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Formation of a low current surface discharge using a negative corona barrier in argon

Bair B. Baldanov

Abstract
We present the results of experimental studies of the barrier negative corona of constant voltage excited by a metal tip over a metal plane covered by a thin film of polytetrafluoroethylene. It is shown that bright surface discharges - streamers - form on the dielectric surface as the voltage increases. The change in the surface properties of PTFE films under the influence of low-current surface discharge plasma initiated by a DC voltage barrier corona in argon has been studied.

Keywords
Barrier negative corona, Surface discharge, Argon, Cold plasma, Point-to-plane, Atmospheric pressure glow discharge.

Institute of Physical Materials Science of the Siberian Branch of the RAS, Russia
*__Corresponding author__: baibat@mail.ru

1. Introduction

One of the most effective and technologically advanced methods to improve the contact properties of polymer surface is treatment in low-temperature nonequilibrium plasma [1]. An important feature of plasma-chemical modification of polymer materials is that only the polymer surface and a thin surface layer of ∼10-1000 nm in thickness undergo changes [2]. Plasma-induced structural and chemical transformations in the surface layer lead to changes in electrical, physical, mechanical, optical, and other properties of the polymer surface [3–8]. A number of gas discharge types used in polymer surface treatment processes, such as corona, dielectric barrier, low-frequency (ac, 50 Hz-1 kHz) glow, radiofrequency (RF, 13,56 MHz), and microwave (MW, 2,45 GHz) discharges, are known to have been used to date [9–12].

A particular place among plasma processing methods for polymers is occupied by low-current surface discharges, which are characterized by a low current density (no more than 10 mA/cm^2) on the surface and low energy densities (less than 10 W/cm^2), a condition that is important for the plasma surface treatment of thermally sensitive polymer materials [13]. Surface discharges occur in either the diffuse or the streamer mode in various gas atmospheres over a wide range of currents and voltages: as a classical dielectric-barrier discharge [14], surface partial discharge [15] appearing for a short time on a dielectric surface when a pulse of either polarity is applied, and an ac barrier corona discharge [16–18]. Akishev et al. [19] noted that there is a big difference in surface streamer propagation conditions between different voltage application modes: unipolar pulses, alternating current, and use of a point or an elongated electrode to which a high voltage is applied. When a long rod (or strip) is used, many closely spaced parallel streamers can simultaneously propagate from it. [20]. If the tip (point electrode) is placed above a dielectric surface, branching of streamers can be more pronounced [18].

Akishev and coworkers [18,21] proposed a new type of dielectric-barrier discharge called an atmospheric-pressure ac barrier corona in argon. It was found that the use of argon as a plasma gas in place of air results in that low-intensity streamers in argon are highly branched on the polymer film surface and propagate far away from the discharge axis along the surface [18]. This property of the barrier corona discharge in argon makes it possible to effectively treat the polymer film surface in atmospheric-pressure plasma compared with barrier corona discharge in air or nitrogen [21].

The aim of this study was to investigate the influence of the surface streamer discharge, initiated by dc barrier corona in an argon atmosphere, on the surface properties of polytetrafluoroethylene films.

2. Experimental setup

The study was conducted in a point-to-plane discharge chamber with the built-in electrodes (Fig. 1).

The point cathode (1) was a steel rod with a tip curvature radius of r = 25 mm, and the plane electrode (2) in this electrode configuration was a steel plate with an area of S = 96 cm^2. A polymer film (polytetrafluoroethylene (PTFE)) of 45 × 45 mm in size was mounted on the planar electrode with special clamps along the edges. The size of the treated area was 40 × 40 mm. This was an unmodified, nonoriented PTFE film (GOST 24222-80) of a 60 ± 3 cm thickness. The distance from the tip of the pointed electrode to the dielectric film was 30 mm. The maximum voltage of a VS-20-10 tunable high-

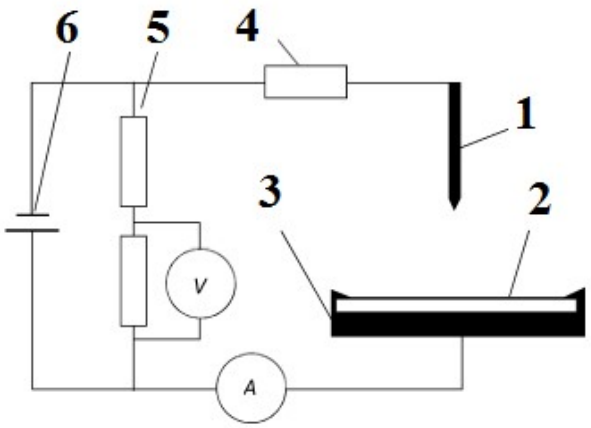

Figure 1. Schematic of the experimental setup: (1)point electrode, (2)plane electrode, (3)dielectric barrier made of polymer film, (4)ballast, (5)voltage divider, and (6) power supply.

voltage power source was 20 kV. To stabilize the discharge, the point electrode was loaded with an adjustable high resistance Rδ ($>$ 1 MΩ). In order to preserve the certified purity of argon, all experiments were performed at low velocities of gas flow through the discharge chamber. Argon flow rate G was measured with an RM-A-0,16GUZ rotameter until 5 $\times$ 10^{-5} kg/s.

The alteration in the surface properties was characterized by the values of contact angle θ, which were determined using the sessile drop technique (accuracy$\pm$1°) with a microscope for the two test fluids water (doubly distilled) and glycerol. The values of contact angles were found using the software package DropSnake – LB-ADSA software suite with the image-processing tool ImageJ [22]. On the basis of these results, total surface energy γ and its polar γ^p and dispersive γ^d components were calculated according to the Fowkes method [23]. In the calculation, the work of adhesion as found from the experimental values of the contact angle with the Dupre-Young formula was used.

The surface topography of the polymer films was examined with a TM-1000 scanning electron microscope equipped with a Hitachi TM-1000 microanalysis system. The composition of the initial and modified PTFE films was determined using a JEOL JSM-6510LV scanning electron microscope with an INCA Energy 350 microanalysis system (Oxford Instruments).

Table 1. Contact angles, work of adhesion, and surface energy of PTFE film.

Polymer	Plasma	Θ, deg		Wa, mJ/m^2		γ, mJ/m^2		
		water	glycerol	water	glycerol	γ	γp	γd
PTFE	Initial	102	90	55.7	63.4	21	0.69	20.33
	Modified	67	63	101.2	92.2	35.2	22.4	12.8

Table 2. Characterization of the surface of initial and plasma-treated PTFE films.

Polymer	Atomic ratio, %		
	F	C	F/C
Initial	66.12	33.88	1.95
Modified	60.72	39.28	1.55

3. Experimental results

A negative corona discharge with a dielectric barrier on the anode is created by applying DC voltage U to the electrode tip-plane structure. The discharge is initiated by raising the voltage to some critical value corresponding to ignition voltage U*. The visual glow pattern of a negative corona discharge with a barrier is qualitatively consistent with the conventional definition of corona and is characterized by the faint luminescence of the zone of generation near the tip, and the drift region remains dark [24]. Figure 2 presents optical micrographs that show the evolution of a surface discharge excited by a negative-polarity corona tip above the polymer film. Raising the voltage further results in the formation of pronounced discharges (streamers) on the dielectric surface.

As is seen, streamers arise at the edge of the dielectric film, and both constricted and diffusive discharge forms are observed (Fig. 2a). Primary streamers at the edge of the dielectric have the form of constricted discharges and begin to branch upon further propagation over the dielectric surface. The streamers disintegrate when they reach distance l = 1.5-2 cm relative to the tip-plane surface on the dielectric and form a region of bulk diffusive plasma covering area S = 3 cm^2. A further increase in voltage U raises the rate of surface streamer repetition; the luminescence grows stronger, and the area occupied by the region of diffusive plasma becomes narrower. In this mode of discharge formation, streamers have a complex spatial structure with a pronounced periodicity of formation and elevated rate of repetition (Fig. 3). Note that low-current discharges are characterized by low current density ($\leq$10 mA/cm^2) on the surface and low power density ($<$10 W/cm^2).

Raising the voltages in the area of diffusive plasma results in individual streamers that are then pulled from the region of plasma to the corona tip (Fig. 2b). When the tip-plane discharge gap is closed by streamers, the discharge transitions to the constricted plasma discharge mode, displaying a bright uniform glow within the plasma channel. The dielectric surface in the constricted plasma discharge mode is almost completely filled with a surface discharge composed of many streamers with different diameters, and with diffusive plasma

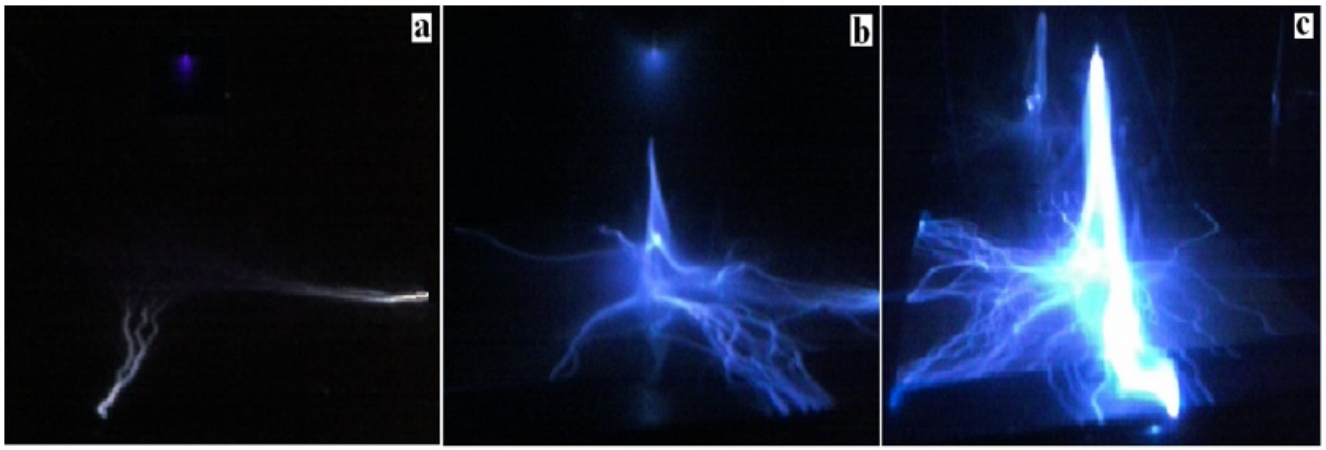

Figure 2. Photographs showing the evolution of the operation of a negative dielectric-barrier corona. The dielectric barrier is a polymer film.

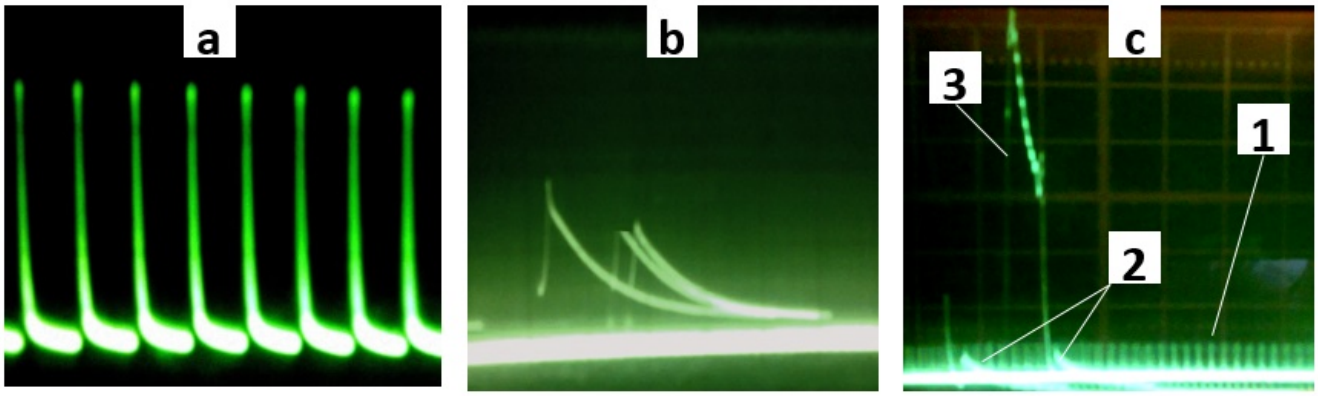

Figure 3. Current pulse oscillograms: (a) negative corona with dielectric barrier (I=184 μA, t=40 μs);(b) low-current surface discharge(I=44 μA, t=1.2 ms); (c) (1) negative corona current pulses; (2) surface discharge current pulses; (3) streamer discharge current pulse (I = 1.4 mA, t = 0.3 ms).

that fills the spaces between streamers (Fig. 2c).

To characterize the surface properties of the PTFE polymer films treated in the low-current surface discharge plasma, we used the values of contact angle θ of water and glycerol. Table 1 shows the surface characteristics of the PTFE films before and after treatment in low-current surface discharge. As can be seen, the surface of the initial PTFE sample had relatively high values of contact angle and a low surface energy of γ = 21 mJ/m^2.

As a result of surface discharge treatment, the surface of the films becomes hydrophilic to have low values of contact angles (Table 1) and its W_a and surface energy γ significantly increase, with the changes being largely due to an increase by many times in the polar component γ^p.

The initial PTFE film had water and glycerol con- tact angles of 102° and 90°, respectively.

The total surface energy and its dispersive and polar components were calculated using the Owens-Wendt-Rabel-Kaelble (OWRK) method [25–27]:

$$\gamma_l(1+\cos\theta) = 2\sqrt{\gamma_l^d \gamma_s^p} + 2\sqrt{\gamma_l^p \gamma_s^p} \quad (1)$$

where γ^l, γ^d, and γ^p are the total surface energy of the liquid and its dispersive and polar components, respectively; θ is the contact angle; and γ^d, and γ^p are respectively the dispersive and polar components of the surface energy of the solid. Water (doubly distilled) and glycerol were used as the test liquids [28]. The total surface energy γ_s of the initial PTFE film is 21.0 mJ/m^2, and its dispersive and polar components are 20.3 and 0.7 mJ/m^2, respectively.

Figure 4 shows the results of calculations of total surface energy γ_s of the PTFE film modified in the plasma of a low-current surface discharge (Fig. 4c) and its dispersive (Fig. 4a) and polar (Fig. 4b) compo- nents. As can be seen, the total surface energy and its dispersive and polar components are inhomogeneous and strongly depend on the character of current spreading over the sample. In the streamer propagation regions [29], the polar component of surface energy predominantly increases: at the points near the reference spots,

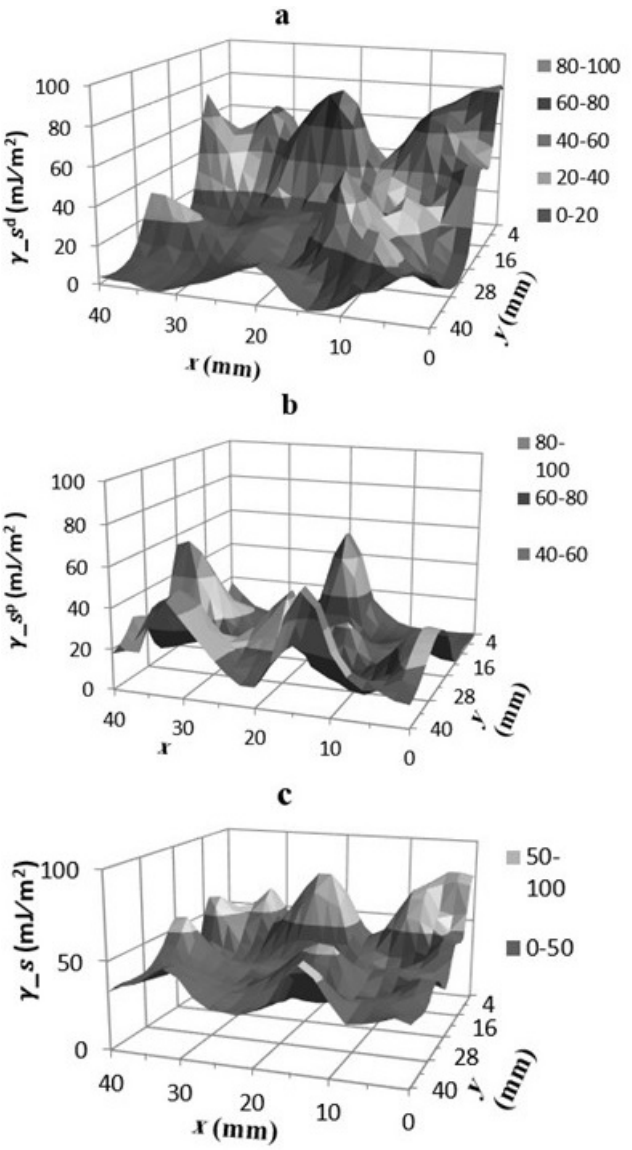

Figure 4. Influence of the character of current spreading on the surface energy of the modified PTFE film: (a)dispersive compo- nent, (b)polar component, and (c)total surface energy.

where the frequency and intensity of streamer luminescence are maximum, the maximum values of the polar component and the minimum values of the dispersive component of the total surface energy are observed, $\gamma^d = 0.8 \pm 0.3$ mJ/m^2 and $\gamma^p = 54 \pm 4$ mJ/m^2 ; in areas with an average frequency and luminescence intensity, $\gamma^d = 1.3 \pm 0.45$ mJ/m^2 and $\gamma^p = 43 \pm 2.5$ mJ/m^2; and in areas with a low frequency and intensity of streamer luminescence, $\gamma^d = 12.5 \pm 4.5$ mJ/m^2 and $\gamma^p = 17 \pm 6$ mJ/m^2. The polar component of the total surface energy increases with an increase in the frequency and intensity of streamer luminescence, which can be associated with an increase in the current and treatment time. The values of total surface energy in regions with high and medium intensities of streamer propagation are in good agreement with the published data [30–34].

An additional effect of the surface discharge is a change in

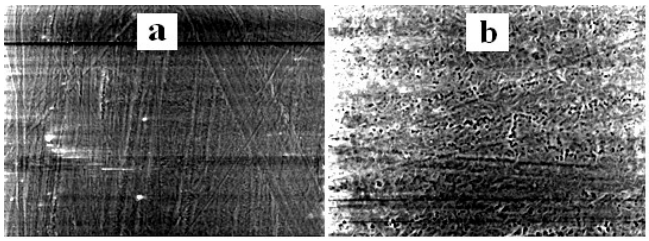

Figure 5. Photomicrographs of the surface of (1)initial and (2)modified PTFE. Magnification, 1500.

surface topography of the sample, consisting in the growth of its roughness. Figure 5 presents photomicrographs of the surface of the initial sample of PTFE film and the sample treated in surface discharge plasma. In contrast to the initial polymer surface (Fig. 5a), the modified surface is textured with characteristic micrometer-sized entities represented by distinct ordered microstructures of about 0.5-3 μm in size (Fig. 5b). The ordered microstructures are mostly micropit chains uniformly distributed over the entire area of the film, with the distribution of microstructures correlating with the distribution pattern of low- current streamers on the PTFE surface. The formation of microsized entities on the film surface after modification in the surface discharge plasma increases the roughness of the PTFE surface [5]. An analysis of the surface microstructure of samples shows that the sur-face roughness increases with increasing treatment time.

The surface-discharge plasma treatment significantly alters the chemical composition of the PTFE surface. The F/C ratio is ∼1.95 in the initial PTFE samples and is decreased to 1.55 by the plasma treatment.

The surface discharge-treated PTFE surface has an increased percentage of carbon and a decreased fluorine percentage. This finding suggests that polymer degradation accompanied by surface depletion in fluorine occurred.

4. Conclusion

The results obtained in this study show that the sur- face streamer discharge initiated by dc barrier corona makes it possible to treat the surface of heat-sensitive polymer films at low densities of electric power. The proposed method for excitation of surface discharge in an argon atmosphere, involving strong streamer branching and the ability of the streamer to propagate over large distances, ensures uniform treatment of a large surface of a polymer film to lead to improvement in the surface properties of the film.

Conflict of interest statement:

The authors declare that they have no conflict of interest.

References

[1] V. E. Fortov. *Encyclopedia of Low-Temperature Plasma*. Moscow: Nauka, 1th edition, 2000.

[2] A. B. Gil'Man. *High Energy Chemistry*, **37**:17, 2003.

[3] A. B. Gil'man and No. 3 14 (1995). V. K. Potapov. *Prikl. Fiz.*, **14**:3, 1995.

[4] A. A. Rychkov, A. A. Malygin, S. A. Trifonov, and D. A. Rychkov. *Russ. J. Appl. Chem.*, **77**:276, 2004.

[5] S. M. Pelagade, N. L. Singh, and R. S. Rane. *J. Surf. Eng. Mater. Adv. Technol.*, **2**:132, 2012.

[6] S. R. Kim. *J. Appl. Polym. Sci.*, **77**:1913, 2000.

[7] L. Guzman, B. Y. Man, and A. Miotello. *Thin Solid Film*, **420**:565, 2002.

[8] E. Njatawidjaja, M. Kodama, K. Matsuzaki, K. Yasuda, T. Matsuda, and M. Kogoma. *Surface and Coatings Technology*, **201**:699, 2006.

[9] C. Z. Lui, J. Q. Wu, and I. Q. Ren. *Mater. Chem. Phys.*, **85**:340, 2004.

[10] C. Jie-Rong and T. Wakida. *J. Appl. Polym. Sci.*, **63**:1733, 1997.

[11] H. Xu, Z. Hu, and S. Wu. *Mater. Chem. Phys.*, **80**:278, 2003.

[12] M. Yu. Yablokov, A. S. Kecheḱ'yan, S. L. Bazhenov, A. B. Gil'man A B, M. S. Piskarev, and A. A. Kuznetsov. *High Energy Chem.*, **43**:512, 2009.

[13] M. Martino, A. P. Caricato, and M. Fernandez. *Thin Solid Films.*, **433**:39, 2003.

[14] B. Eliasson, M. Hirth, and U. Kogelschatz. *J. Phys. D: Appl. Phys.*, **20**:1421, 1987.

[15] C. Heuser and G. Pietch. *VI International Conference on Gas Discharges and Their Applications*, , 1980.

[16] S. Mailis, F. Reekie, and S. Pissadakis. *Appl. Phys. A.*, **69**:671, 1999.

[17] A. P. Caricato, M. De Sario, and M. Fernandez. *Appl. Surf. Sci.*, **208-209**:632, 2003.

[18] Yu. S. Akishev, A. V. Deḿ'yanov, and V. B. Karaĺ'nik. *Fiz. Plazmy.*, **29**:90, 2003.

[19] Yu. S. Akishev, G. I. Aponin, and V. B. Karaĺ'nik. *Fiz. Plazmy.*, **30**:1088, 2004.

[20] A. B. Saveliev and G. I. Pietch. *International Symposium on High Pressure, Low Temperature Plasma Chemistry*, **19**:229, 2002.

[21] Yu. S. Akishev, M. E. Grushin, A. E. Monich, A. P. Napartovich, and N. I. Trushkin. *High Energy Chem.*, **37**:286, 2003.

[22] W. S. Rasband. *National Institutes of Health*, :Bethesda, Maryland, USA, 2014.

[23] P. P. Pugachevich, E. M. Beglyarov, and I. A. Lavygin. *Surface Phenomena in Polymers*, , 1982.

[24] B. B. Baldanov, A. P. Semenov, and Ts. V. Ranjurov. *J. Electrostatics.*, **100**:103351, 2019.

[25] D. Owens and R. Wendt. *J. Appl. Polym. Sci.*, **13**:1741, 1969.

[26] W. Rabel. *Farbe Lack.*, **77**:997, 1971.

[27] D. Kaelble. *J. Adhesion.*, **2**:66, 1970.

[28] C. Rulison. *Hamburg: KR¨ÜSS GmbH.*, , 2000.

[29] B. B. Baldanov and Ts. V. Ranzhurov. *High Energy Chem.*, **50**:60, 2016.

[30] M. S. Piskarev, A. B. Gil'man, N. A. Shmakova, and A. A. Kuznetsov. *High Energy Chem.*, **42**:137, 2008.

[31] S. M. Pelagade, N. L. Singh, R. S. Rane, and S. J. Mukherjee. *Surf. Eng. Mater. Adv. Technol.*, **2**:132, 2007.

[32] L. Zhou, G. H. Lu, W. Chen, W. Chen, H. Pang, G. L. Zhang, and S. Z. Yang. *Chin. Phys. B.*, **20**:065206, 2011.

[33] A. De. Sarani, N. Geyter, A. Yu. Nikiforov, R. Morent, C. Leys, J. Hubert, and F. Reniers. *Surf. Coat. Technol.*, **206**:2226, 2012.

[34] W. Chen, C. Jie-rong, and L. Ru. *Appl. Surf. Sci.*, **254**:2882, 2008.