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Confined photo-catalytic oxidation: a fast surface hydrophilic modification method for polymeric materials

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Abstract

When a very thin persulfate salt aqueous solution layer (μm) was sandwiched between two polymer films and strong UV light irradiated the assembly from the side transparent to UV light, a fast surface hydrophilic modification method for most of commercial polymeric materials was developed. For example, irradiating for 90 s and using 30 wt% ammonium persulfate, the static surface water contact angles of polymeric substrates decreased from 100 to 44° for LDPE, from 107 to 34° for HDPE, and from 73 to 15° for PET. The increases in surface hydrophilicity came from the formation of a sulfate salt group ($SO_4^- NH_4^+$)-ionized surface, which was characterized by XPS and ATR-FTIR. The surface topography of the modified polymer substrates were observed by SEM and AFM, and no visible etching effect to original surface were found. A possible reaction model named by 'confined photo-catalytic oxidation' was put forward to interpret the above results.

Keywords: Surface oxidation; Persulfates; Surface modification

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1. Introduction

The surface hydrophilicity of polymeric material is a key property in many technological fields such as gluing, painting, inking, anti-fogging and biomedical application [1,2]. Many methods [3] have been developed to introduce the hydrophilicity to the surfaces or interfaces of polymeric materials, including glow and corona discharge [4], grafting [5], chemical wet oxidation [6], sequential surface chemical derivation [7], layer-by-layer deposition [8], blending [9], flame [10], photooxidation [11] etc.

In chemical wet oxidation methods, strong oxidants such as CrO_3/H_2SO_4, $K_2Cr_2O_7/H_2SO_4$, $KClO_3/H_2SO_4$, $KMnO_4/H_2SO_4$, HNO_3 and H_2SO_4 can provide an effective approach to surface modification with main drawbacks such as damages to substrates and pollution to environment [12]. Persulfate salt aqueous solution is a kind of milder oxidizing agents and its main drawbacks in surface modification application are slow oxidizing speed and poor modification efficiency. As to overcome these problems, many efforts have been reported to enhance the oxidation ability of this system [13–17]. Morris [13] used ammonium persulfate (APS) solution under heating to modify polyethylene surface, and Ag^+ salt as catalyst was utilized to promote this oxidation. Zhang et al. [14] also used APS solution under heating to modify polyethylene surface, and at 70 °C for 6 h, surface water contact angle decreased from 99 to 61° for HDPE, and from 102 to 83° for LDPE. Bamford and AI-Lamee [15] used potassium persulfate (KPS) solution plus heating as a way to implant hydroxyl groups onto polymer surface, which was used as further grafting polymerization sites. Price [16] developed a method to ultrasonochemically-assisted modification of PE surface with using KPS and APS aqueous solution, which resulted in a decrease of surface water contact angle from 95 to 60° at 35 °C after ultrasonicating for 24 h. Kubota et al. [17] reported a UV assisted surface oxidation method where LDPE film was put in a rotary Pyrex glass tube containing KPS aqueous solution (0.01–0.30 mol l^{-1}), and after UV irradiation for a certain time (~ 12 h) at 50 °C, a number of carbonyl groups

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and hydroxyl groups were introduced onto the oxidized surface. Along with ceric salt, these hydroxyl groups could initiate surface grafting polymerization.

In 1996 Rånby and Yang reported a ‘bulk surface photografting process’ where a Film Interface Photopolymerization (FIP) setup was devised [18], which consisted of top layer transparent to UV light, middle graft-reaction solution layer and bottom layer. From then on, kinds of grafting systems have been extended with this special technique [19]. Recently, when we deliberately replaced the graft-reaction solution (including monomer and initiator) layer in FIP with persulfate salt aqueous solution, some unexpected results were observed, e.g. surface water contact angle of the modified surface could decrease 30–40° in a few seconds and a high hydrophilic surface could be obtained in about one and half minutes. The paper will report the experimental setup, main results and chemistry involved in.

2. Experimental

2.1. Materials

Main polymeric materials used are common commercial samples, of which details are listed in Table 1, which include films ($5 \times 5\ \text{cm}^2$) and plates ($4 \times 2\ \text{cm}^2$). Solvent used in persulfate salt solution is tri-distilled water with conductivity being less than $0.5\ \mu\text{S cm}^{-2}$. Acetone, KPS and APS are of analytical grade, trifluoroacetic anhydride (TFAA) is of chemical grade. All reagents were obtained from Beijing Chemical Reagents Company and used without further purification.

2.2. Photoirradiation procedures

Films and plates were cleaned with deionized water and acetone. The UV irradiation system used was shown schematically in Fig. 1. A predetermined amount of persulfate salt aqueous solution (100 μl) was deposited on the bottom film or plate with a micro-syringe. A top layer transparent to UV light covered this solution and the drop of solution was spread into an even and very thin liquid layer (about 2 μm) under suitable pressure from a quartz plate. BOPP has good ultraviolet light transmission as shown in Fig. 2, and is used as top layer covering the substrates opaque to UV light. PET absorbs largely UV light at about $\lambda < 310$ nm (Fig. 2), so BOPP is used as top layer when PET is prepared to be modified. In this work, we examined the transparence of all substrates to UV light at $\lambda = 254$ nm and the results were listed in Table 1. According to Fig. 2 and Table 1, the top–bottom assemblies were used as follows: CPP–CPP, LDPE–LDPE and BOPP-other substrate as listed in Table 1. Top layer for CPP, LDPE, BOPP and bottom layer for other substrates were used to characterize and analyze. The assembled unit was irradiated by UV radiation (UV lamp: high-pressure mercury lamp, 1000 W; UV intensity at $\lambda = 254$ nm was measured by spectrometer) from the topside at room temperature for a certain time. After the irradiation, top and bottom layers were separated and soaked into deionized water for 10–15 min, then, rinsed by deionized water and acetone, respectively three times to clean the treated surface absolutely, dried in air at room temperature and kept in sealed plastic bag for measurements.

Table 1
The substrates used in this work

Material	Thickness (μm)	T (%)[a]	Material	Thickness	T (%)[a]
CPP	28	79.2	PVC	88 μm	12.7
BOPP	19	83.8	PVF	48 μm	44.6
LDPE	62	73.2	Nylon6	15 μm	59.0
HDPE	13	68.3	EPDM	2 mm	0
TPX	48	65.2	NBR	2 mm	0
PET	98	0.92	SBR	2 mm	0
PC(yellow)	25	15.8			

[a] T(%), the transmission ratio of UV light at $\lambda = 254$ nm, which is defined as the ratio of UV intensity after and before penetrating film.

2.3. Characterization methods

The UV absorption spectrum of APS aqueous solution was recorded by GBC Cintra 20 spectrophotometer (Australia). Surface static contact angles were measured with 5 μl of distilled water droplet being placed on the treated film by a micro-syringe, and observed through a traveling microscope fitted with a goniometer eyepiece, all measurements were at the room temperature and were the average of at least nine readings at different positions across the surface. X-ray photoelectron spectra (XPS) were obtained by using ESCA Lab 220i-XL (VG Scientific) instrument and Al K-alpha excitation at one 15° angle. Fourier Transformed Infrared spectra were recorded on a Nicolet Nexus 670 spectrometer with $4\ \text{cm}^{-1}$ resolution, a variable-angle attenuated total reflectance (ATR) accessory (PIKE ATRMax II) was utilized with ZnSe ($n = 2.43$) as internal reflection element wafer. Scanning electron micrographs (SEM) were obtained with S250HK3 (Cambridge) instrument. Atomic force microscopy (AFM) was carried out with Nano Scope III a (DI, USA) microscope. Gravimetric analysis was performed with BP211D electrobalance (Sartorius AG, Germany) with the accuracy being 0.00001 g.

3. Results and discussion

3.1. Hydrophilic modification of polymer surfaces

Static water contact angle was not only a major factor of characterizing surface hydrophilicity, but also just a

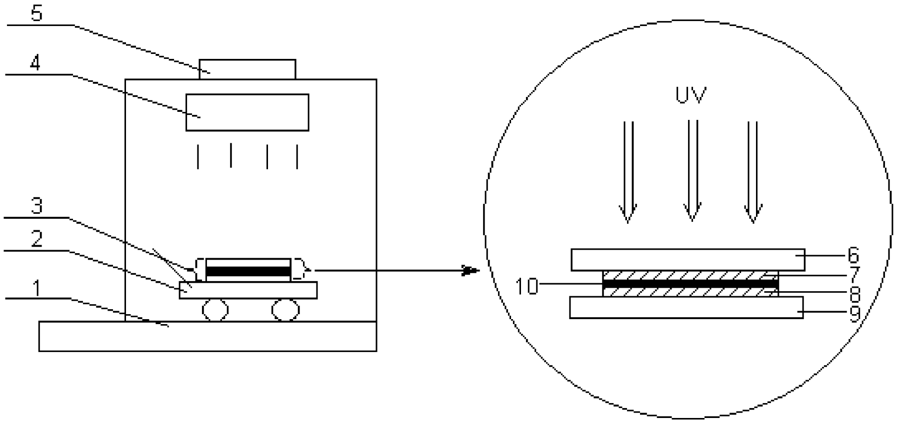


Fig. 1. Schematic diagram of photoirradiation apparatus (the right part is the amplification of reaction assembly system: the sandwich structure (3)): 1. Track; 2. Mobile sample holder; 3. Reaction assembly system: the sandwich structure; 4. UV lamp (high pressure mercury lamp, 1000 W); 5. Ventilation; 6. Top quartz plate; 7. Top layer; 8. Bottom layer; 9. Bottom quartz plate; 10. Persulfate salt aqueous solution.

sensitive indication of the chemical nature of a surface in terms of the outermost few tenths of a nanometer [20].

Fig. 3 showed the variation in surface static water contact angle (CA) with changes of irradiation time. The plot indicated that in very beginning (only a few seconds), CA of the samples underwent a significant change (about 30–50°), then decreased gradually and leveled off to minimum values about 44° (LDPE), 34° (HDPE) and 15° (PET) at last (after about 90 s). Comparing with the promotion methods reported such as Ag^+ catalyzing [13], heating [14] (HDPE, from 99 to 61° at 70 °C after 6 h), ultrasound-promoting [16] (PE, from 95 to 60° at 35 °C after 24 h), the modifying speed and CA decrease of the present process were unusual. Inspired by the above success, we extended this method to a wider range of common polymeric materials, and the results were shown in Fig. 4. Fig. 4 spelled out that this method was very effective to a lot of polymeric materials including PP (CPP and BOPP), PE (LDPE and HDPE), PET, TPX, PVC, PVF, PC, NBR, SBR, EPDM, Nylon6 [21].

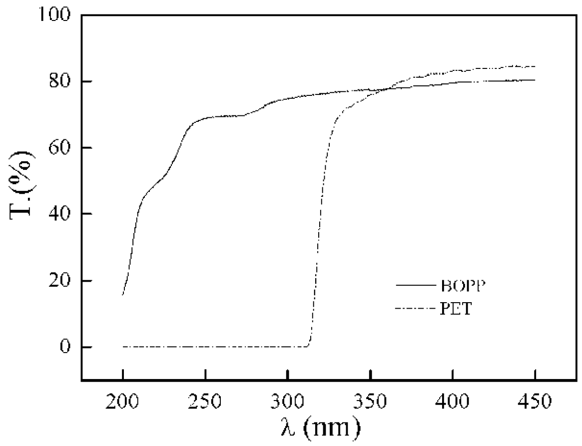


Fig. 2. The transparency of BOPP and PET films to UV light.

Fig. 5 illustrated the dependence of CA on concentrations of APS with the irradiation time being 90 s. It was obvious that the modify extent was enhanced by increasing persulfate concentration. For example, under low concentration such as 10 wt%, CA of modified PET, HDPE and LDPE were about 25, 47 and 55°, respectively, while at the concentration of 30 wt%, these values decreased to 15, 34 and 44°. At room temperature, the saturated concentration of APS was about 30 wt%, so higher concentration could not be plotted in Fig. 5. KPS was also a kind of alternative oxidant, and its saturated concentration at room temperature was about 5 wt%. When 5 wt% KPS aqueous solution was used to modify CPP film surface, CA decreased to about 74° with irradiation time being 90 s.

In this photo-catalytic oxidation reaction, the wavelength and intensity of UV irradiation are important reaction parameters. The UV absorption spectrum of APS was shown in Fig. 6. It was believed that the maximum quantum efficiency of the photolytic decomposition of persulfate was about 0.6 at $\lambda = 254$ nm [22]. By using PET film to filter far UV wavelength ($\lambda \leq 300$ nm), the modification experiment

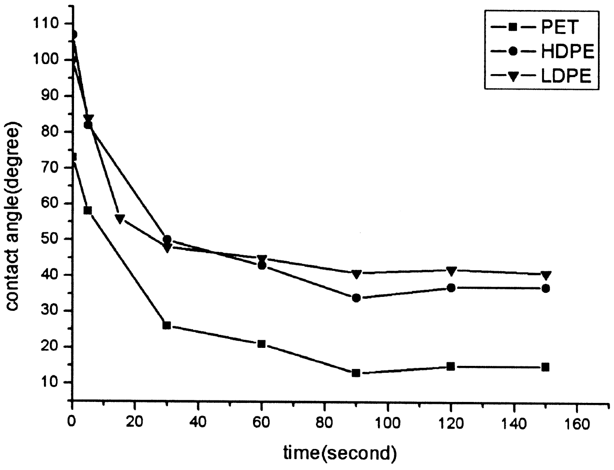


Fig. 3. Changes in water contact angle of polymer surface with irradiation time. (UV intensity: 6500 μw cm^{-2}; $(NH_4)_2S_2O_8$, 30 wt%.)

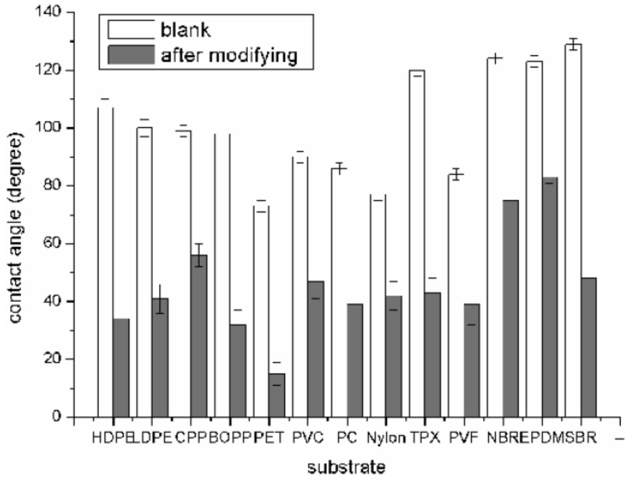


Fig. 4. Water contact angles of the modified polymer surfaces. (UV intensity: 6500 μw cm^{-2}; $(NH_4)_2S_2O_8$, 30 wt%; irradiation time: 120 s for NBR, SBR, PC, PVF and 90 s for others.)

of PET was performed and the results were plotted in Fig. 7. From Fig. 7, it was observed that under the same reaction conditions, filtering by PET film and without filtering showed quite large difference in CA, e.g. in 90 s, the latter decreased to 15° while the former was 70° close to that of untreated PET (76°). Fig. 7 presented that strong absorption in far UV wavelength ($\lambda \leq 300$ nm) took main responsibility for photolytic decomposition of persulfate.

The effect of UV irradiation intensity (at $\lambda = 254$ nm) on CA was illustrated in Fig. 8. Fig. 8 displayed that for LDPE, when irradiation time was less than 30 s, CA of the modified surface decreased with increasing UV intensity. For example, increasing UV intensity from 6000 to 13,800 μw cm^{-2} with irradiation time being 10 s, CA decreased to about 64° from 84°. When irradiation time was more than 30 s, the effect of UV intensity on CA was not obvious, and CA at different UV intensity leveled off gradually to reach same minimum values about 44°. These results showed that at the beginning of irradiation, the increase of UV intensity accelerated the oxidation reaction; after irradiation for a certain time, CA at different UV intensity reached same minimum values, which may mean that the surface oxidation reaction reached a stable state and was insensitive to UV intensity.

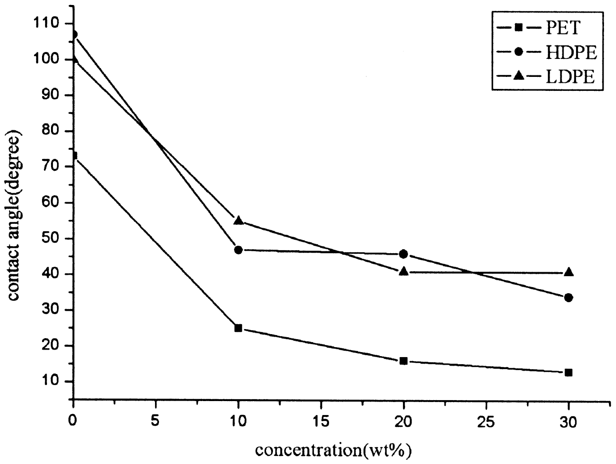


Fig. 5. Changes in water contact angle of polymer surface with the concentrations of $(NH_4)_2S_2O_8$. (UV intensity: 6500 μw cm^{-2}; irradiation time: 90 s.)

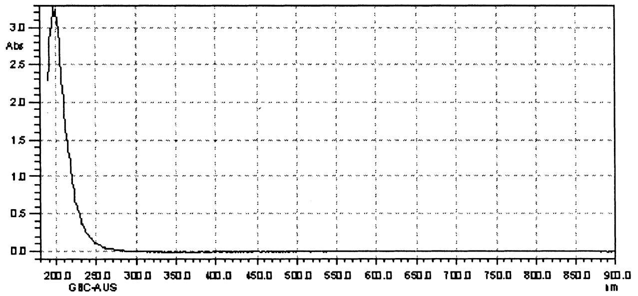


Fig. 6. UV absorption spectroscopy of persulfate ammonium aqueous solution (1 wt%, water as solvent).

3.2. *Physical and chemical changes of the modified polymer surfaces*

Surface hydrophilicity was determined by topographical structure and chemical composition of polymeric material surface. Here we investigated topographical changes of modified polymer surface, following chemical changes to reveal the origin of the high hydrophilic modified surface.

Conventional chemical wet oxidation systems, such as CrO_3/H_2SO_4, $K_2Cr_2O_7/H_2SO_4$, $KClO_3/H_2SO_4$, $KMnO_4/H_2SO_4$, HNO_3 and H_2SO_4, had a strong etching effect on treated surface to increase surface roughness. Glow discharge had several kinds of damages on modified surfaces, including etching, smoothing or cross-linking [23]. Either etching or smoothing effect could result in a measurable decrease in the weight of treated polymer film. In this work, we followed the topological changes of a number of the treated samples (CPP, BOPP, LDPE and

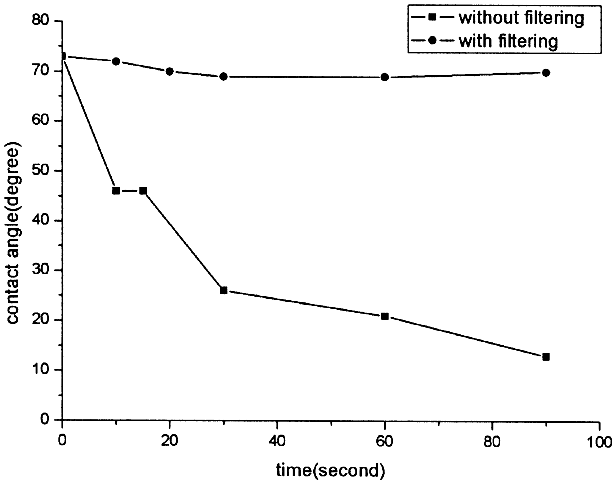


Fig. 7. Effect of ultraviolet wavelength range on water contact angle of treated PET surface. (UV intensity: 6500 μw cm^{-2}; $(NH_4)_2S_2O_8$, 30 wt%.)

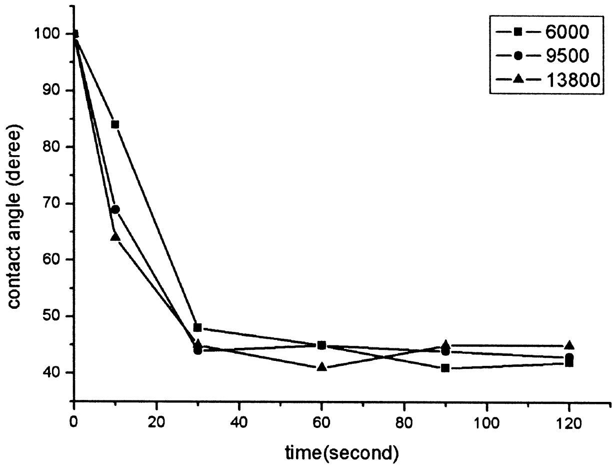


Fig. 8. Effect of UV intensity (μw cm^{-2}) on water contact angle of treated LDPE surface. ($(NH_4)_2S_2O_8$, 30 wt%.)

PET) with different irradiation time by SEM (at resolution of 20 nm) and AFM (at resolution of 5 nm) [24], but no observable changes on surface topography were found. Further gravimetric analysis showed that no measurable changes were found in all treated samples (by electrobalance with accuracy being 0.00001 g), so smoothing effect also could be excluded. The results above, in other word, meant that there was little surface etching effect and smoothing effect in the oxidation process.

ATR-FTIR could provide a route to characterize surface chemical structure within the order of μm (1–10) [20]. For polymer samples used in this method, of which thickness varied from 20 to 100 μm, this meant that the outer surface (a few μm) of samples could be characterized by ATR-FTIR, and of course, the sensitivity for the change of chemical nature of the outer surface would decrease with the increase of measured thickness. We investigated ATR-FTIR spectra of some samples (CPP, LDPE and PET) treated by this method with APS as oxidant, but did not find the existence of carbonyl and hydroxyl groups in treated samples. Kubota and Price [16,17] carried out the reaction between TFAA and hydroxyl group to confirm the formation of hydroxyl group on the oxidized surface. In similar conditions, we carried out this reaction on modified LDPE film surface [25], but no ester carbonyl bond at 1785 cm^{-1} and C–F bond at 1223 cm^{-1} were found, which proved no hydroxyl groups were attached onto oxidized surface.

XPS could indicate the change of chemical element within the order of 1–5 nm [20], much thinner than that of ATR-FTIR, so it was able to characterize the chemical changes of the outmost surfaces of samples. From the XPS spectra of the treated samples with persulfate ammonium as oxidant (LDPE and CPP), the peaks of S and N elements were observed. Fig. 9 was the XPS spectra of the treated and blank CPP where 168.6 eV (S_{2p}) and 399.8 eV (N_{1s}) peaks were attributed to S (SO_4^-) and N (NH_4^+) respectively [26], while the two peaks were not found in XPS spectra of blank CPP surface. The fact that co-existence of S and N implied some sulfate anion groups were implanted onto the outmost surface with counterpart ion groups being NH_4^+. The introduction of ion groups onto the very surface could more effectively raise surface hydrophilicity than other polar groups such as hydroxyl, carbonyl groups.

The different results obtained by ATR-FTIR and XPS reflected the fact that a very thin single molecular sulfate salt group layer was introduced covalently onto the surface of polymer substrates. Because the thickness of the single sulfate salt layer was the order of Å, it was difficult to be detected by ATR-FTIR, and this result was in agreement with gravimetric analysis.

3.3. Possible reaction model

Reactions (1)–(6) in Scheme 1 showed conventional oxidation route of persulfate salt aqueous for polymer surface [15,17], which resulted in the formation of hydroxyl, carbonyl etc. groups on modified surface. In this route, the sulfate anion free radical ($SO_4^-\cdot$) produced by the decomposition of $S_2O_8^{2-}$ (reaction (1)) may attack water molecule to give out HO· (reaction (2)) or abstract hydrogen atom from C–H bonds of polymer surface. Consequently, $SO_4^-\cdot$ and HO· exist in reaction solution, and both are able to abstract hydrogen atom from polymer surface and combine with surface free radical to attach them onto the surface covalently (reactions (3) and (4)). The SO_4^- groups attached on surface could also hydrolyze into hydroxyl groups in the aqueous as shown in reaction (5). The formation of carbonyl groups (reaction (6)) come from the participation of O_2 produced in the reaction system. In relative solution chemistry [22a–c], the coefficient of the reaction (2) is about 10^3–10^4 s^{-1}, while the coefficient of $SO_4^-\cdot$ attacking organic compounds is about 10^7 l mol^{-1} s^{-1}. But for heterogeneous surface or interface reaction (for example, surface modification), since HO· is a kind of neutral free radical which is easy to contact with or diffuse into hydrophobic polymeric substrates, while $SO_4^-\cdot$ is a kind of high hydrophilic ion free radical which is difficult to spontaneously adsorb onto the hydrophobic surfaces of substrates, and therefore, in the reported oxidation methods of persulfate salt aqueous solution, the abstraction hydrogen and following combination of HO· (reaction (3)) play main part rather than $SO_4^-\cdot$ (reaction (4)).

In the present experimental setup, since there was large difference in polarity between persulfate salt aqueous solution and polymeric substrates, the solution did not diffuse into substrates but would keep a continuous phase with μm thickness. This setup not only made the reaction solution and polymer surface realize most intimate contact which increased the relative concentration of C–H on organic substrates to biggest extent, but also made the continuous aqueous phase lose flowing ability due to the thinness. Under strong UV

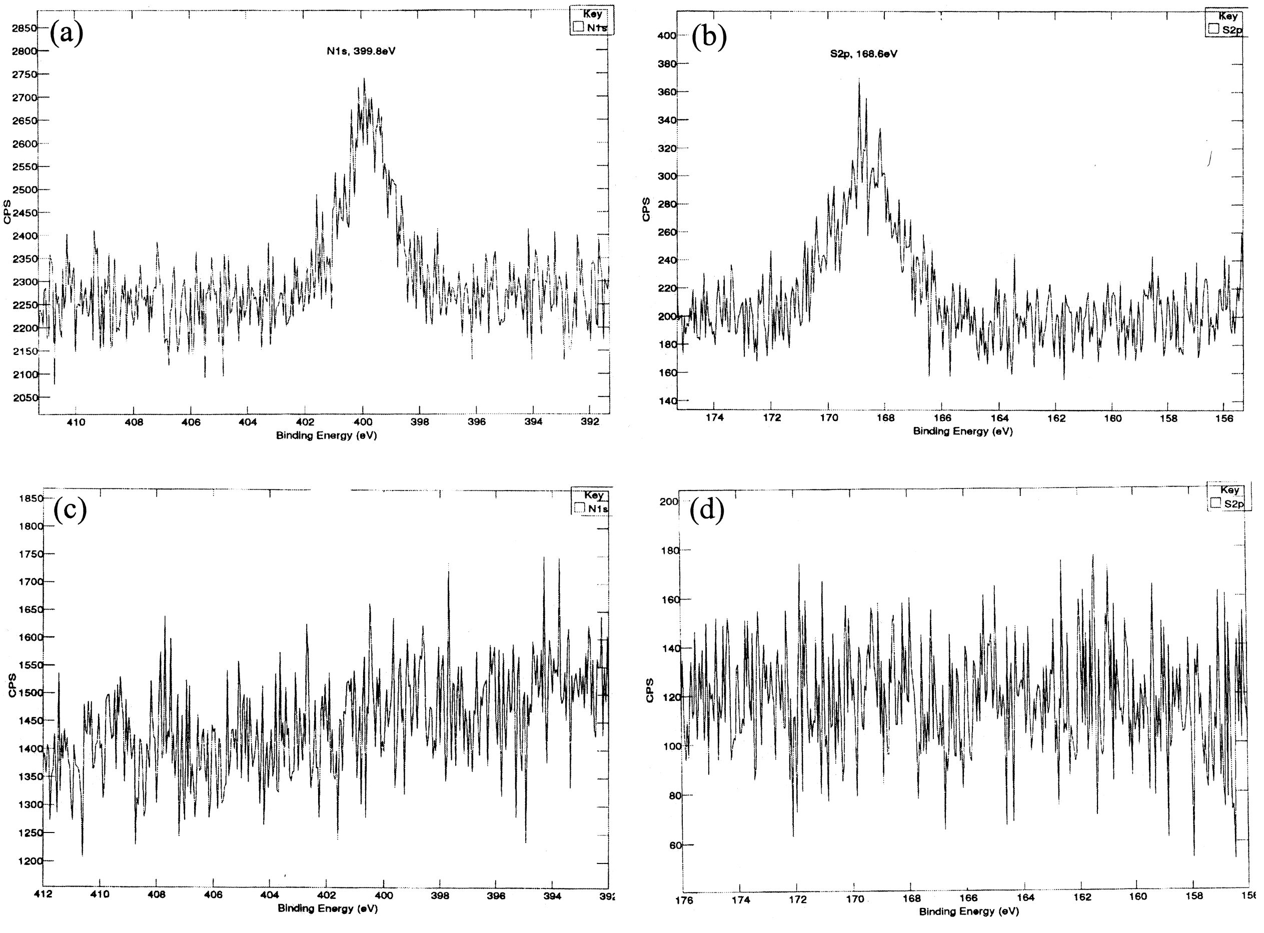
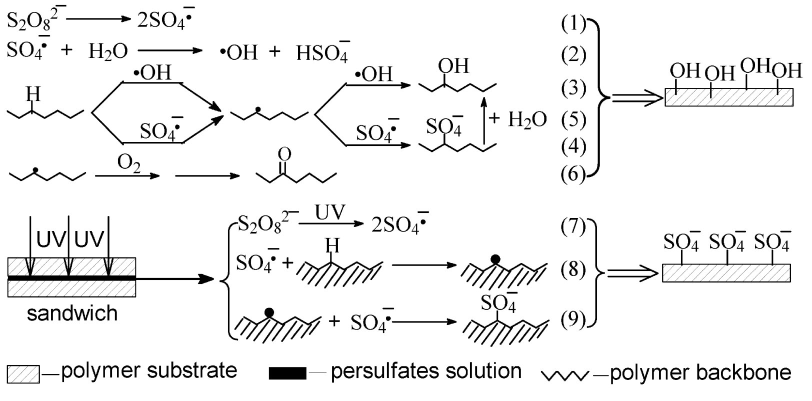


Fig. 9. XPS spectra of treated CPP surfaces: $N_{1\,s}$ peak ((a) and (c)); S_{2p} peak ((b) and (d)), the upper: after treated; the lower: before treated. (UV intensity: 6500 μw cm^{-2}; $(NH_4)_2S_2O_8$, 5 wt%; irradiation time: 90 s.)

irradiation, a great amount of $SO_4^{-}\cdot$ could be produced in very short time. Since the reaction coefficient of $SO_4^{-}\cdot$ attacking organic substrates is much bigger than with H_2O, the reactions of $SO_4^{-}\cdot$ with polymer surface would dominate whole reaction course where some of $SO_4^{-}\cdot$ abstracted surface hydrogen atoms and produced surface free radicals, and some of them coupled with the surface free radicals, at last, to form surface SO_4^{-} group as shown reactions (7)–(9). The great polar difference between salt aqueous solution and organic substrate made the oxidation reactions only take place at the outmost surface of substrates. The outmost surface limitation plus short irradiation time were also main reasons for no observable etching and smoothing effect. For convenience, here, we proposed tentatively a concept, 'confined photo-catalytic oxidation', to summarize the experimental



Scheme 1. The possible reaction model for surface oxidation by persulfates: the conventional and the 'sandwich' methods.

setup, reaction route and reaction uniqueness, i.e. the ‘confining’ from special setup forced the oxidation reaction proceed in a new direction (reaction (4)) not conventional way (reaction (3)).

For further convincing this interpretation, we did a comparative test where under the same conditions (UV intensity, APS concentration), film samples were put (floating) onto the surface of reaction solution as shown in Fig. 10(b), and the results were listed in Table 2. The setup in Fig. 10(b) modeled conventional photochemical reactions commonly carried out in reaction solution [17] with less self-screening effect. As presented in Table 2, with the ‘sandwich’ setup (shown in Fig. 10(a)), the minimum CA for CPP and LDPE were about 56, 44° respectively; while with the conventional setup, the surface hydrophilicity of samples increased little, even prolonging irradiation time (the minimum CA for CPP and LDPE modified by this setup were around 74, 75°, respectively).

4. Conclusions

By using a new strategy of confined photo-catalytic oxidation, an array of sulfate anion groups could be attached covalently on the outmost surface. This strategy provided an effective surface hydrophilic modification method suitable for most of commercial polymeric materials with the advantages of fast, mild (to environment and substrate), facile and low cost technological process. The sulfate salt-ionized surface with little etching effect implied that a number of molecular engineering could be initiated on the premise of keeping original surface topography, such as surface molecular self-assembling based onto polymer substrate, organic–inorganic hybrid synthesis, surface functionalization and so on. The concept of confined in this method may be beneficial to other photochemical reaction in aqueous system. Moreover, the sulfate anion groups onto surface could be transformed further into hydroxyl groups by simple hydrolysis, so a hydroxylated surface could be also obtained easily which will be reported later.

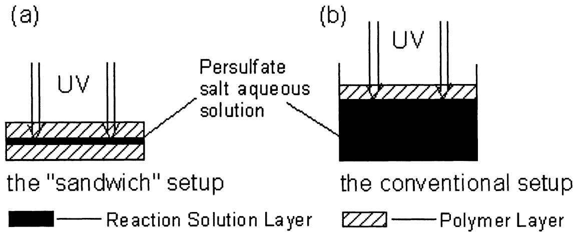


Fig. 10. Two kinds of setups to modify polymer surface: (a) the ‘sandwich’ setup; (b) the conventional setup.

Table 2
The surface water contact angles of polymer films modified by two methods

Substrate	Setup	Reaction time (s)	Contact angle (degree)
LDPE	Fig. 10(b)	90	76
LDPE	Fig. 10(b)	240	75
CPP	Fig. 10(b)	90	83
CPP	Fig. 10(b)	120	78
CPP	Fig. 10(b)	150	77
CPP	Fig. 10(b)	180	74
CPP	Fig. 10(b)	210	74
CPP	Fig. 10(b)	240	76
LDPE	Fig. 10(a)	90	44
CPP	Fig. 10(a)	90	56

Reaction conditions: 6500 μw cm^{-2}; $(NH_4)_2S_2O_8$, 30 wt%.

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[24] The samples for SEM were BOPP, CPP and LDPE films, irradiation time: 0, 30, 60 and 90 s, $(NH_4)_2S_2O_8$ aqueous solution was used, 30 wt% The samples for AFM was PET film, irradiation time: 0, 30, 60 and 90 s, $(NH_4)_2S_2O_8$ aqueous solution was used, 30 wt%.

[25] Irradiated LDPE films were soaked in TFAA in a sealed tube for 40 min at 35 °C, taken out and soaked in ethyl ether for at least 3 h, taken out and washed with ethyl ether, ethanol, water and acetone in this order, then dried under reduced pressure in 20 °C for at least 24 h.

[26] Liu S, Wang D. X-ray photoelectron spectra analysis. Beijing: Science Press. 1988. N_{1s} peak (399.8 eV) lie between N_{1s} for NH_4^+ (401–402 eV) and for NH_2 (398.7 eV), surface NH_4^+ maybe have different measuring environment from that shown in Ref. [26], so resulted in the deviation from NH_4^+ (401–402 eV) in Ref. [26].