Supporting Information

Experimental Section

Materials
Tetraethyl orthosilicate (TEOS, reagent grade 98%), aqueous Ammonia (25-28%), Ethanol (5% Methanol), Titanium (IV) Butoxide (TBT, 97%), Polyvinylpyrrolidone (PVP, MW 55,000), Absolute Ethanol (ACS reagent > 99.5%), anhydrous Sodium Hydroxide pellet (NaOH, ACS reagent > 97%), Ethyl Cellulose, Triton X-10, Terpineol (α-Terpineol >80%), Acetic acid, Copper(II) acetate monohydrate (98+ % extra pure). All the chemicals were used as received.

Synthesis of SiO$_2$ Nanospheres
24 ml of ammonia, 81 ml of ethanol and 4.2 ml of TEOS were mixed and stirred for 1h at room temperature. The precipitated silica nanospheres were washed with deionized water and ethanol, and then dried in the oven.

Synthesis of SiO$_2$@TiO$_2$ core-shell structure
0.1 g of as-prepared SiO$_2$ nanospheres were mixed with 0.235 ml of TBT in 2 ml of absolute ethanol and stirred for 20 min. The mixture of 0.3 g of PVP, 1 ml of deionized water and 20 ml of absolute ethanol were added to the solution and stirred for 1 h. Then the precipitate was washed and calcined in the furnace at 450 °C for 2 h.

Synthesis of hollow TiO$_2$ structures
Hollow TiO$_2$ structures were obtained by soaking the SiO$_2$@TiO$_2$ sample in 0.1M NaOH solution for 24 hours. The mixture was then washed a few times with deionized water and dried in the oven.

Synthesis of TiO$_2$/CuO hollow nanocomposite
CuO nanoparticles were synthesized by an aqueous precipitation method. TiO$_2$/CuO nanocomposite was prepared by adding desired amount of CuO nanoparticles to 0.04 g of hollow TiO$_2$ (or SiO$_2$@TiO$_2$ core-shell) powder in 20 ml ethanol to achieve different loading percentage ranging from 3 to 10 wt%. The solution was stirred in water bath at 90 °C for 3 h.
Fabrication of TiO$_2$/CuO film on glass substrate

0.040 g of the TiO$_2$/CuO hollow nanocomposites were mixed with 0.040 g of ethyl cellulose, 2 drops of triton x-100, 2.4 ml of Terpineol and 20 ml of ethanol. The solution was stirred in water bath at 90 °C for 3 h. Various substrates were coated using spin-coater and dried before annealing at 450 °C for 30 min.

Simulation conditions

The simulations are conducted by the Finite-difference time-domain (FDTD) simulations with the Lumerical software. In this simulation, the incident wave is set to be 300 nm from the bottom. The nanoparticle is placed in the water matrix. The refractive index of the TiO$_2$ material is taken from the literature. As the TiO$_2$ shell is made of the nano-particles, it is not fully packed with TiO$_2$ material. In our simulation, we assume that the solid loading factor of the TiO$_2$ is 66%. In the supplementary material, we also presented the transmittance at other solid loadings. The conclusions are coherent for other solid loading. The refractive index of water is 1.34. The refractive index of SiO$_2$ is set to be 1.48. The boundary condition is set to be perfect absorber. The dimension of the simulation areas is 1 µm$^2$. The transmission is calculated by placing a detector 0.5 µm away from the center of the nanoparticle. The transmittance is only measured at the incident wavelength.

Material Characterization

The scanning electron microscopy (SEM) characterization was carried out using a JEOL FEG JSM 6700F field-emission operating at 215 kV. The EDX characterization was performed with an Oxford Instruments Energy Dispersive X-ray (EDX) System. The crystalline structures were analyzed using transmission electron microscopy (TEM, Phillips FEG CM300) operated at 200 kV and X-ray diffraction (D5005 Bruker X-ray diffractometer equipped with graphite monochromated Cu Kα radiation at $\lambda = 1.541$ Å). Absorption and transmittance spectra were obtained using a Shimadzu UV-3600 UV-vis spectrophotometer. Brunauer–Emmett–Teller (BET) measurements were conducted using Quantachrome Nova 1200 with N$_2$ as the adsorbate at liquid nitrogen temperature.

The H$_2$ evolution measurements were carried out using 1 mg of photocatalyst and 10 ml DI water (10% methanol) contained in a quartz vial and illuminated with a 300 W Xe lamp (Excelitas, PE300BFM). The wavelength range and light intensity of the Xe lamp is 300–1100
nm and 100 mW cm$^{-2}$, respectively. The reaction mixture was purged with Ar gas for 15 min prior to measurements. The reaction mixture was syringed drawn (100 μl) to sample the gas composition using gas chromatographer (Shimadzu, GC-2014AT).

For photochromism measurements, the as-prepared samples dispersed in solution or coated on substrates were irradiated with a UV light source (365 nm) with light intensity of 35.3 mW cm$^{-2}$ for various periods of time with water-methanol solution (10 wt%). The reverting process was done by low-temperature heating with various periods of time. The same UV light source was used for photochromic printing, while the solar light source used for photochromic printing is a 300 W Xe lamp (Excelitas, PE300BFM). The wavelength range and light intensity of the Xe lamp is 300–1100 nm and 100 mW cm$^{-2}$, respectively. The high-magnification images were obtained by microscope.
Fig. S1 SEM images of (a) SiO$_2$@TiO$_2$ core-shell nanocomposites and (b) hollow TiO$_2$ nanospheres.

Fig. S2 TEM image of SiO$_2$@TiO$_2$ core-shell nanocomposite with its respective element mapping images.

Fig. S3 XRD spectra of hollow TiO$_2$ nanospheres, SiO$_2$@TiO$_2$ core-shell nanocomposites and SiO$_2$ nanospheres.
Fig. S4 (a) EDX spectrum and (b) TEM image of TiO$_2$/CuO nanocomposite with CuO nanoparticles evenly distributed on TiO$_2$ surface.

Fig. S5 H$_2$ production of P25, SiO$_2$@TiO$_2$ core-shell and hollow TiO$_2$ nanocomposites with 1 wt %, 3 wt %, 5 wt %, 7 wt % and 10 wt% of CuO loading.
Fig. S6 N\textsubscript{2} adsorption–desorption isotherm and the pore size distribution curves (inset) of (a) SiO\textsubscript{2}@TiO\textsubscript{2} core-shell nanocomposites, (b) hollow TiO\textsubscript{2} nanospheres and (c) P25 TiO\textsubscript{2} nanoparticles.

Fig. S7 H\textsubscript{2} production cycling test for hollow TiO\textsubscript{2}/CuO nanocomposites with 5 wt % CuO loading.
Additional simulation results

Section 1: Table for the transmittance

Simulations are conducted to investigate the transmittance of the nano-particles in the matrix. The simulations are conducted by the Finite-difference time-domain (FDTD) simulations with the Lumerical software. In this simulation, the incident wave is set to irradiate from the bottom. The nanoparticle is placed in the water matrix. The refractive index of the TiO$_2$ material is taken from the literature. The refractive index of water is 1.34. The refractive index of SiO$_2$ is set to be 1.48. The boundary condition is set to be perfect absorber. The dimension of the simulation areas is 1 µm$^2$. The transmission is calculated by placing a detector 0.5 µm away from the center of the nanoparticle. The transmittance is measured at the 300 and 350 nm wavelengths respectively. The full solid loading and the 66% solid loading are investigated. For each of the simulation, the SiO$_2$@TiO$_2$ core shell structure with the same solid loading factor is set as the reference group. The transmittance of this system is normalized to be 1. The transmittance of the TiO$_2$ hollow shield structure is normalized compared to the core shell structure at that condition respectively.

<table>
<thead>
<tr>
<th>Wavelength/nm</th>
<th>TiO$_2$ (66% Solid Loading)</th>
<th>TiO$_2$ (100% Solid Loading)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.94</td>
<td>0.98</td>
</tr>
<tr>
<td>350</td>
<td>0.80</td>
<td>0.85</td>
</tr>
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</table>

Table S1: Normalized Transmittance at different conditions

For both the 300 and 350 nm, the hollow TiO$_2$ structure has lower transmittance than the SiO$_2$@TiO$_2$ core shell structure, indicating the better light matter interaction. It should be noted that at the wavelength of 300 nm. The absorption factor (imaginary part of the refractive index) for TiO$_2$ is very large, so most of the light was already absorbed by the TiO$_2$ shell. In this case, the core area does not play as importantly as the case of 350 nm. It should be noted that the number indicate the transmittance difference compared to the SiO$_2$@TiO$_2$ core shell structure. At the 300 nm, the transmittance of the reference group is 28.1%. At the 350 nm, the transmittance of the reference group is 55.1%. So the absolute transmittance of the hollow TiO$_2$ sphere at the 300 nm wavelength is lower than the 350 nm.
Section 2: The explanation of the optical performance

Although the transmittance difference of the individual nano-particle is low, the accumulated effect accounts for the large difference of the optical behavior in the macro-system. One example is given below to explain the absorption curve measured in our experiments:

![Hollow TiO2 nanospheres](image)

**Fig. S8** Mechanism for the accumulated effect contributed from the each of the individual nanospheres.

For each of the nano-particle, assume the transmittance is $T_{\text{effective}}$. In the macro-system, the light transmit through a number of the nano-particle. We assume that number is $n$. Each of this individual nano-particle shall interact with light separately. In this case, the overall transmittance ($T_{\text{overall}}$) will be:

$$T_{\text{overall}} = (T_{\text{effective}})^n$$

This shall account for the absorption curve measured in the experiments.

Section 3: Multiple Ball system

We have also conducted the simulations to study the coupling effect between the neighboring nano-particles. The parameters settings for the material properties are identical as the previous simulations. To simplify the case, we focus on the neighboring effect between two nano-particles, which is the building block for most of the complicated systems. As the hybrid system composed of two nano-particles are asymmetric, we need to study two cases: a) when the co-axis (defined as the axis that connects the center of the two nano-particles) is perpendicular to the incident direction of the light; b) when the co-axis is in parallel to the incident direction of the light. The simulations results for each of these cases are presented below:
Fig. S9 E-field distribution of the 2-ball systems at 300 nm wavelength with 66% solid loading: a) SiO$_2$@TiO$_2$ core-shell structure in the perpendicular direction; b) Hollow TiO$_2$ structure in the perpendicular direction; c) SiO$_2$@TiO$_2$ core-shell structure in the vertical direction; d) Hollow TiO$_2$ structure in the vertical direction;

For the E field map distribution, it can be concluded that the 2-balls systems have the similar effect as the individual nano-particle systems. The hollow TiO$_2$ favors the light matter interaction while the SiO$_2$@TiO$_2$ core-shell structure favors the focusing effect. As the consequence, there exist more enhanced areas (red areas) in the E field distribution map of the hollow TiO$_2$ structure compared to the SiO$_2$@TiO$_2$ core-shell structure. This simulation results double confirms our conclusions discussed in the manuscript.

Calculations of optical properties

The transmitted intensity of different ranges of light (UV: 300 – 400 nm, VIS: 400 – 750 nm, NIR: 750 – 1500 nm) can be obtained by the transmittance spectra and standard solar spectrum using the following formula:

$$I_T = \int F(\lambda)T(\lambda)d\lambda$$

where $F(\lambda)$ and $T(\lambda)$ are the incident photon flux intensity and the transmittance at wavelength $\lambda$.

The transmitted efficiency (TE) of different ranges of light is calculated using the following formula:
\[ TE = \frac{I_T}{I_{\text{total}}} \times 100\% \]

where \( I_{\text{total}} \) is the total light intensity of different ranges of light (UV, visible, and NIR).

The shielding efficiency (SE) of different ranges of light is calculated using the following formula:

\[ SE = 1 - TE \]

<table>
<thead>
<tr>
<th>Type of Film</th>
<th>Transmitted intensity (mW cm(^{-2}))</th>
<th>Transmitted efficiency (TE, %)</th>
<th>Shielding efficiency (SE, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV</td>
<td>Vis</td>
<td>NIR</td>
</tr>
<tr>
<td>P25_Oxd</td>
<td>3.31</td>
<td>38.6</td>
<td>30.2</td>
</tr>
<tr>
<td>P25_Red</td>
<td>3.34</td>
<td>37.8</td>
<td>29.5</td>
</tr>
<tr>
<td>SiO(_2@TiO_2) core-shell_Oxd</td>
<td>2.21</td>
<td>29.8</td>
<td>25.8</td>
</tr>
<tr>
<td>SiO(_2@TiO_2) core-shell_Red</td>
<td>2.12</td>
<td>27.1</td>
<td>24.4</td>
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<tr>
<td>HollowTiO(_2) Oxd</td>
<td>1.90</td>
<td>34.8</td>
<td>29.0</td>
</tr>
<tr>
<td>HollowTiO(_2) Red</td>
<td>1.53</td>
<td>29.3</td>
<td>26.7</td>
</tr>
</tbody>
</table>

Table S2 Summary of Transmitted intensity, transmitted efficiency and shielding efficiency calculated according to the formulae above. The total light intensity from standard solar light: UV (300–400 nm) = 9.16 mW cm\(^{-2}\), Vis (400–750 nm) = 49.0 mW cm\(^{-2}\), and NIR (750–1500 nm) = 36.3 mW cm\(^{-2}\).

Fig. S10 (a) Digital photo of transparent TiO\(_2\)/CuO nanocomposites coated on glass substrate. SEM images of (b) the cross section and (c) top-down view of TiO\(_2\)/CuO film.
Fig. S11 (a) Micro-scale photochromic patterning of TiO$_2$/CuO films using UV lithography with (b) high-magnification images at different spots.

Fig. S12 (a) Transmittance spectra of hollow TiO$_2$/CuO film with various UV light irradiation time, and (b) respective digital photos of the printed words.

Fig. S13 Comparison between photochromic patterning of TiO$_2$/CuO films using (a) UV and (b) solar light lithography.
Fig. S14 digital photos of the printed pattern leaving in ambient condition with normal office lighting (500lx) at various time.

Fig. S15 Transmittance spectra of hollow TiO$_2$/CuO film with various heating temperature of (a) 85°C, (b) 95°C and (c) 105°C with respect to time, and respective digital photos of the printed pattern before and after erasing process (insets).

Fig. S16 The switchable photochromogenic transmittance at 600 nm and 1000 nm for hollow TiO$_2$/CuO nanocomposite coating on glass. 0$^{th}$ to 10$^{th}$ cycles and 10$^{th}$ to 25$^{th}$ cycles are measurements made 6 months apart.
Reference

