-1}, etc. It is interesting that acrylamide and acrylic acid were reported to undergo polymerization on Ag colloid surfaces[18,21].

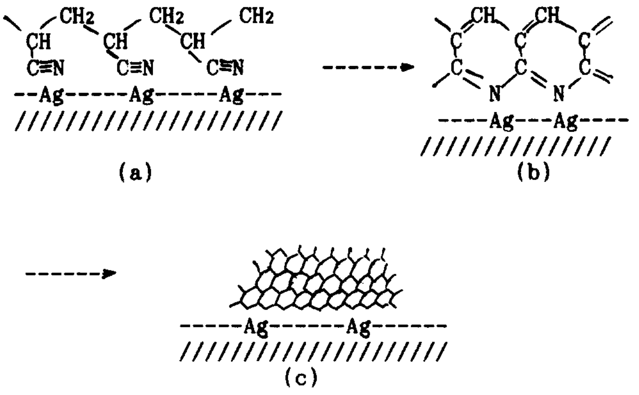
Table 1 Bonding characteristics of acrylonitrile on Ag(111) (see *Table 1a*)

	Free AN monolayer	a	b	c	d
Overlap population					
C≡N	1.635	0.675	0.666	0.665	0.838
C=C	1.229	0.975	0.956	0.962	0.922
Occupations					
HOMO^{-1} (n)	2.00	1.91	1.92	1.92	1.88
HOMO (π)	2.00	1.88	1.91	1.90	1.99
LUMO (π^*)	0.00	1.78	1.83	1.82	1.96
LUMO^{+1} (π^*)	0.00	1.89	1.86	1.87	1.48

Table 1a Atomic orbital parameters used for extended Hückel (EH) calculation. (The EH parameters for Ag were taken from ref. 54. The bond lengths and angles in an AN molecule were taken from ref. 55. The AN molecule is so large that a P(3 × 3) unit cell is used. For simplicity, calculations were performed only at the Brillouin zone centre)

Orbital	H_{ii} (eV)	zeta$_1$	zeta$_2$	C_1[a]	C_2[a]
H1s	−13.60	1.30			
C2s	−21.40	1.625			
C2p	−11.40	1.625			
N2s	−26.00	1.95			
N2p	−13.40	1.95			
Ag5s	−7.56	2.244			
Ag5p	−3.83	2.244			
Ag4d	−11.58	6.07	2.663	0.5889	0.637

[a] Contraction coefficients used in double-zeta expansion



Scheme 1 Proposed structural changes of PAN on Ag after different stages: (a) adsorption of PAN chains on silver through C≡N group coordination; (b) adsorption-induced cyclization of PAN chains forming double-coupled conjugated aromatic rings standing up on the surface; (c) carbonization of cyclized rings forming a graphitic structure

Graphitization of neat PAN usually needs a temperature of about 1000°C. Besides the induction of laser irradiation, the extremely low cyclization and graphitization temperature on rough Ag surface may also be attributed to the surface-complex induced activation effect of transition metals. This activation effect, observed in many transition metal surface reactions of polar compounds, indicates that surface reactions leading to bond weakening and breakage are promoted by surface complex formation and charge transfer[51-53]. Silver in particular is known to function as a catalyst for thermal dehydrogenation of hydrocarbon compounds. Based on the above SERS results, we propose a surface reaction mechanism of PAN as shown in *Scheme 1*.

CONCLUSIONS

The above SERS results indicate that the surface reactions of acrylonitrile and poly(acrylonitrile) on Ag that occur after chemisorption seem to follow an aromatization or cyclization pattern. Under high laser power irradiation, a further graphitic formation will take place. Heating is also favourable for graphitization of a PAN layer on Ag. The reaction mechanism may be ascribed to the surface-complex induced activating effect as well as the laser induction effect on metal surface species.

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