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Graphene Oxide Transparent Hybrid Film and Its Ultraviolet Shielding Property

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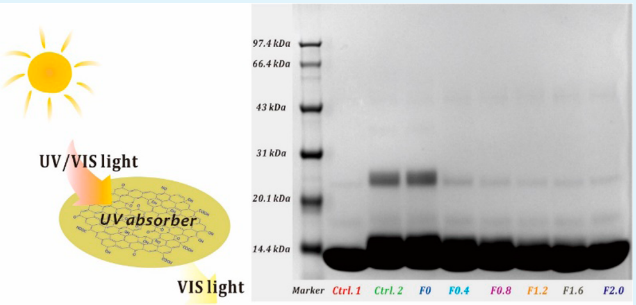
Supporting Information

ABSTRACT: Herein, we first reported a facile strategy to prepare functional Poly(vinyl alcohol) (PVA) hybrid film with well ultraviolet (UV) shielding property and visible light transmittance using graphene oxide nanosheets as UV-absorber. The absorbance of ultraviolet light at 300 nm can be up to 97.5%, while the transmittance of visible light at 500 nm keeps 40% plus. This hybrid film can protect protein from UVA light induced photosensitive damage, remarkably.



KEYWORDS: *graphene oxide, visible light transparency, ultraviolet shielding, photosensitive damage*

Ultraviolet (UV) radiation is widely applied in many fields, including UV detection, photography, optical sensors, disinfection, medical diagnosis and therapy, and polymer process, because of its short wavelength and high energy exposure. However, every coin has two sides, and so does UV radiation. It has been proved that prolonged exposure to UV radiation would result in acute and chronic health effects on the skin, eyes, and immune system of humans.[1] Consequently, the development of UV protective materials, especially UV shielding coatings, which allow good transmission to visible light but block most UV light, has grabbed much more attention from the scientific community.[2]

Apart from conventional organic UV absorbers (e.g., avobenzone, oxybenzone, and octyl methoxycinnamate) and inorganic blockers (e.g., titanium dioxide, indium oxide, zinc oxide), some novel designs of nanomaterials have been reported recently to be used to prepare UV shielding materials with good transparency in visible region. For instance, the layered double hydroxides (LDHs) based UV-shielding materials have been reported that show significantly enhanced performance compared with organic UV absorbers,[3] but without side-effect, i.e., self-degradation of organic absorbers,[4] photocatalytic activity of inorganic blockers.[5] LDHs is a sort of inorganic layered material with positively charged hydroxide basal layer, which are electrically balanced by the intercalation of anions in the interlayer space.[6] The organic UV absorbers, generally anionic molecules can be intercalated into interlayers of LDHs host by replacing the anions in LDHs precursor and form new intercalated LDHs materials.[7] To a certain extent, this structure is similar to that of graphene oxide (GO) nanosheets, which consists of graphitic structure core and oxygen-containing edge.[8] In consideration that the conjugated aromatics is well-known absorber of UV light[9] and GO nanosheets are stable in chemistry, it may be feasible to use GO as UV absorber for preparation of UV shielding materials.

In the past decade, graphene nanosheets, the 2D nanocarbon materials with just one atom thickness are absolutely the most shining star in scientific community because of its amazing properties and multiple applications.[10] Recently, there is an emerging recognition on the special properties of GO, the precursor of chemical modified graphene (CMG), for many material applications, such as energy material,[11] hydrogen storage materials,[12] drug or biomolecule carriers,[13] and so on. However, the optical performance of GO nanosheets seems to attract less attentions as of now. According to previous reports, the optical band gap of GO is about 1.5 eV, which means it has good absorption in ultraviolet (UV) zone, but weak absorption in visible range.[14] In a typical UV−vis absorption spectrum of a GO dispersion in water (Figure S1), it shows an absorption peak at 230 nm and declined sharply absorption line from 400 nm. Does this phenomenon indicate GO nanosheets could be able to act as UV absorber or blocker?

Similar to many nanocarbon sp^2 components, such as the single-walled carbon nanotube fullerene, to be used in optoelectronic devices, many interesting works have been published recently by using graphene as the functional

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component to build up electronic and optical devices owing to its UV absorption.[15] Moreover, W. He et al. prepared a kind of nitrogen-doped graphene sheets (NGSs) by reducing GO with ammonia—water at 100 °C.[16] The as-prepared NGSs can dramatically enhance the photostability of Food Black under UV irradiation and exhibit greatly applied potential as a multifunctional UV absorber for new-generation inkjet inks that can simultaneously integrate the advantages of dye-based and pigment-based inks. M. Tian et al. reported their novel strategy to prepare functional cotton fabrics with UV blocking property by using graphene nanoplates as a novel UV absorber, which was immobilized onto the surface of cotton fabric at low content via pad-dry-cure method.[17] The obtained fabrics performed ultrastrong protection against UV radiation, up to 10-fold increment of ultraviolet protection factor (UPF). In our previous work, we prepared flexible transparent conductive films by γ radiation reduced GO nanosheets coupling with polymer matrixes.[18,19] We found that the ultraviolet light absorption and visible transmittance of these films are relative to the reduction degree of GO nanosheets. The visible transmittance of film building by GO with higher reduction degree would be lowered, while the UV-absorption is basically unchanged. Considering its good visible transmittance and favorable dispersibility in water and some organic solvents, GO would become a good UV absorber or blocker for preparing UV-shielding transparent materials.

GO can be well-dispersed in water, and thus hydrophilic polymers such as poly(vinyl alcohol) (PVA), because of their hydroxyl groups, are able to make GO nanosheets well-dispersed in PVA solution, even at the molecular level.[20,21] Herein, we design a novel route to prepare GO-based UV-shielding transparent polymeric hybrid films as shown in Figure 1. GO nanosheets, with 1.05 nm thickness (i.e., monolayer) as shown in Figure S2, here was synthesized by modified Hummer's method as previously reported,[6,19] dispersed in deionized water to obtain stable GO dispersion, then, mixed with a PVA solution. The resultant GO/PVA dispersions were further casted on a fresh cleaned quartz substrate and dried in a 60 °C oven for 2 h, and the resultant film is designated as GO/PVA hybrid film. In consideration that PVA film is prone to etching and dissolution when contacts to water, we treated the GO/PVA hybrid film at 100 °C. After several hours, the thermal-treated film is still dissolved in water. To get out of the water erosion, an additional coating on surface of GO/PVA hybrid film with some water-proof materials to isolate GO/PVA layer from water would be feasible.

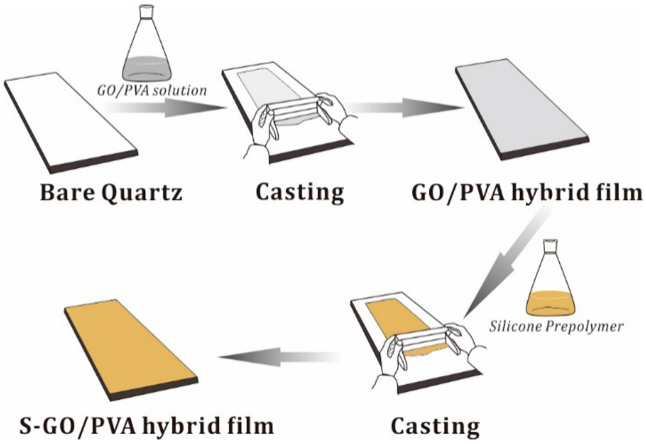

Figure 1. Schematic diagram of the GO-based UV-shielding transparent hybrid film preparation.

As we known, silicone is a general category of synthetic polymers with a siloxane main chain made up of repeating silicon to oxygen bonds, and two pendant organic groups attached to each silicon atom. Different functional pendant groups will allocate it with different properties. Up to now, silicone has been wide-used in sealants, adhesives, lubricants, medicine, and thermal and electrical insulation. Besides, silicone prepolymer is liquid under ordinary conditions and show high wettability to almost all solid surfaces,[22] and can be anchored to semi/porous substrates via mechanical interlocking mechanism, or to smooth substrates via chemical reaction, which contain unreacted —OH or —COOH groups on surface.[23] Herein, we coated a silicone prepolymer, STARKON SI-200 on the above GO/PVA hybrid films, and then dried in oven at 60 °C. After 12 h, the GO/PVA hybrid film was completely coated with a smooth and hardened layer of silicone. The S-GO/PVA hybrid film is obtained which refers to the GO/PVA hybrid film with silicone coating. The details have been provided in Experimental Section S3 in the Supporting Information.

In Figure 2a and 2b, water droplets were dripped on the GO/PVA and S-GO/PVA hybrid film, respectively. After wiping off the water droplets, the S-GO/PVA hybrid film still exhibited uniform tiny yellow (Figure 2b, left), while a white spot could be found on the bare GO/PVA hybrid film (Figure 2b, right). It indicates that the silicone coating is effective to prevent GO/PVA damage from water. Furthermore, we characterized the surface property of GO/PVA film before and after silicone coating through water contact angle test. It reveals that the water contact angle of hybrid film increased from 55.6° to 97.9° after silicone coating (Figure S3). This result indicates silicone coating allocates GO/PVA film with hydrophobic property. As it well-known, silicone is both hydrophobic and lipophobic. When it is spotted with oily organic matters, the hybrid film with silicone coating, is supposed to be cleaned easily. Herein, we dripped some lubricant oil on the surface of S-GO/PVA hybrid film. And we found it can be wiped off with tissue paper readily, which shows easy cleanability to oily contamination (as shown by Video S1). Therefore, these results can be seen as the indication that silicone coating on GO/PVA hybrid film could make it water-resistant and oil-resistant.

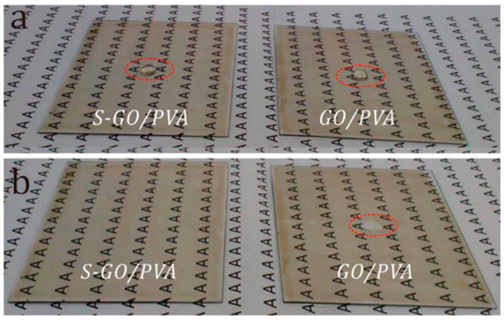

Figure 2. Photographs of water droplet on GO/PVA hybrid film with silicone coating (S-GO/PVA) and without silicone coating (GO/PVA) with 1.2 wt % GO content: (a) before and (b) after wiping off.

Figure 3**a and** 3**b** shows the surface and cross-section morphology of the GO/PVA hybrid film characterized by scanning electron microscope (SEM). It can be found that the

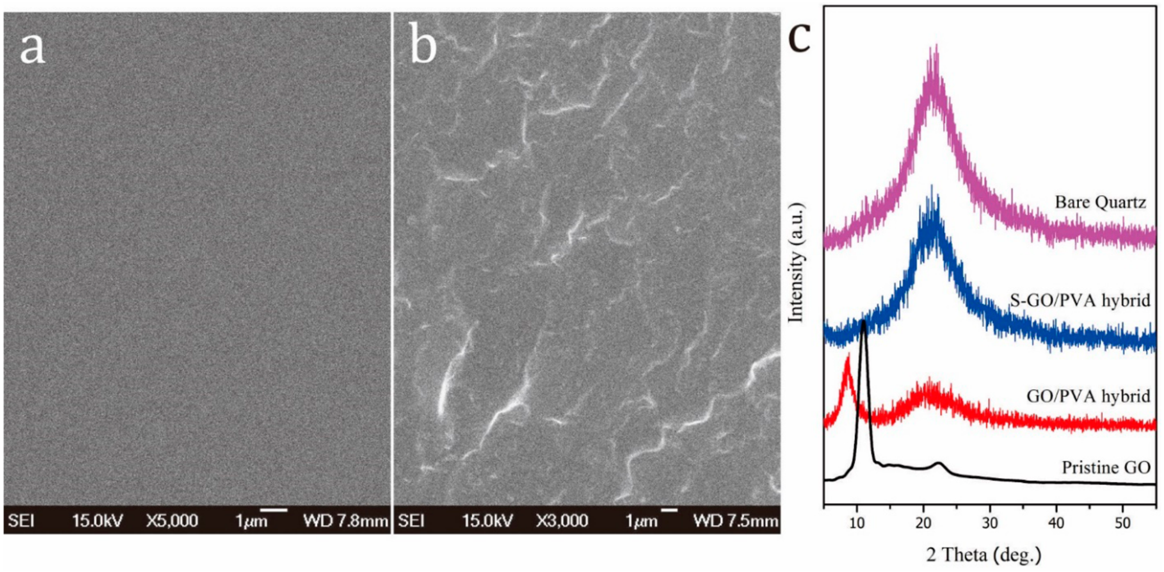

Figure 3. SEM images of (a) surface and (b) cross-section morphology of GO/PVA hybrid film with 1.2 wt % GO content; (c) XRD patterns of bare quartz, GO/PVA, and S-GO/PVA hybrid film with 1.2 wt % GO content.

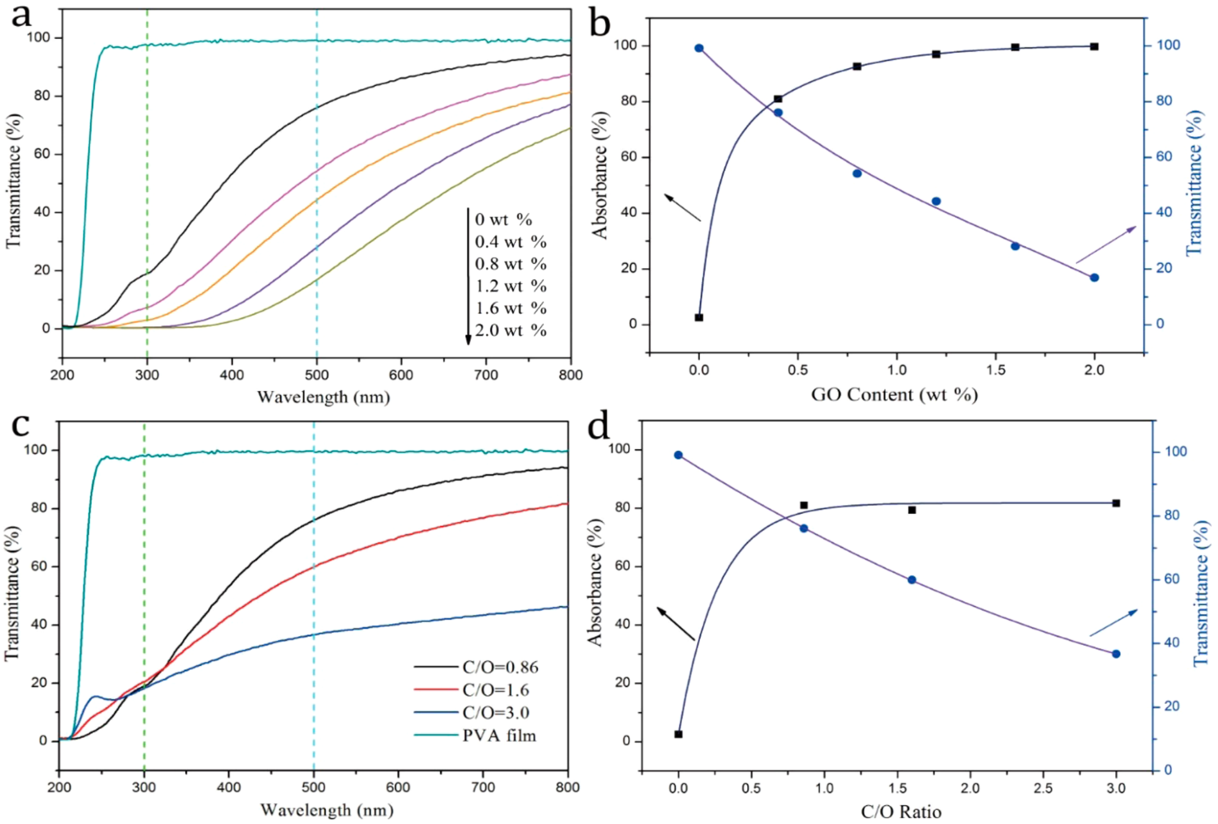

Figure 4. (a) UV−vis light transmittance spectra of S-GO/PVA hybrid films with different content of GO, which GO is at 0.86 of C/O ratio; (b) ultraviolet light absorbance at 300 nm and visible light transmittance at 500 nm of S-GO/PVA hybrid films with different content of GO. (c) UV−vis light transmittance spectra of S-GO/PVA hybrid films with different C/O ratio, which is 0.4 wt % of GO content; (d) ultraviolet light absorbance at 300 nm and visible light transmittance at 500 nm of the S-GO/PVA films with different C/O ratio. The thickness of GO/PVA film is 190 ± 5 μm and the silicone coating is 100 ± 5 μm thickness in all of the above-mentioned hybrid films.

surface of GO/PVA film is very flat without any bulges or aggregations (Figure 3a). On the cross-section of GO/PVA film, some irregular but uniform fringes were found, which would be formed by the irregular breakage of GO/PVA film after liquid nitrogen immersing (Figure 3b). This phenomenon was also observed on the cross-section of PVA film (Figure S4). By comparison to the PVA film, the fringes on GO/PVA hybrid film increased obviously. That may be owing to the GO dispersed in PVA matrix. And the uniform fringes also indicates that GO was well dispersed in PVA matrix without obvious

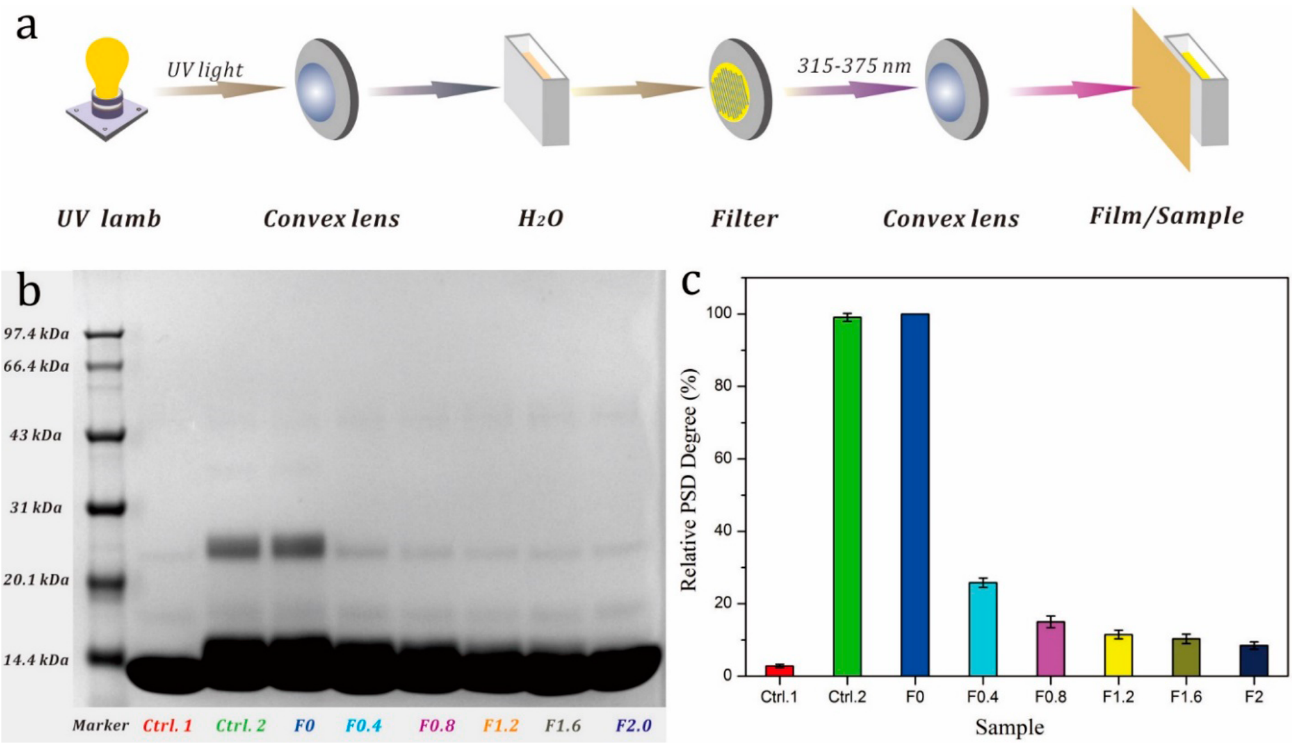

Figure 5. (a) Schematic diagram of steady state irradiation by UVA light, (b) gel electrophoresis patterns indicating the effect of shielding UV by S-GO/PVA hybrid films with different content of GO, and (c) relative photosensitive damage (PSD) degree of lysozyme of each sample. Ctrl 1: lysozyme solution without any film shielding, ctrl. 2: lysozyme and riboflavin (RF) solution without any film shielding, F0: lysozyme and RF solution with a bare quartz shielding, F0.4–F2.0: lysozyme and RF solution with S-GO/PVA hybrid film shielding with 0.4, 0.8, 1.2, 1.6, and 2.0 wt % of GO content, respectively.

aggregation.[20] In Figure 2**c,** the typical diffraction peak of GO observed in the GO/PVA hybrid film at about $2\theta = 8.6°$, is obviously decreased in comparison with that of pristine GO (10.8°), i.e. the interlayers distance increased, which should be due to the well-dispersed PVA chains encircling GO nanosheets, hindering the nanosheets stacking compactly and make the interlayers distance of GO be increased.[24] It would demonstrate PVA and GO are mixed thoroughly at molecular level. The XRD patterns of bare quartz plate and GO/PVA hybrid film with silicone coating are almost identical. The broad diffraction peak at 20–25°, is typical of an amorphous silicon dioxide. The pattern confirms that GO/PVA hybrid film on quartz plate has been covered thoroughly with silicone layer.

Silicone is free obvious absorption in UV–vis region (200–800 nm), as shown in Figure S5. While the UV–vis transmittance of quartz palate will be decreased evidently when the thickness of silicone coating comes up to around 300 μm. It may be due to the different refractive index of silicone and quartz makes the incident light deviate from original path and some deviated light has not be recorded by detector. In order to eliminate the influence of silicone coating on the optical property of GO/PVA hybrid film, we coated a very thin silicone layer on GO/PVA hybrid film with just 100 ± 5 μm of thickness. Herein, we compared the UV–vis absorption spectra of GO/PVA and S-GO/PVA hybrid film, and found the two curves are almost overlapping, without any new absorbance in the whole range, which means the thin silicone coating (100 ± 5 μm of thickness) has few effects on the transmittance performance of hybrid film (Figure S6).

Figure 4a shows UV–visible transmittance spectra of silicone coated GO/PVA hybrid films containing different GO content on quartz substrate in the wavelength range from 200 to 800 nm. Here, there is almost no absorbance of PVA film in UV region from 220 to 400 nm, while a sharp absorbance increasing in UV region is observed when GO nanosheets are introduced into PVA film, even the content as low as 0.4 wt %. It indicates an enhanced UV light shielding capacity by GO nanosheets in the spectra of interest. The resulting hybrid film containing 0.8 wt % of GO can block almost 100% of UVC (100–280 nm), more than 90% of UVB (280–315 nm) and more than 80% of UVA (315–400 nm), which are quite harmful to human skin and eyes in circumstances. When the GO content increases to 2.0 wt %, the UV light is almost completely shielded, but the visible light transmissibility is still retained. For quantify the UV shielding performance and visible light transparent ability, we investigated the absorbance at 300 nm and transmittance at 500 nm of S-GO/PVA hybrid films with different GO content, and results are shown in Figure 4b. It shows the absorbance of S-GO/PVA hybrid films at 300 nm increases along with increase in GO content, and about 99.7% of UV light is shielded by the S-GO/PVA hybrid films with 2.0 wt %. Although the transmittance at 500 nm decreased as GO content increasing, when hybrid film containing 1.2 wt % GO, 97.5% of UV light can be shielded, 44.3% of visible light still can be transmitted, which illustrates good UV shielding and visible transparency. The UV-shielding performance of obtained films is much comparable to that using other inorganic UV-absorbers,[5,25] which indicates GO can be used as a good UV-absorber for predation of transparent UV shielding hybrid film.

As we known, the reduction of GO nanosheets would make the absorption peak red-shift, and result in stronger background absorption in whole spectrum.[6] It is found that the UV absorbance and visible light transmittance depend on the C/O ratio of GO nanosheets obviously (Figure S7). In other words, GO nanosheets with different C/O ratio would make an effect to the UV-shielding and visible transmittance of S-GO/PVA hybrid films. In Figure 4c, we can find the C/O ratio of GO used here almost has no effect to the UV absorption of hybrid film, but obvious influence on the visible light transparency, which makes its transparency decreased as the C/O ratio increasing. As Figure 4d shows, the absorbance of hybrid films at 300 nm keeps at about 80%, when GO content is 0.4 wt %, whatever the C/O ratio is. Meanwhile, Figure 4d also shows that the transmittance at 500 nm declines progressively as the C/O ratio increasing from 0.86 to 3.0. It could be reasoned as that GO with higher C/O ratio is more prone to aggregation or stacking, which driven by the van der Waals force of graphitic structure.[6] Furthermore, we also find absorption of UV light below 270 nm are also declined. It is accountable that the absorption peak of GO at around 230 nm would be red-shifted to about 270 nm by reduction process.

UVB (290−320 nm) and UVA (320−400 nm) can cross the epidermis and reach the dermis,[26] which can interact with endogenous chromophores and photosensitizers resulting in the generation of reactive oxygen species (ROS) causing damage to DNA, proteins and lipids.[27] Owing to more than 95% of the solar ultraviolet radiation that reaches the Earth's surface, is the longer wavelengths of UVA, the UVA shielding effect of UV-protecting materials is the more pragmatic requirement. As we know, Riboflavin (RF), an endogenous photosensitizer, can be excited by visible and UVA light irradiation to singlet states and could transform to triplet states easily through intersystem crossing (ISC)($\Phi_{ISC} = 0.67$).[28] The triplet of RF can induce protein damage directly by proton/electron transfer (Type I) or first react with oxygen to form ROS, which interact with protein subsequently and result in protein dimerization or trimerization (Type II).[29] Therefore, it is an effective method to evaluate the UV-shielding property of the S-GO/PVA hybrid film by comparing the protein damage degree with or without its shielding.

Herein, we use a UVA light steady state irradiation coupling with sodium dodecyl sulfate−polyacrylamide gel electrophoresis (SDS−PAGE) to test the UV-induced damage of Lysozyme in the presence of RF with or without S-GO/PVA hybrid films shielding. Figure 5a is the schematic diagram of the UVA light steady-state irradiation. Solutions consist of 0.5 mmol L^{-1} Lysozyme and 0.1 mmol L^{-1} RF, were irradiated by UVA light (315−375 nm) with simultaneous air bubbling. After irradiation for 40 min, the solution was analyzed by SDS-PAGE. And the details of process are described in following Experimental Section. Lysozyme has barely any absorption of UVA,[30] so that ctrl. 1 shows a negligible damage of Lysozyme after UVA irradiation as shown in Figure 5b. After adding RF, 26−29 kDa and 42−44 kDa macromolecular protein fragments, the dimer and trimer of lysozyme, were observed in ctrl. 2, which indicates an obvious damage of lysozyme has been initiated in this condition. Bare quartz is well-transparent to UVA light, so that the lysozyme is also damaged dramatically in F0. When the quartz was coated with GO/PVA (i.e., S-GO/PVA hybrid film), the damage of Lysozyme was decreased abruptly. Moreover, the degree of damage is apparent negative correlation with the GO content of S-GO/PVA hybrid film, which has been demonstrated in F0.4−-F2.0 of Figure 5b.

To make a semiquantitative assessment of UVA light-induced damage degree of lysozyme in the presence of RF, we defined and calculated relative photosensitive damage (PSD) degree by the relative intensity of dimers and trimers bands of lysozyme (see Experimental Section). Figure 5c shows that the PSD of ctrl. 2 and F0 are very strong and almost identical, whereas by being shielded with s-GO/PVA hybrid film, the relative PSD has been down sharply to 30% less in F0.4 and even to 10% less when the hybrid film contain 2.0 wt %. It has fully proved that the hybrid film prepared by GO, working as UV-absorber, possesses outstanding UV-shielding performance, and this hybrid film would be used as UV-proof material in many fields such as building decoration, automobile caring, packaging material of UV-sensitive matters and senior show window for artworks/antiques and so forth.

In summary, we have successfully prepared GO/PVA hybrid film using simple solution processing technique like solution-casting and air-drying. The coating of silicone on GO/PVA hybrid film not only improves its water-resistance, and makes it easy to be cleaned, but also remains its optical property without any disturbance. The hybrid film has been illustrated possesses a strong UV-shielding ability as well as satisfactory visible light transmittance, which indicates GO acted as UV absorber in hybrid film. The UV-blocking ability and visible light transparency of hybrid film is well-related to GO content. However, increasing the C/O ratio of GO in hybrid film cannot improve its UV absorption but binge down the visible transparency. Steady-state irradiation and SDS−PAGE experiment demonstrated that the S-GO/PVA hybrid film can shield the UVA light and protect protein against photosensitive damage, such as dimerization and trimerization. All in all, these results here have proved a simple and low-cost process to prepare UV-shielding and visible light transparent hybrid film using GO as UV absorber, which is promising to large-scale production of UV-shielding transparent materials, and can be used as good UV protective material for photosensitive substance.

EXPERIMENTAL SECTION

Steady-State Irradiation and SDS−PAGE. This experiment is carried out according to previous reports.[30] The detail procedure as follows, UV light is generated from a 500W xenon lamp, and then focused by convex lens. After through a cuvette filled with water, the light penetrated a filter with a wave band of 315−375 nm, then it was focused on the sample cell filled with solution containing 0.5 mmol L^{-1} Lysozyme and o.1 mmol L^{-1} RF. Each sample solution was irradiated and simultaneously bubbled with air for 40 min. Then, all sample solutions were dotted on polyacrylamide gels separately and analyzed by Sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) (Mini-PROTEIN 3 Cell). After 2 h electrophoresis at 120 V, the gels were stained with Coomassie Brilliant Blue G-250 solution, distained with methanol/acetic acid mixed solution subsequently, and then scanned on a Quantity One scanner (Bio-Red) to quantify band intensity. The S-GO/PVA hybrid films with different GO content were placed in front of sample cell. Lysozyme solution, Lysozyme and RF mixture solution without any film shielding were also irradiated on above procedure, which are designated as the control 1 and 2. Relative PSD degree is defined as the criteria to evaluate the effect of S-GO/PVA hybrid film shielding on the damage degree of lysozyme by RF-sensitizing UVA damage. It can be calculated by following equation

$$R = \frac{I_s}{I_o} \times 100\% \tag{1}$$

Where R, I_o, and I_s refer to the relative PSD degree, dimers and trimers band intensity of Lysozyme in the sample cell with a bare quartz shielding (i.e., F0) and other samples.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04231.

> Experimental details of graphene oxide preparation; UV−vis spectra of GO with different C/O ratio; GO/PVA film before and after silicone coating are involved (PDF)
>
> Video of lubricant oil drop being wiped from hybrid film (AVI)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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