The photothermal conversion and UV resistance of silk fabrics being achieved through surface modification with C@SiO$_2$ nanoparticles

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Abstract

With the improvement in people’s living standards, the development and application of smart textiles are receiving increased attention. In this study, a carbon nanosurface was successfully coated with a SiO$_2$ layer to form C@SiO$_2$ nanomaterials, which improved the dispersion of carbon nanomaterials in aqueous solution and enhanced the absorption of light by the carbon nanoparticles. C@SiO$_2$ nanoparticles were coupled on the surface of silk fabric with a silane coupling agent KH570 to form C@SiO$_2$ nanosilk fabric. The silk fabric that had undergone such surface modification was endowed with a special photothermal function. The results obtained with scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), and infrared spectroscopy (FTIR) showed that C@SiO$_2$ nanoparticles were successfully modified on the surface of the silk fabric. In addition, under the irradiation of near-infrared light with a power of 20 W and a wavelength of 808 nm, the C@SiO$_2$ nanosilk fabric was rapidly warmed from 23 °C to 60 °C within 30 s. After subjecting the functional fabric to hundreds of photothermal experiments and multiple washes, the photothermal efficiency remained largely unchanged and proved to be durable and stable. In addition, the thermogravimetric (TG) analysis results showed that the C@SiO$_2$ nanoparticles contributed to the thermal stability of the silk fabric. The UV transmittance results indicated that C@SiO$_2$ nanofabric is UV-resistant. The silk modification method developed in this study is low-cost, efficient, and environmentally friendly. It has some prospects for future applications in the textile industry.

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Keywords: C@SiO$_2$ nanomaterials; photothermal conversion; UV resistance; clean production;

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Highlights
A fast photoresponsive photothermal fabric
C@SiO$_2$ nanosilk fabric is a low cost UV resistant fabric
Low cost and environmentally friendly way to modify the surface of fabrics

1. Introduction
Silk from silkworms is a natural polymer material. Silk fabrics are characterized by a unique pearl-like lustre, breathability, high moisture absorption, and smooth hand feel. In addition, silk fabrics are also strong and ductile, highly biocompatible, biodegradable, and environmentally stable [1]. Although silk fabrics excel in many aspects, they also have some drawbacks: Silk fabrics are prone to yellowing and wrinkling, which seriously affect their esthetics and longevity. Additionally, the poor UV resistance and heat resistance of silk fabrics are problems [2]. To overcome these drawbacks, the current performance of silk fabrics should be enhanced through modification to achieve special properties. As such, researchers have focused on the modification of silk fabrics and the functional finishing of fabrics. Through continuous technological innovation and research and development, we hope to further expand the applications of silk fabrics [3,4].

With global energy shortages and environmental pollution becoming increasingly serious, people are increasingly concerned about low carbon energy saving and environmental protection. In indoor life, thermal comfort is achieved with electrical devices such as air conditioners and heaters; yet, these devices consume large amounts of energy. Therefore, a smart wearable fabric should be developed that can protect the body from the cold in cold environments but can also absorb the energy of sunlight and turn it into heat or use reflected far-infrared radiation from the human body for heating and insulation [5,6], thus providing protection against the cold in extremely harsh climatic conditions. To achieve thermal comfort for the human body while reducing energy consumption for warmth, personal thermal management is an effective solution [7-9]. Traditional smart textiles include the photovoltaic effect [10], electrothermal conversion [11], and photothermal conversion [12]. Here, solar energy, as an abundant, safe, and sustainable energy source, is widely used in photothermal conversion technology and can provide a convenient and reliable solution for personal temperature regulation.

Solar energy is an inexhaustible and renewable resource, which is why photothermal textiles have been extensively studied. Photothermal conversion materials absorb near-infrared light and generate heat through plasma resonance thermal effects, semiconductor nonradiative chirality, and molecular thermal vibrations, resulting in rapid localized warming [13,14]. The general photothermal conversion nanomaterials are classified as metallic [15], semiconductor [16], and carbon-based nanomaterials [17]. Among them, carbon-based nanomaterials are simple to prepare, low-cost, and have good heat transfer and excellent chemical and physical properties [18]. Therefore, they can be used as photothermal conversion materials [19], anti-UV materials [20], and electromagnetic shielding materials [17,21]. Because carbon-based nanomaterials have SP$^2$ and SP$^3$ hybrid orbitals with very close energy levels and π-electron clouds, they show excellent photothermal conversion performance and high efficiency due to their strong absorption of near-infrared light with a wide range of visible light absorption wavelengths [22,23]. Therefore, they can be used as a photothermal conversion material for wearable smart fabrics. In addition, silica is considered a promising material because of its low cost, chemical inertness, good mechanical properties, and thermal stability and due to being nonpolluting [24]. Nanosilica has very low photocatalytic activity and high UV and IR shielding and reflecting abilities [25]. Therefore, it has a wide range of promising applications in textile surface modification.
To combine the advantages of carbon and silica nanoparticles, in this study, a carbon silicon composite photothermal nanomaterial was prepared by coating a layer of silica on carbon nanoparticles. As shown in Scheme 1a, carbon nanoparticles have a high surface energy and are prone to agglomeration and precipitation in solution. After modification with PVP, the carbon nanoparticles were less agglomerated and better dispersed in a solution, and the affinity of the carbon nanoparticles for the SiO$_2$ precursor was strengthened [26]. In this study, a modified Stober method was used to form silica layers on the surface of carbon nanoparticles under alkaline conditions to form core–shell nanostructures [27,28]. The employed coating process substantially increased the dispersion of carbon nanoparticles in solvents such as water and ethanol [29]. The C@SiO$_2$ nanoparticles bonded to the silk surface using a silane coupling agent (KH570) to form functional fabrics. The C@SiO$_2$ silk fabrics exhibited excellent photo-thermal conversion and UV resistance properties. In addition, a layer of silica was coated on the surface of the carbon nanomaterials to improve the carbon nanodispersion and absorption of light, enhancing the safety of the wearable fabric. The photo-thermal and UV resistance of silk fabrics enables the use of silk for smart wearable textiles.

2. Experimental

2.1. Materials

Silk fabric (19 mm, density: 114 g/m$^2$) was purchased from Ningbo Yunling Textile Trading Co. (Ningbo, China) Carbon nanomaterials particle size: 50 nm, purity: 99.99% were purchased from Suzhou Beasley New Materials Co. (Suzhou, China) We purchased 3-(trimethoxysilyl)propyl methacrylate (KH570), polyvinylpyrrolidone (PVP), and tetraethyl silicate (98%) (TEOS) from Aladdin Biochemical Technology Co. (Shanghai, China); ammonia (25%) was purchased from Xi long Science Co. (Shantou, China) A plug-in thermal imager (312-Z5mini) was obtained from Shenzhen Chuang zhi Fei Technology Co., Ltd. (Shenzhen, China), and an 808 nm NIR LED lamp (20 W) was obtained from Fang pu Optoelectronics Co. (Shenzhen, China).

2.2. Preparation of C@SiO$_2$ nanoparticles:

Firstly, 6 g of carbon nanoparticles was added to 600 mL of deionized water and sonicated and dispersed for 30 min; secondly, an equal amount of polyvinylpyrrolidone (PVP) was added and stirred for 12 h at 1500 rpm to allow sufficient dispersion. Thirdly, the product was centrifugally dried and again sonicated and dispersed into 1000 mL of anhydrous ethanol. 22.4 mL of deionized water and 32 mL of ammonia solution at a concentration of 0.1 M were added and then well stirred. Fourth, 92.8 mL of tetraethyl silicate (TEOS) was added and stirred in a water bath at 38 °C for 5 h. Finally, C@SiO$_2$ nanoparticles were obtained by centrifugal drying. As shown in Scheme 1 a.

2.3. Preparation of C@SiO$_2$ silk fabric:

The silk fabric was boiled in 7 mg/mL Na$_2$CO$_3$ solution for 30 min, followed by repeated washing with deionized water. The dry degummed the silk fabric was cut into 4×4 cm$^2$ pieces, 10 mL of C@SiO$_2$ nanodispersion solution with different concentrations (1.25 mg/mL, 2.5 mg/mL, 5 mg/mL, 10 mg/mL, or 20 mg/mL) was configured. The silk fabric was immersed in the solution and the nanoparticles were dispersed by ultrasonication. Then, 200 μL of silane coupling agent KH570 was added and shaken in a water bath at 80 °C for 30 min. The silk fabric was then removed and transferred to an oven and dried at 120 °C. By repeating this operation several times, sufficient amount of nanoparticles C@SiO$_2$ were successfully modified onto the surface of the silk. To remove the unbound nanoparticles, the dried silk fabric needed to be repeatedly rinsed with de-ionized water and put into the oven again to dry. As shown in Scheme 1 b.

2.4. Characterization

Transmission electron microscopy (TEM) was used to observe the nanomorphology. An amount of nanoparticles was dispersed in a volume of anhydrous ethanol solution and sonicated for 30 min, and then a microdrop of the solution were taken onto a copper grid using a pipette gun and dried in air. After drying, they were placed in Transmission electron microscopy (TEM) for characterization. The absorption of the nanoparticles at different optical wavelengths was tested using UV-Vis-NIR absorption spectroscopy. Fixed
amounts of carbon nanoparticles and C@SiO$_2$ nanoparticles were dispersed in aqueous solution, separately, and sonicated for 30 min. The nanoparticles dispersion were then pipetted into a quartz cuvette with a pipette and their UV–Vis–NIR absorption spectra were measured. And, the carbon nanoparticles and C@SiO$_2$ nanoparticles dispersions were added to separate beakers and sonicated for 30 min, then the supernatants were then aspirated at different times to determine their UV absorbance values. The chemical structure of the nanoparticles and the silk fabric was observed using infrared spectroscopy (FTIR). Trace sample mixed with a small amount of potassium bromide and then dried in an oven, ground, and pressed to form very thin slices for infrared spectroscopy measurements in a dry environment. The infrared spectra were measured in the 4000 cm$^{-1}$ to 400 cm$^{-1}$ band with a resolution of 4 cm$^{-1}$ and 256 cumulative scans. Scanning electron microscopy (SEM) was used to analyze the surface morphology of the silk fabrics. In addition, the surface of the silk fabric was scanned for elements using energy dispersive spectrometer (EDS). The thermal stability of the fabrics was tested using thermogravimetry (TG). The silk fabric was cut up and tested for thermal stability using a thermogravimetric analyzer STA-2500 NE-TZSCH, Germany, under a nitrogen atmosphere. The sample mass was 6–8 mg, the temperature range was 25 degC to 800 degC, the heating rate was 10 degC/min, and the protective gas flow rate was 20 mL/min.

### 2.5. Characterization of Photothermal Conversion Properties

The untreated silk fabric, the silk fabric treated with silane coupling agent KH570, and the silk fabric cotreated with different concentrations of C@SiO$_2$ nanoparticle solutions were exposed to 808 nm near-infrared light and sunlight, and the changes in the silk fabric were observed via thermal imaging with increasing irradiation time and temperature.

### 2.6. Washing durability test

The photothermal properties of the samples were tested according to FZ/T73023-2006 “Antimicrobial Knitwear” by performing 10, 30, and 50 standard washes to assess the washing resistance of the photothermal effect of the finished silk fabric.

### 2.7. UV resistance test

The UV transmittance of the fabric was tested using a UV spectrophotometer (Shimadzu UV-2600, Japan) with a slit width of 2 nm in the range of 190–800 nm. The transmittance was measured by first using barium sulfate as a base for baseline calibration and then using a sample holder to hold the sample under test and scanning at wavelengths 190–800 nm. According to GB/T18830-2009 “Evaluation of textile UV protection performance”, the UV protection factor and UV transmittance T(UVA) and T(UVB)) of the samples were measured at 290–400 nm using a UV protection factor (UPF) tester.
3. RESULTS AND DISCUSSION

When the carbon nanoparticles and C@SiO$_2$ nanoparticles were observed through a transmission electron microscope (TEM), we observed that the surface of the carbon nanomaterials, as shown in Figure 1a,b, was smooth, showing a regular spherical shape. When a layer of SiO$_2$ was modified on the surface of the carbon nanomaterials, we observed a transparent layer of SiO$_2$ was wrapped around the surface of the carbon nanomaterials, as shown in Figure 1c,d. From the TEM results, we observed that the core–shell structure of the C@SiO$_2$ nanoparticles was successfully prepared.

Figure 1. TEM of (a,b) C nanoparticles and (c,d) C@SiO$_2$ nanoparticles.

Carbon and C@SiO$_2$ nanoparticles were dispersed in aqueous solution, and the UV-Vis-NIR absorption spectra were measured, as shown in Figure 2a. The results showed that the absorbance of the C@SiO$_2$ nanoparticle dispersions was stronger than that of the carbon nanoparticle dispersions at the same mass concentration due to the rich hydrophilic hydroxyl functional groups on the surface of the C@SiO$_2$ nanoparticles, which allowed the C@SiO$_2$ nanoparticles to be more easily dispersed in aqueous solution. In addition, C@SiO$_2$ nanoparticles can reduce light reflection and increase light absorption [30,31]. To verify the stability of the C@SiO$_2$ nanoparticles in aqueous solution, we measured the absorbance of the carbon nanoparticles and C@SiO$_2$ nanoparticles dispersed in aqueous solution at a wavelength of 808 nm at different times as shown in Figure 2b. We found that the carbon nanoparticles completely precipitated after only 3 h in aqueous solution, as shown in Figure 2c, and the absorbance of the supernatant was close to zero. In contrast, the luminosity of the C@SiO$_2$ nanoparticles remained almost unchanged over 7 days. This indicated that the C@SiO$_2$ nanoparticles were more dispersed in aqueous solutions and did not precipitate or coalesce. As such, these nanoparticles are more feasible for practical application in textile processes.
Figure 2. (a) UV-Vis-NIR absorption spectra of C and C@SiO$_2$. (b) Colloidal stability of C and C@SiO$_2$ were measured using changes in the UV-Vis absorption spectrum over a period of 7 days. (c) Optical images of C and C@SiO$_2$ in aqueous solution at different times.

From the scanning electron microscopy (SEM) results shown in Figure 3a, we found that the surface of the untreated silk fabric was smooth and flawless; after the C@SiO$_2$ nanotreatment, the surface of the C@SiO$_2$ nanosilk fabric was rough, which indicated that the C@SiO$_2$ nanoparticles were successfully modified on the silk surface, which may have been caused by the condensation reaction of the silane coupling agent KH570 in grafting the C@SiO$_2$ nanoparticles on the silk fabric surface [32]. By comparing the energy dispersive spectrometer (EDS) results of the untreated silk fabric with those of the C@SiO$_2$-nanoparticles-treated silk fabric, as shown in Figure 3b, we found that the content of elemental silicon in the untreated silk fabric was 0%, whereas that in the C@SiO$_2$-nanoparticles-treated silk fabric was 29.59%, which proved that the C@SiO$_2$ nanoparticles were successfully modified on the silk surface. In addition, Figure 3b shows that elemental Si was uniformly distributed on the silk surface, indicating that the C@SiO$_2$ nanoparticles were uniformly distributed on the silk surface.
As shown in Figure 4a, the carbon nanoparticles mainly showed the antisymmetric -OH stretching vibration peak at 3420 cm$^{-1}$. When the carbon nanoparticles were wrapped with a layer of SiO$_2$ on the surface, we found that the antisymmetric -OH stretching vibration peak at 3420 cm$^{-1}$ significantly enhanced when comparing the IR spectra, and the new characteristic peaks at 1630 cm$^{-1}$, 1097 cm$^{-1}$, and 468 cm$^{-1}$ corresponded to the stretching and bending vibration of the silicon–oxygen bond. The strong absorption peak at 1097 cm$^{-1}$ corresponded to the asymmetric vibration of the Si-O-Si in the sample. The absorption peak at 468 cm$^{-1}$ corresponded to the bending vibration of Si-O [33]. The IR results demonstrated the successful wrapping of a layer of SiO$_2$ on the carbon nanosurface. The results in Figure 4b show that the characteristic peaks of the random coils in amide I and the $\beta$-folded structure in the amide II band, both of which belong to the main characteristic peaks of silk proteins, appeared at 1648 cm$^{-1}$ and 1527 cm$^{-1}$, respectively [34]. The silk fabric modified with the silane coupling agent KH570 showed an asymmetric -CH$_3$ stretching vibration peak at 2927 cm$^{-1}$, C-O-C absorption peak at 1300.7 cm$^{-1}$, and C=O stretching vibration peak at 1722.1 cm$^{-1}$ [35,36]. The silk-modified nanoparticles then showed a C-O stretching vibration peak linked to an alkyl group at 1037 cm$^{-1}$. The Si-O-Si bonds may have formed due to the hydrogen bonding between the Si-OH generated by the hydrolysis of Si-CH$_3$ in KH570 and the hydroxyl groups on the silica surface [37]. We found that C@SiO$_2$ was modified on the silk surface with the silane coupling agent KH570 in the form of grafting through chemical bonding.
The untreated silk fabric, the silk fabric treated with silane coupling agent KH570, and the silk fabric cotreated with different concentrations of C@SiO$_2$nanoparticle solutions were each subjected to NIR light irradiation at a power of 20 W and a wavelength of 808 nm. The change in temperature of the silk fabric over time was observed via infrared thermography, and the results are shown in Figure 5a. Notably, the C@SiO$_2$silk fabric rapidly warmed from 23 °C to 60 °C within 30 s, demonstrating its remarkable rapid heating ability under 808 nm NIR light. In addition, to determine the photothermal conversion of the C@SiO$_2$ silk fabric under natural light, the samples were placed together under natural light. The temperature change in the silk fabric over time was observed with infrared thermography, and the results are shown in Figure 5b. The results showed that the temperature of the C@SiO$_2$ nanosilk fabric increased from an outdoor temperature of 22 °C to 45 °C within 8 min, proving that a high photothermal conversion efficiency under sunlight. Based on the results of the photothermal data obtained in near-infrared and natural light, we found that the difference in the photothermal effect of the silk fabrics with different nanoparticle concentrations was minimal. This occurred because the C@SiO$_2$ nanomaterial is a highly efficient photothermal material, requiring only a small amount to produce a powerful photothermal effect. Therefore, the C@SiO$_2$-nanomaterial-modified silk fabrics have considerable potential as functional fabrics for photothermal conversion. Furthermore, by observing the photothermal efficiency of the C@SiO$_2$ and carbon nanosilk fabrics under 808 nm NIR light, we found that the photothermal effect of both materials was strong, but that of the C@SiO$_2$ silk fabric was stronger. This occurred because the C@SiO$_2$ nanoparticles were more uniformly dispersed on the silk surface and did not agglomerate, resulting in a stronger photothermal effect. In other words, the C@SiO$_2$-nanomaterial-modified silk fabric provides additional advantages and is more suitable as a material for functional fabrics for photothermal conversion.

Next, to test the reproducible photothermal performance of the C@SiO$_2$ silk fabric, we placed it under 808 nm NIR light, repeatedly warmed and cooled the fabric, and observed its temperature change over time, with the results shown in Figure 5d. The experimental results showed that the C@SiO$_2$ silk fabric quickly warmed and reached equilibrium after 30 s. The results of 100 repeated photothermal conversion experiments showed that the material warmed up from 23 °C to approximately 60 °C in 30 s and demonstrated good photothermal stability: its photothermal efficiency was not reduced by repeated use.
Figure 5. Comparison of the heating rate of photothermal fabrics under (a) NIR light and (b) solar light; (c) comparison of the photothermal warming rates of C and C@SiO$_2$ fabrics in near-infrared light. (d) Photothermal condition of C@SiO$_2$ fabric repeatedly warmed 100 times in near-infrared light. (e) Infrared image of sunlight-heated fabric.

To test the effect of the number of washes on the experimental effect of the photothermal conversion of the C@SiO$_2$-nanoparticle-treated silk fabric, different numbers of washes were applied, and a comparative experiment was conducted. The experimental results showed that the photothermal conversion effect of the C@SiO$_2$-treated silk fabrics differed little after 0, 10, 30, and 50 washes under either 808 nm NIR or sunlight, which proved that the bond between the C@SiO$_2$ nanoparticles and silk fabrics was strong and not easily broken.
Figures 6. Comparison of the heating rate of photothermal fabrics under (a) near-infrared light and (b) solar illumination for different number of washes. (c) Infrared image of a fabric heated by sun-light.

The thermal stability of the fabrics was effectively assessed with thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses, as shown in Figure 7a,d. In general, silk has a small mass loss in the range of 40–200 °C, mainly due to the evaporation of water; in the range of 320–480 °C, silk fabrics show a large mass loss, which is due to their thermal degradation [3]. Therefore, we concluded from the readings that the thermal degradation temperature of the untreated silk fabric was 324 °C and that of the C@SiO\textsubscript{2}-nanoparticle-treated silk fabric was 320 °C. We noted a slight acceleration in the decomposition, possibly occurring due to the ability of C@SiO\textsubscript{2} nanoparticles to increase the absorption of heat by the fabric. Furthermore, by comparing the residual mass, we found that the percentage of residual mass of the C@SiO\textsubscript{2} nanomodified silk fabric was 33.8%, which was 7.4% higher than that of the untreated silk fabric. This also indicated that the silk surface was successfully modified with C@SiO\textsubscript{2} nanoparticles. Overall, these results indicated that C@SiO\textsubscript{2} nanoparticles can effectively improve the thermal stability of silk.

Figures 7. (a) TG and (b) DTG analyses of untreated and treated silk fabrics.

To verify the UV resistance of the C@SiO\textsubscript{2} silk fabric, the UV transmittance of the fabric was measured, as shown in Figure 8. and the UV protection factor (UPF), UVA, and UVB transmittance of the fabric were calculated. The results are shown in Table 1. The UPF of the untreated silk fabrics was only 38.57. Different concentrations of C@SiO\textsubscript{2}-nanoparticle-treated silk fabrics had UPF values of up to 165.76, indicating that the C@SiO\textsubscript{2} silk fabrics had a certain UV resistance. This performance mainly depended on the UV
absorption capacity of the carbon nanomaterials and the UV reflection capacity of SiO₂. Therefore, C@SiO₂ silk fabric is a promising functional fabric for development.

Figure 8. UV transmission rates of untreated silk fabrics and silk fabrics treated with different concentrations of C@SiO₂ nanoparticles.

Table 1. UPF value and transmittance of untreated and treated samples

<table>
<thead>
<tr>
<th>Silk Fabric Sample</th>
<th>UPF</th>
<th>UVA</th>
<th>UVB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>38.57</td>
<td>36.17</td>
<td>20.54</td>
</tr>
<tr>
<td>1.25 mg/mL C@SiO₂</td>
<td>103.83</td>
<td>11.63</td>
<td>8.02</td>
</tr>
<tr>
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<td>126.03</td>
<td>9.37</td>
<td>6.79</td>
</tr>
<tr>
<td>5 mg/mL C@SiO₂</td>
<td>126.08</td>
<td>8.63</td>
<td>6.78</td>
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<tr>
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<td>7.55</td>
<td>5.86</td>
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<tr>
<td>20 mg/mL C@SiO₂</td>
<td>165.76</td>
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4. Conclusions

In conclusion, we successfully prepared C@SiO₂ nanoparticles by coating silica on the surface of carbon nanoparticles, and we modified the surface of silk with C@SiO₂ nanoparticles through grafting via chemical bonding with a silane coupling agent KH570. By comparing the transmission electron microscopy (TEM) and infrared spectroscopy (FTIR) results of the carbon and C@SiO₂ nanoparticles, we found that SiO₂ was successfully modified on the surface of the carbon nanoparticles to form nanoparticles with a core–shell structure. By comparing the absorbance of carbon and C@SiO₂ nanoparticles in the UV–Vis–NIR spectra and the UV absorbance at different time periods in aqueous solution, we found that C@SiO₂ nanoparticles were more dispersed and stable than carbon nanoparticles in aqueous solution. The infrared spectroscopy (FTIR) and energy dispersive spectrometer (EDS) results showed that C@SiO₂ nanoparticles were successfully used
to modify the surface of silk. The results of the photothermal conversion experiments demonstrated that C@SiO$_2$ silk fabrics possess suitable photothermal conversion properties. To determine the strength of the bond of the C@SiO$_2$ nanoparticles to the silk fabric, we tested the C@SiO$_2$ silk fabric after repeated rinsing. We found that the photothermal effect of C@SiO$_2$ silk fabric was basically the same after different numbers of washes, proving that the nanoparticles were firmly bonded to the silk fabric. The UPF value of the C@SiO$_2$ silk fabric was calculated by measuring the UV transmission rate of C@SiO$_2$ silk fabric, which showed good UV resistance. In this study, low-cost, thermally efficient, and environmentally friendly C@SiO$_2$ silk fabrics were prepared. This material shows potential for future application in the textile industry.

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