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Enhancement of anatase functionalization and photocatalytic self-cleaning properties of keratins by microwave-generated plasma afterglow

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ABSTRACT

A microwave-generated plasma afterglow (MWGPA) treatment was applied to keratin fibers to improve their adhesion to anatase nanocrystals by modifying their surface chemical and physical structure. The induced photocatalytic self-cleaning property has significantly been improved by 70% as evidenced by complete stain decomposition in 6 h only. The effects of gas mixtures, gas flow, treatment distance, treatment duration and power flow of the MWGPA treatment on keratin's surface were investigated. The MWGPA-induced alteration of keratin's surface structure resulted in an increase in the uptake of anatase crystals and thus enhanced photocatalytic self-cleaning activities. The contact angle, absorption time, deposition behavior, adhesion and stability of anatase coating of keratin fibers are discussed. The anatase uptake and coating uniformity were characterized quantitatively using Time-of-Flight Secondary Ion Mass Spectrometry. This efficient and low energy plasma surface activation approach demonstrated potential toward the practical application of anatase in keratinous materials.

1. Introduction

Protein fibrous material with photo-induced self-cleaning property has recently been developed [1–9]. Through a simple treatment with a colloid of anatase nanocrystals at ambient conditions [5–9], protein fibers can become capable of decomposing adsorbed contaminant, dirt, and harmful microorganisms through an advanced oxidation triggered by incident light [1–9]. This research has aroused interest both academically and commercially. Although self-cleaning keratinous materials hold promise in many anticipated applications such as medical treatment and military use, the practical application of these materials has been impeded due to the instability of anatase coating on protein fiber surface [5,8].

The poor binding ability of protein fibers is mainly attributed to its heterogeneous structure [10]. Titanium dioxide binds efficiently to carboxyl groups via strong electrostatic interactions; however, these groups are not uniformly allocated throughout the protein fiber resulting in poor anatase–fiber interaction. Moreover, both hydrophilic and hydrophobic groups can be found in proteins because of its randomly grouped 19 naturally-occurring amino acids, which contribute to an eventual uneven distribution of anatase particles along the fibers after coating [10]. Our previous studies showed that the anatase–fiber interaction can be enhanced by wet chemical pre-treatment with succinic anhydride or nonionic wetting agents through the introduction of carboxyl groups or improvement of the fiber hydrophilicity, respectively [5,8]. In these processes, large consumption of chemicals and water is required to achieve the desired effect. In addition, the generation of harmful waste may lead to ecological problems. Therefore a more environmental friendly and economical alternative method, such as plasma surface treatment, would be highly preferred.

Physical surface modification of fibrous materials has generally been conducted by laser irradiation, electron beam, UV irradiation, ion beam, microwave irradiation, and plasma at an industrial scale [11–14]. Among these methods, the plasma technique has widely been investigated in a large range of applications over the past decades [13–15]. Microwave-generated plasma technology has been proven to be a promising surface modification process due to its simplicity, efficiency and environmental friendly features, such as in the saving of consumption of water and chemicals and in eliminating costly treatment of effluents from wet chemical processing [13]. It was reported that the surface properties of biopolymers can be improved while maintaining their bulk properties [13–18]. Unlike glow discharge plasma, less attention was given to microwave-generated plasma afterglow (MWGPA) because no ions or electrons are produced. However, with the incorporation of various plasma gases, free species such as neutral particles, photons and excited atoms/molecules can be generated to modify the surface reactivity and increase the free surface area of a substance

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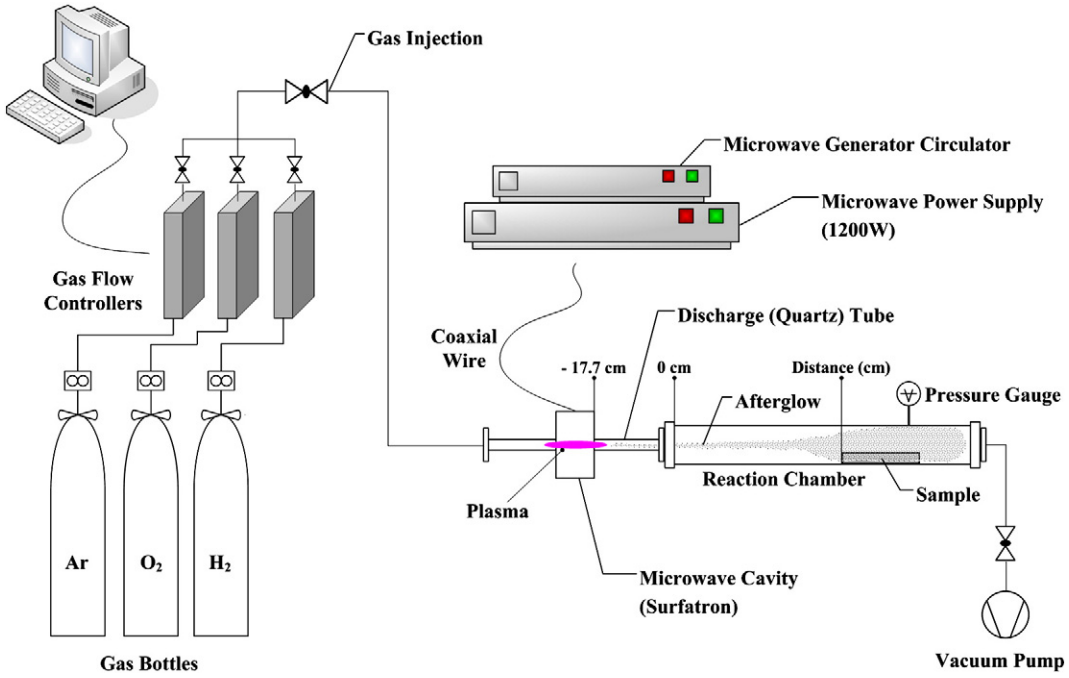

Fig. 1. Schematic diagram of the MWGPA set-up.

surface at a relatively low temperature that is favorable for delicate materials with low chemical and thermal stability such as wool, silk, and spider silk [1–9,16,17,19,20]. Thus, it is anticipated that with MWGPA treatment, the reactivity of keratinous materials toward anatase particles and their conferred self-cleaning properties can be improved.

This paper discusses the modification of the surface reactivity of a representative protein fiber, wool, by MWGPA as a pre-treatment in the self-cleaning functionalization process. The effect of power flow, gas mixture, gas flow, sample distance and treatment duration on the deposition, coating uniformity, photocatalytic activity and its reproducibility of the anatase-modified keratin fibers are thoroughly discussed.

2. Materials and methods

2.1. MWGPA surface modification

MWGPA was employed in a surface modification pre-treatment process for improving the surface reactivity of protein fibrous materials. Fig. 1 shows a schematic diagram of the microwave-generated plasma

Table 1
Experimental parameters of MWGPA surface modification.

Sample No.	Power (W)	Pressure (Pa)	Carrier gas	Carrier gas flow (ml/min)	Reacting gas	Reacting gas flow (ml/min)	Distance (cm)	Duration (min)
O1	50	100	Ar	100	O_2	25	10	5
O2	50	100	Ar	100	O_2	25	10	3
O3	100	100	Ar	100	O_2	25	10	5
O4	50	100	Ar	100	O_2	25	4	5
O5	50	100	Ar	100	O_2	50	10	5
O6	50	100	Ar	100	O_2	25	10	10
O7	200	100	Ar	100	O_2	25	10	5
O8	50	100	Ar	100	O_2	25	16	5
O9	50	100	Ar	100	O_2	75	10	5
H1	50	100	Ar	100	H_2	25	10	5
H2	50	100	Ar	100	H_2	25	10	3
H3	100	100	Ar	100	H_2	25	10	5
H4	50	100	Ar	100	H_2	25	4	5
H5	50	100	Ar	100	H_2	50	10	5
H6	50	100	Ar	100	H_2	25	10	10
H7	200	100	Ar	100	H_2	25	10	5
H8	50	100	Ar	100	H_2	25	16	5
H9	50	100	Ar	100	H_2	75	10	5
HO1	50	100	Ar	100	H_2/O_2	25/25	10	5
HO2	50	100	Ar	100	H_2/O_2	25/25	10	3
HO3	100	100	Ar	100	H_2/O_2	25/25	10	5
HO4	50	100	Ar	100	H_2/O_2	25/25	4	5
HO5	50	100	Ar	100	H_2/O_2	50/50	10	5
HO6	50	100	Ar	100	H_2/O_2	25/25	10	10
HO7	200	100	Ar	100	H_2/O_2	25/25	10	5
HO8	50	100	Ar	100	H_2/O_2	25/25	16	5
HO9	50	100	Ar	100	H_2/O_2	75/75	10	5