Efficient Photooxygenation of Furans using Oxygen with Wool-Immobilizing Rose Bengal as Green Photosensitizer

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A new type of solid-supported photosensitizer was prepared from Rose Bengal and wool *via* acid dye dyeing process. The wool-Rose-bengal photosensitizer was characterized by Fourier transform infrared spectrometer (FTIR), scanning electron microscope and fastness test. This sensitizer was used as heterogeneous photocatalyst to promote furans oxidation to the corresponding butenolides in excellent yields (90 %). The sensitizer could be easily recovered from the reaction mixture by filtration and reused in the new cycle of the reaction.

Keywords: Wool, Rose bengal, Sensitizer, Photooxidation, Furans, Singlet oxygen.

INTRODUCTION

Much of the attention of the scientific community is currently directed toward developing new benign and clean processes[1]. Photochemical oxidation reaction by singlet oxygen ($^1O_2$) is an attractive process. It provides access to useful derivatives, such as endoperoxides or allylic hydroperoxides, by using molecule oxygen and solar radiation. So it is an example of a "green" process. Typically, a heterogenized form of photosensitizer was used[2], which makes the isolation of photosensitizer easier and is much closer to sustainable chemistry principles. The pioneering work of Schappe and Neckers[3] with Rose bengal immobilized onto low crosslinked polystyrene beads has shown the success of this approach. In addition to polystyrene beads, some other supported photosensitizers[4] have been reported. The representative solid supports are polyacrylamine resins[5], polycyanoacrylates[6], silica[7] and zeolites[8]. However, many of these approaches suffer from complicated synthetic routes and are unable to generate multigram quantities of the supported photosensitizer. Recently we focused on the design of heterogeneous versions of $^1O_2$ generator. We succeeded in discovering one type of support with wool, which is so widely used as textile fibers. Wool has several useful properties including ready availability, nontoxicity, biodegradiation and renewability. To the best of our knowledge, wool have not been empolyed for the immobilization of singlet oxygen photosensitizers. Because wool has the property of a positive-charged surface in water, anionics can bind to wool tightly. To date, no reports from other research group exist on

heterogeneous $^1O_2$ photooxidations with wool as a solid support. In this study, we design and develop a convenient way to prepare the novel supported photosensitizer by immobilizing a photosensitizer-rose bengal onto wool surface through a normal acid dye dyeing process. Rose bengal, an anionic dye, is a disodium salt, which can be dissolved in water or strongly polar solvents. Rose bengal is an excellent photosensitizer for reactions under visible light and their covalent immobilization on polymeric matrices has been shown to give very active singlet oxygen-generating materials[9]. Thus the Rose bengal can form ionic bonds with wool surface under dyeing conditions. This new photoactive material, which can be produced at a multigram scale and in a quantitative fashion, might also yield $^1O_2$ under irradiation for photooxygenation reactions.

For such purpose we selected the oxidation of furans **1** to butenolides **2** as the benchmark reaction (Fig. 1). Butenolides **2** is a key constituent of the potent analgesic and antiinflammatory agent manoalide and many other natural and unnatural products of biomedical importance[10]. Our initial results were published[11]. In this paper, we further report the preparation of RB-rose bengal, characterization, application and recovery in detail.

EXPERIMENTAL

2-Furoic acid, 2-furfural, 5-hydroxymethylfurfural and Rose bengal sodium salt (Rose bengal) were purchased from Alfa Aesar and were used without further purification. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was purchased from

1a: R = CHO;   R₁ = H
1b: R = CHO;   R₁ = CH₂OH
1c: R = COOH; R₁ = H

2a: R₁ = H
2b: R₁ = CH₂OH
2a: R₁ = H

RB-wool sensitizer =

Fig. 1. Synthesis of butenolides **2** from photooxygenation of furans **1** using RB-wool photosensitizer

Aldrich. Acetonitrile, acetone, chloroform, benzene, ethyl acetate, hexane and other chemicals were analytical reagent grade. Water was purified by the MilliQ system. The wool was provided by Dr. Wang Baihua of BIFT (originally from Inner Mongolia).

Immobilization of Rose bengal: Pure new wool (60 g) was scoured with a solution that contained 2 g/L non-ionic detergent (Labolene) at 30-35 °C for 0.5 h. The scoured wool was thoroughly washed with tap water and dried at room temperature. The scoured material was then soaked in clean water for 0.5 h prior to dyeing. Pretreated pure new wool were treated in a two-step dyeing process. First, dyeing bath temperature was raised to 50 ºC at a heating rate of 5 ºC/min from 20 °C and then was increased to 95 ºC by a rate of 2 ºC/min and kept at 95 ºC for 1 h. Dye concentration was ranging from 0.5 % to 2.5 % on weight of wool fabric (owf). Dyeing bath pH was adjusted to 3-4 by using hydrochloric acid. The dyed wool were then dipped into a saturated brine solution (50 g in 250 mL water) for 15 min at room temperature. This acted as a dye-fix. Then, it was thoroughly rinsed in a tap water and allowed to dry in open air. The dyed wool was washed thoroughly with hot water and solvent to remove free Rose bengal before use. The amount of Rose bengal on the wool was determined by the absorbance of the dye bath before and after dyeing at λ_{max} 548 nm. The UV-visible absorption spectra were recorded with Thermo UV300 spectrophotometer in 1 cm quartz cell at room temperature.

Irradiation of samples: Photoirradiation was carried out by using a PLS-LAM 400W medium pressure mercury lamp (Perfect light). Light of the appropriate wavelength was selected by using a cut off optical filter (Hoya). The procedure is as follows. The photosensitizer RB-wool (2 g), Rose bengal (6.5×10^{-4} M) was added to a oxygen-equilibrated solution of 2-furfural (**1a**, 200 mg, 2.08 mmol, 6.9×10^{-2} M) in CH₃CN (30 mL). The resulting mixture in a Pyrex vessel was vigorously stirred at room temperature under O₂ and irradiated with a 400 W mercury lamp through a UV-cutoff filter to give light wavelengths of $\lambda > 500$ nm. Substrate concentrations were determined by GC-FID (Agilent 7820). GC analysis

indicated complete oxidation of **1a** after 10 h. Removal of the sensitizer by filtration of the reaction mixture and removal of the solvent under vacuum gave the crude product of **2a** which was further purified by flash chromatography to afford pure compound **2a** (142 mg, 82 %). The structure of **2a** was confirmed by ¹H NMR and EI-MS. Flash column chromatographic separation was carried out on Merk Kieselgel 60 (230-400 mesh) using ethyl acetate and hexane as the eluents. **1b** and **1c** could also be transformed to **2b** and **2a**, respectively in a similar manner.

Characterization of the product **2a** and **2b**. The follows data are in agreement with the literature[12].

2a: ¹H NMR (600 MHz, d-acetone) δ: 7.45 (1H, d, $J = 6$ Hz), 6.70 (1H, s), 6.26 (1H, s), 6.22 (1H, d, $J = 5.4$ Hz); MS(EI): m/z 55 [(C₃H₃O)⁺, 100 %], m/z 72 [(C₃H₄O₂)⁺, 40 %], m/z 100 [(C₄H₄O₃)⁺, 15 %].

2b: ¹H NMR (500 MHz, d-acetone) δ: 7.41 (1H, d, $J = 2.5$ Hz), 6.52 (1H, s), 6.20 (1H , d, $J = 3.5$ Hz), 4.46 (1H, s), 3.79 (2H, d, $J = 7.5$ Hz); ¹H NMR (500 MHz, MeOD + D₂O) δ: 7.41 (1H, d, $J = 6$ Hz), 6.26 (1H, d, $J = 6$ Hz), 3.79 (2H, s).

Instrumentation and product analysis: UV-visible spectra were recorded with a Thermo UV300 spectrophotometer in 1 cm quartz cell at room temperature. IR spectra were measured on an FT-IR infrared spectrophotometer (Nicolet Nexus 670). The analytical instruments for SEM was a Hitachi S4800 Field-Emission Scanning Electron Microscope (Japan). The structure of target compounds were confirmed by ¹H NMR and MS. ¹H NMR spectra were obtained on a Bruker AVANCE III 600 MHz spectrometer and Bruker AVANCE II 500 MHz spectrometer, tetramethylsilane used as the internal standard. MS spectra were obtained using Agilent 6890-5973N GC/MS spectrometer. Gas chromatographic analysis for the reaction kinetics was performed on a Agilent 7820A GC spectrometer using a hydrogen flame ionization detector, equipped with an integrator processor. Nitrogen was used as the carrier gas. The inner column (length 30 m; internal diameter 0.25 mm, film thickness 0.25 μm) was packed with a Agilent HP-5 5 % phenyl-methyl siloxane film. The reaction products were identified by comparison of their retention times with the corresponding standard samples. For GC analysis of the 2-furfural oxidation reaction, operating conditions were as follows: Injection temperature, 200 °C; nitrogen as carrier gas at a flow rate of 2 mL/min and the detection temperature at 250 °C. The column temperature was maintained at 60 °C for 2 min, then programmed at 15 °C/min to 150 °C, increased to 250 °C at a rate of 5 °C/min and held for 10 min.

Dye uptake property: The dye uptake property (*i.e.*, dye exhaustion percentage, E %) was calculated according to the following eqn. (1):

$$E (\%) = [A0 - Ar / A0] \times 100 \qquad (1)$$

where A0 and Ar are, respectively, the absorbance of the dye bath before and after dyeing at λ_{max} 548 nm of the dye used. The absorbance was measured on a Thermo UV300 spectrophotometer at 548 nm of the dye used.

Fastness testing of dyed wool: The color fastness to light used QB/T 2925-2007; the color fastness to washing empolyed AATCC Test Method 61-2010. A Xenoster was used to test the light fastness of the dyed wool. A Thermolab wash wheel was used to test the washing fastness. Gray scale for color change and gray scale for staining.

SEM of dyed wool: Wool which adsorbed Rose bengal was subjected to SEM-EDX analysis. After SEM observation of the chemical reagent adsorbing on wool, elementary analysis of carbon, oxygen, iodine, chloride and sulfur were performed. The analytical instruments for SEM was a Hitachi S4800 Field-Emission Scanning Electron Microscope. Observation conditions of SEM: Acceleration voltage was 15 kV and pressure was 1-10 Pa.

RESULTS AND DISCUSSION

Preparation and characterization of wool-immobilizing Rose bengal: Rose bengal, an anionic dye, is a disodium salt, which was immobilized on wool fibers by using an acid dyeing progress. The carboxylic groups could react with amino on wool to form ionic bonds. So the dyes are incorporated onto the fabrics (Fig. 2). The Rose bengal dyed wool fibers became red after dyeing.

The dye uptake property (*i.e.*, the Rose bengal content in the solid wool sensitizer) was approximately 97.7 %, which was calculated from the UV-visible spectra. The pretreated wool could adsorbed 99 % of the Rose bengal, but did release it about 1 % by hot water and solvent washing. These results suggested that Rose bengal was adsorbed to the wool by ionic bonding. In order to clarify the mechanism of adsorption of Rose bengal to the wool fabrics, the dyed wool was then subjected to the fastness test according to standard methods. The washing and light fastness exhibit to be 3-4 grade. The results show that dyed wool exhibits good fastness properties.

Elementary analysis of the halogenated xanthene compound Rose bengal which was adsorbed on wool showed the presence of chlorine and iodine (Figs. 3 and 4). These images show that halogenated Rose bengal compound is bound to the surfaces of the wool.
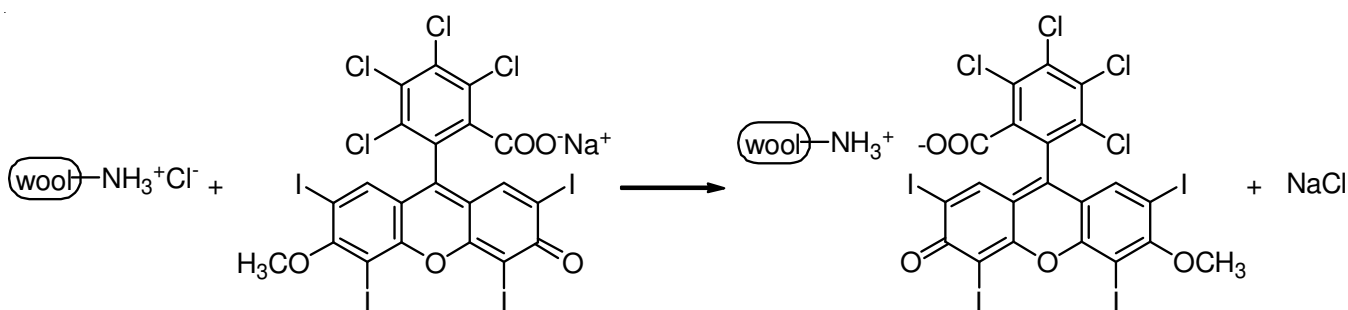

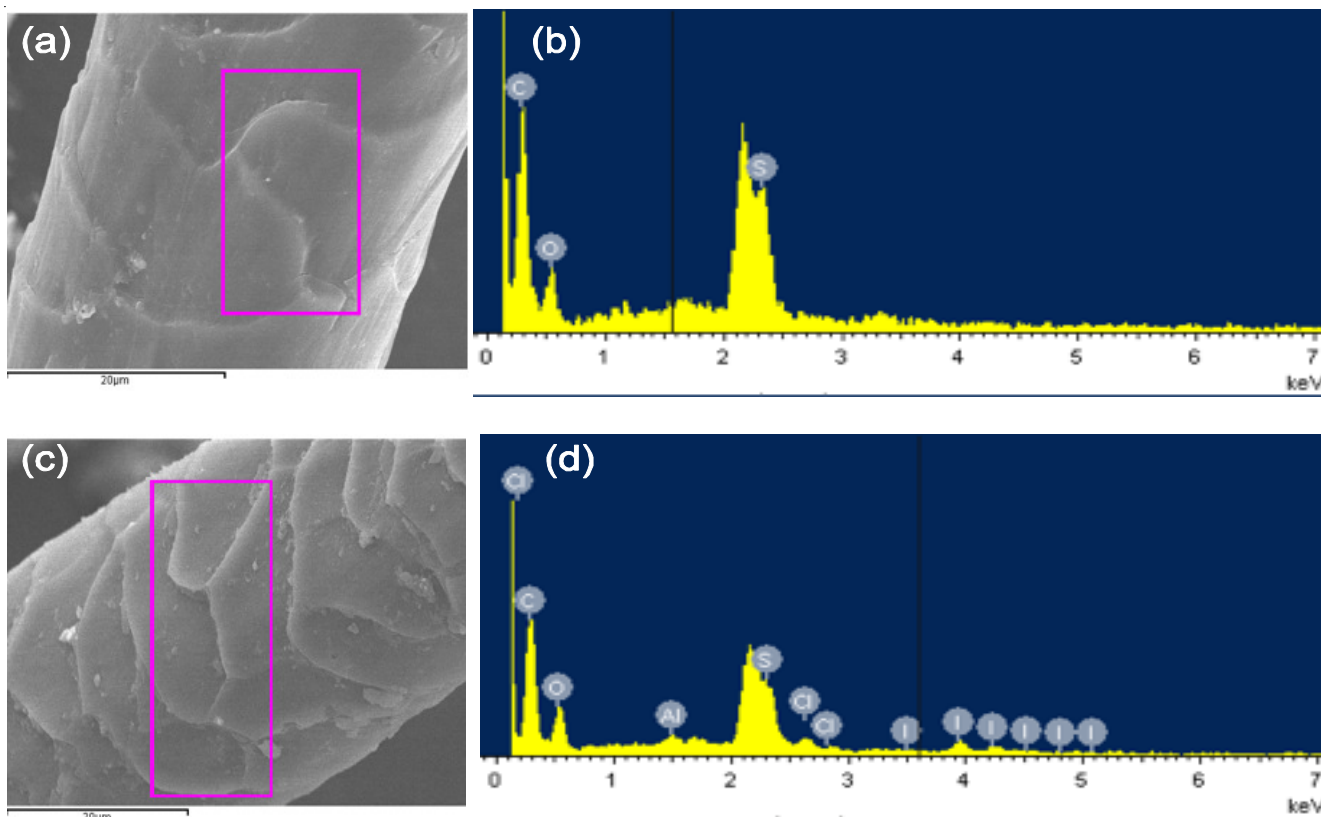Fig. 2. Anchorage of Rose bengal dye to the wool

Fig. 3. SEM-EDX spectras: (a) SEM photograph of the surface of the wool, Bar indicates 20 µm (b) Results of elemental analysis in SEM-EDX of the surface of the wool (c) SEM photograph of the surface of the RB-wool system, Bar indicates 20 µm (d) Results of elemental analysis in SEM-EDX of the surface of the RB-wool system
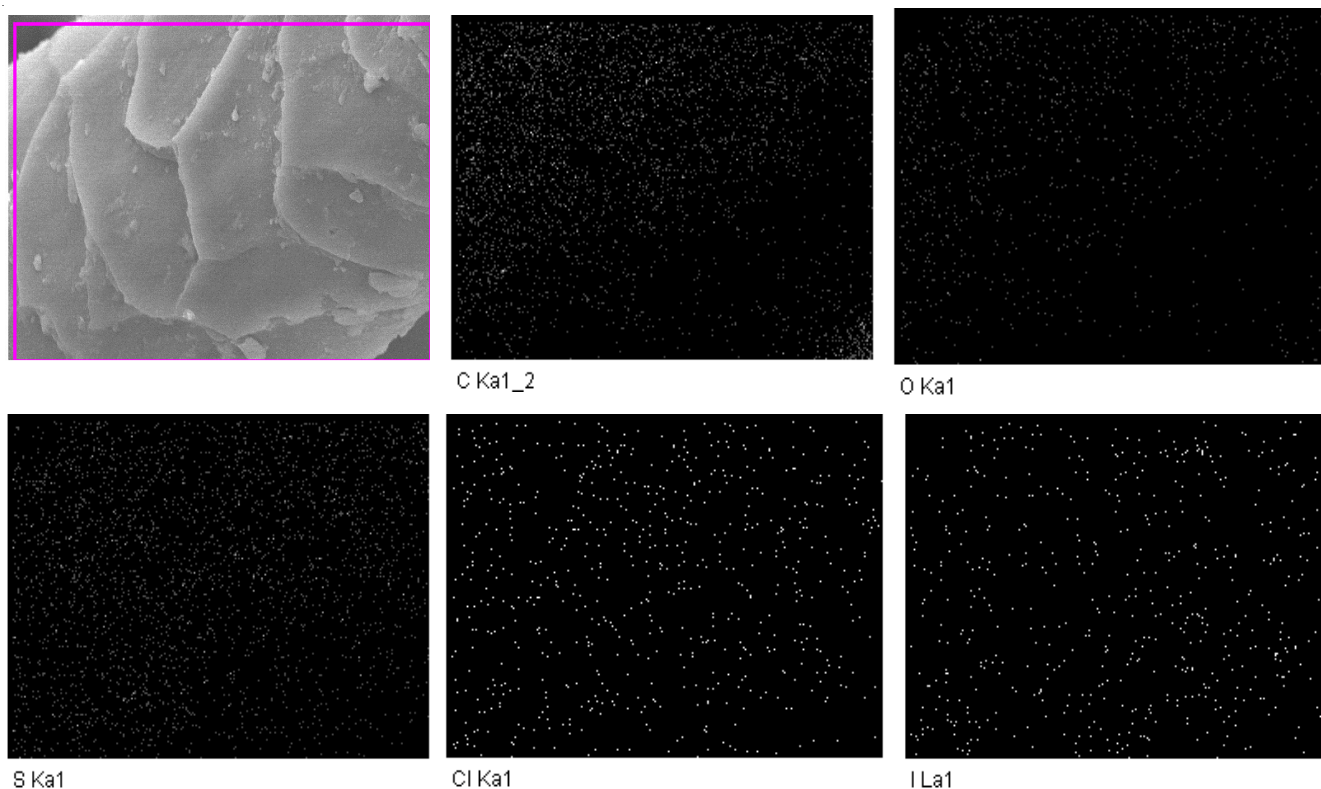
Fig. 4. Results of mapping analysis in SEM-EDX of the surfaces of wool immoilized with Rose bengal

We further analyzed the difference between the wool and RB-wool system by means of infrared spectroscopy (IR). IR spectroscopy of Rose bengal shows characteric absorption at 1,334 cm^{-1} due to -Cl and 951 cm^{-1} due to -I, which was not observed in IR spectra of the wool. However, new absorption at 1,338 and 953 cm^{-1} could be observed for the IR spectra of RB-Wool system, which slightly shifted to left can be assigned to the functional groups of -Cl and -I present on the surface of wool (Fig. 5).

It is worth noting that the wool-bound rose bengal was obtained in a multigram scale in a two-step dyeing process, which represents an important advantage over other time-consuming methodologies that may lead to the milligram or lower scale.

Photooxidation of furans: As reported, Rose bengal as a sensitizer could promote the photooxygenation of 2-furfural to butenolides **2a**. We would like to explore the wool-supported Rose bengal's activity of promoting photooxygenation of furan derivatives. The RB-wool system was washed repeatedly with hot water and CH$_3$CN until the final filtrate was colorless before use. The irradiation of all the samples was achieved by passing the light of a Hg lamp through a cut off optical filter in order to select the wavelength of > 500 nm, as described in the experimental section. The progression of the reaction was monitored by means of GC spectrometry.

To find out the optimal conditions for the photooxidation reactions, photooxidation of 2-furfural (**1a**) using RB-wool photocatalyst was first examined at room temperature. The effects of light, molecular oxygen and solvent on the photo-oxygenation of 2-furfural were investigated under differernt conditions. In the dark, 2-furfural was not oxygenated by oxygen. Under light irradiation, oxygenation of 2-furfural
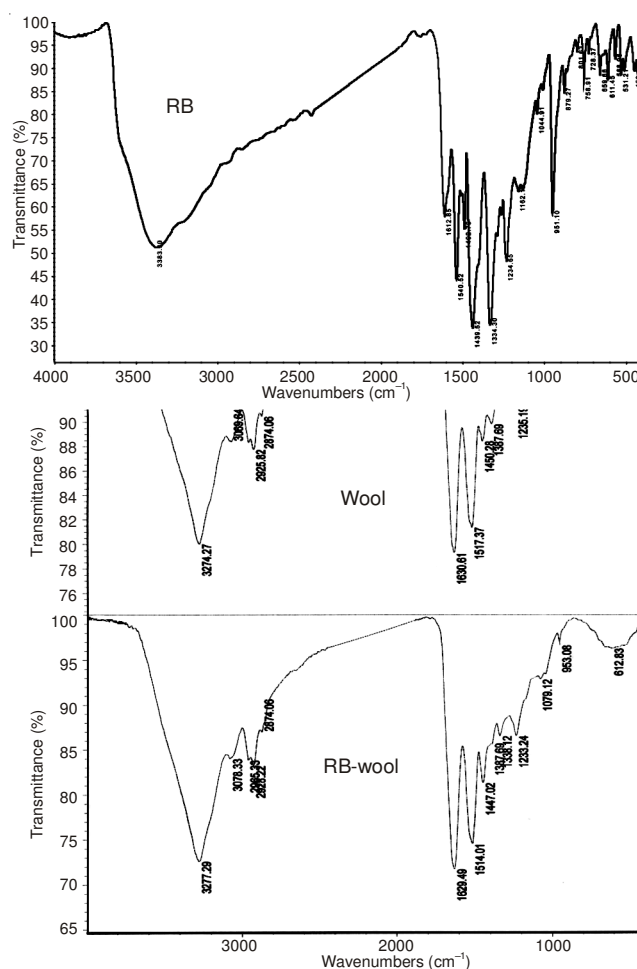

Fig. 5. IR spectroscopy of Rose bengal, Wool and RB-wool

to butenolide **2a** with a yield of 82 % was achieved when oxygen was continuously added during reaction, whereas the yield was lower when oxygen was added only before the irradiation. In methanol, no **2a** was formed under the same conditions, because the **2a** can react with methanol. In the absence of dioxygen, the photooxidation of 2-furfural did not occur in any solvents. Therefore, both oxygen and light are essential to the oxygenation reaction. We also investigated the photooxygenation of 2-furfural in different solvents by dioxygen. The results are summarized in Table-1. The reported yields and conversion were determined by GC analysis.

TABLE-1
SOLVENT EFFECT FOR PHOTOOXIDATION OF 2-FURFURAL
(**1a**) WITH RB-WOOL SYSTEM AS THE SENSITIZER

Solvent	Reaction time (h)	Conv (%)	Yield (%)
Acetonitrile	8	83	82
Chloroform	8	81	89
Acetone	8	55	83
Benzene	8	40	55
Hexane	8	11	64

Here, the conversion is defined as the percentage of starting material consumed and the yield is referred to as the percentage of product actually obtained based on the consumed starting material. As shown in Table-1, the photooxygenation yield of 2-furfural with dioxygen is the highest in polar solvent, but the lowest in nonpolar solvent. This shows that the solvent polarity has a dramatic effect on this reaction, which is consistent with the general rules of solvent effect on the photooxygenation[13]. Chloroform is the most preferable solvent, which leads to 81 % conversion with a higher yield. Although a good yield is also obtained with acetone as solvent, the relatively low conversion is a problem.

The influence of dye concentration (owf) on photooxidation of 2-furfural was also investigated in present study. The results are summarized in Table-2. 59 % conversion rate was observed under 5 h irradiation in acetonitrile when dye concentration on wool reached 2 %. At the low dye concentration (0.5 %, owf), the conversion rate was only 44 %. Because Rose bengal are photosensitive, by increasing dye concentration, more dyes can be immobilized on the surface of wool and be excited to produce more singlet oxygen during irradiation. Singlet oxygen are responsible for oxygenation of substrate. But when dye concentration on wool reached 2.5 %, the conversion rate of 2-furfural and yield of butenolides **2a** were all decreased. This may be caused by the self-quenching of the Rose bengal in excited triplet states due to aggregation of Rose bengal on the surface of the wool. Thus, the concentration of singlet oxygen was lower.

TABLE-2
PHOTOCATALYTIC ACTIVITY OF WOOL WITH
DIFFERENT ROSE BENGAL CONCENTRATION
(OWF) UNDER 5H IRRADIATION IN MECN

Entry	Rose bengal (owf)	Wool (g)	Conv (%)	Yield (%)
1	0.5	2	44	82
2	1.0	2	53	82
3	2.0	2	59	83
4	2.5	2	50	73

Apart from the substrate **1a**, the photoxygenation of other furan derivatives with oxygen were also examined, for which 2-furoic acid and 5-hydroxymethylfurfural were selected as substrates (Fig. 1). A fourth sample containing Rose bengal disodium salt as the photosensitizer was also irradiated in order to establish a comparison with the polymeric photocatalysts. After irradiation, the samples were filtered, concentrated under reduced pressure and analyzed by ^{1}H NMR and GC, confirming the product **2** in different yields (Table-3).

TABLE-3
PHOTOOXIDATION OF FURANS IN ACETONITRILE

Substrate	Photocatalyst	Reaction time (h)	Conv (%)	Yield (%)
1a	RB-wool	10	84	84
1b	RB-wool	8	88	89
1c	RB-wool	12	74	92
1a	Rose bengal	5	89	90

As shown in Table-3, all of the substrates could be smoothly converted to the expected products in high yields under heterogeneous conditions. For the oxidation of **1c**, the reaction was relatively slow under irradiation. On comparison of the photocatalytic activity of RB-wool and Rose bengal, we found that the photoreactivity of RB-wool was comparable to that of Rose bengal based on the yields. But the conversion rate is lower in the case of wool-Rose bengal. This may be caused by the introduction of a polymeric support into the system which results in increase of viscosity, which in turn influences the diffusion of oxygen to the rose bengal sites in the heterogeneous system.

It is generally believed that the [1]O2 molecules was involved in the photooxygenation of furans. It was further supported by the finding that the reaction rate was reduced drastically by the addition of 1,4-diazabicyclo[2,2,2]octane (DABCO; an efficient quencher of [1]O2) at a concentration of 10 mol %. Under irradiation, the sensitizers will be excited to the singlet state, then the singlet sensitizers will transfer to more stabilized triplet state through intersystem crossing. The triplet state sensitizers can collide with triplet oxygen molecules to form reactive [1]O2. In this case, furans **1** were subjected to the described [1]O2 photooxidation mechanism.

Conclusion

In summary, the utilization of RB-wool as a efficiently "green" sensitizer for photooxygenation of furans **1** to butenolides **2** in excellent yields have been demonstrated. The reaction occurs with participation of singlet oxygen. The polymeric sensitizer was prepared by a general dyeing procedure. It can be easily separated from the low molecule weight reactants and reused in the new cycle of the reaction. It represents a practical alternative to soluble Rose bengal for relatively high photostability, recyclability, sensitizing activity and sustainable development.

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