Supporting Information

Highly Sensitive and Stable SERS Substrate Using Hybrid Tungsten Dioxide/Carbon Ultrathin Nanowire Beams

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Experimental Section

Synthesis of Carbon Fibres

0.5 g of WO$_2$/C ultrathin nanowire beams was added into 200 mL of H$_2$SO$_4$ solution (10 M). The mixed solution was heated to 60 °C and kept for 5 hours under agitation. Finally, the black products were collected, purified with absolute ethanol and distilled water, and dried in air at 50 °C.

Calculation of EFs

To calculate the EF of the WO$_2$/C ultrathin nanowire beams, the ratio of SERS to normal Raman spectra (NRS) of R6G was determined by using the following calculating formula

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{NRS}/N_{NRS}}$$

(1)

$$N_{SERS} = N_A n S_{irr}/S_{diff}$$

(2)

$$N_{NRS} = d S_{irr} h N_A / M$$

(3)

where $I_{SERS}$ and $I_{NRS}$ refer to the peak intensities of the SERS and NRS, respectively. $N_{SERS}$ and $N_{NRS}$ correspond to the number of probe molecules excited in the SERS and NRS tests. In the SERS measurements, Raman scattering peak, $R_1$ at 612 cm$^{-3}$ was selected for the calculations of the EF. For comparison, the peak intensities of the R6G (1 $\times$ 10$^{-2}$ M, aqueous solution) directly placed on bare glass were detected as NRS data. To decrease the measuring error, the intensities were obtained by continually ran the test procedure at randomly selected 50 points and took the average. $N_{SERS}$ is calculated by formula 2, where $N_A$ refer to the Avogadro's constant, $n$ correspond to the molar quantity of the probe molecule, $S_{irr}$ refer to the irradiation area under the laser beam (5
m in diameter), and \( S_{\text{dif}} \) refer to the diffusion area of the substance to be tested on the substrate. In a typical test, one drop (20 microliter) of the probe solution was dropped onto the SERS substrate, and the probe solution was spread into a circle with a diameter of 4 mm when the solution is completely dry. \( N_{\text{NRS}} \) is determined by the formula 3, where \( d \) is the packing density of R6G molecules in the surface of substrate \((1.4 \times 10^{21} \text{ molecule/cm}^3)\), \( h \) refer to the laser confocal depth \((26 \, \mu\text{m})\), \( M \) correspond to the molecule weight of R6G \((479)\).

**Electronic Structure Calculations**

The density functional theory based calculations are carried out by the Vienna ab initio Simulation Package (VASP), within the projector-augmented-wave approach.\(^{[1-4]}\) And the generalized gradient approximation (GGA) with the function of Perdew and Wang (PW91) was employed for the exchange correlation functional,\(^{[5-6]}\) where the W-5d\(^4\)6s\(^2\) states and the O-2s\(^2\)2p\(^4\) states were treated as valence states. The cutoff energy was chosen at value of 600eV, Brillouin zones (BZ) integrations were carried using Monkhorst-Pack sampling grids\(^{[7]}\) with resolution of \( 2\pi \times 0.2 \, \text{Å}^{-1} \) and \( 2\pi \times 0.1 \, \text{Å}^{-1} \) for structure optimizations and DOS calculations, respectively. The high symmetry path was determined by materials tools.\(^{[8]}\) The atomic positions and lattice constants were optimized using the conjugate gradients (CG) scheme until the force components on each atom were less than 0.02 eV/Å. All the electronic structure calculations were calculated by hybrid functional (HSE06). Both monoclinic phase WO\(_3\) (space group P2\(_1\)/c) and WO\(_2\) (space group P2\(_1\)/c) were modeled in our calculations and the optimized lattice parameters were \( a=5.59, b=4.94, c=5.71 \, \text{Å}, \alpha=\gamma=90^\circ, \beta=120.48^\circ \) for
WO$_2$ and $a = 7.52$, $b = 7.71$, $c = 7.85$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 90.18^\circ$ for WO$_3$, which agree well with the previous experimental and calculation results.$^{[1,9-10]}$

**Reference**


Figure S1. Morphology, structure, and crystal phase characterizations of the $\text{W}_{18}\text{O}_{49}$/PVP ultrathin nanowire beams: (a) TEM image; (b) HRTEM image; (c) XRD pattern.
Figure S2. The WO$_2$/C UNBs can of g-scale by this simple reaction route.
Figure S3. XRD pattern of the as-synthesized WO$_2$/C ultrathin nanowire beams by heating W$_{18}$O$_{49}$/PVP ultrathin nanowire beams in N$_2$.

Figure S4. Raman spectrum of the WO$_2$/C ultrathin nanowire beams. This spectrum clearly demonstrates that the WO$_2$ nanowires are highly crystalline, while the carbon layers are amorphous carbon.
Figure S5. Additional HRTEM images of the obtained WO$_2$/C ultrathin nanowire beams, which can be seen that the WO$_2$ nanowires are highly crystalline and the carbon layers are amorphous.
**Figure S6.** EDS component analysis of the WO$_2$/C ultrathin nanowire beams.

![EDS Component Analysis]

**Figure S7.** N$_2$ adsorption/desorption isotherms of the as-synthesized WO$_2$/C ultrathin nanowire beams, which shows the WO$_2$/C ultrathin nanowire beams have a large specific surface area of 101.5 m$^2$ g$^{-1}$.

![N$_2$ Adsorption/Desorption Isotherms]
Figure S8. XPS of the WO$_2$/C ultrathin nanowire beams. In the spectra, the peaks located at 32.9 and 34.8 eV can be indexed into the W$^{4+}$ and W$^{5+}$ respectively, while the peaks located at 35.8 and 37.9 eV can be indexed into W$^{6+}$. These W$^{6+}$ and W$^{5+}$ atoms are derived from oxidized W atoms on the surface of the WO$_2$ nanowires. Because the diameter of the nanowires is only about 1 nm, and the detection depth of XPS is up to 2-3 nm, the ratios of W$^{6+}$ and W$^{5+}$ atoms is relatively high.
**Figure S9.** Characterization of the as-synthesized WO$_3$ obtained by oxidizing the WO$_2$/C ultrathin nanowire beams at 600 °C in air. (a-b) SEM image and TEM images of the prepared chain-like WO$_3$ nanowires. (c) XRD pattern of the sample can be indexed with monoclinic WO$_3$ (JCPDS No.: 43-1035). (d) XPS spectrum of the WO$_3$ chain-like WO$_3$ nanowires.
Figure S10. The structure evolution from WO$_2$/C to WO$_3$ can be reflected by the Raman spectra changes.
Figure S11. The UV-Vis spectra of the WO$_2$/C ultrathin nanowire beams, commercial WO$_2$ powders (a), and the carbon fibres obtained by removing the WO$_2$ from the WO$_2$/C ultrathin nanowire beams (b). Inset in Figure S11a: SEM image of the commercial WO$_2$ powders; Inset in Figure S11b: SEM image of the carbon fibres.
Figure S12. photocurrent spectra of the WO$_2$/C ultrathin nanowire beams and the chain-like WO$_3$ nanowires.
Figure S13. (a) Differential thermal analysis (DTA) of the WO$_2$/C UNBs. (b) DTA of the commercial WO$_2$ powders.

Note: because of the strong interference of carbon in the analysis process of the WO$_2$/C UNBs, we chose commercial pure WO$_2$ as the reference sample. In Figure S16a, it is evident that there are fluctuations in the two regions (I and II) of the weightless trend line. Compared with the Figure S16b, it can be found that the two fluctuation regions shown in Figure S16a correspond to the oxidation threshold temperature and the fast transition temperature of pure WO$_2$. Combined with the two figures, it can reasonably conclude that the starting temperature of WO$_2$ ultrafine nanowires transformed to WO$_3$ is about 400 °C. The weight gain during the transition (from WO$_2$ to WO$_3$) is mostly neutralized by the loss of carbon contained in the WO$_2$/C UNBs.
Figure S14. Comparison of oxidation resistance of WO$_2$/C ultrathin nanowire beams and W$_{18}$O$_{49}$ nanowires: these results clearly demonstrate that WO$_2$/C has much higher antioxidant activity than W$_{18}$O$_{49}$. 
Figure S15. The substrate preparation and sample test process.
Figure S16. Relative standard deviation (RSD) of statistically obtained from more WO$_2$/C substrates by using the intensities of $R_1$, $R_2$, $R_3$, and $R_4$ at 10$^{-4}$ M. For each concentration, a total of 40 intensity values were collected from one WO$_2$/C substrate.
Figure S17. Relative standard deviation (RSD) of statistically obtained from more WO$_2$/C substrates by using the intensities of $R_1$, $R_2$, $R_3$, and $R_4$ at $10^{-5}$ M. For each concentration, a total of 40 intensity values were collected from one WO$_2$/C substrate.
Figure S18. Relative standard deviation (RSD) of statistically obtained from more WO$_2$/C substrates by using the intensities of R$_1$, R$_2$, R$_3$, and R$_4$ at $10^{-6}$ M. For each concentration, a total of 40 intensity values were collected from one WO$_2$/C substrate.
Figure S19. Relative standard deviation (RSD) of statistically obtained from more WO$_2$/C substrates by using the intensities of R$_1$, R$_2$, R$_3$, and R$_4$ at $10^{-7}$ M. For each concentration, a total of 40 intensity values were collected from one WO$_2$/C substrate.
Figure S20. The PDOS of W atoms in WO$_2$ nanowires grown along the [100] directions and bulk crystal. Obviously, WO$_2$ nanowires grown along the [100] direction have more free electrons compared with bulk WO$_2$. 
Figure S21. UV-Vis absorption spectra for R6G-modified WO\textsubscript{2}/C compared with neat WO\textsubscript{2}/C and R6G.
**Table S1:** Some of the Previously Reported EFs for Semiconductor Substrates

<table>
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<tr>
<th>Material</th>
<th>Probe molecule</th>
<th>EF</th>
<th>Excited wavelength (nm)</th>
<th>Author</th>
</tr>
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<tr>
<td>core–shell TiO$_2$–Ag</td>
<td>4-Mpy</td>
<td>6.5×10$^5$</td>
<td>514</td>
<td>X. X. Zou et al.[1]</td>
</tr>
<tr>
<td>TiO$_2$ photonic microarray</td>
<td>MB</td>
<td>2×10$^4$</td>
<td>532</td>
<td>D. Qi et al.[2]</td>
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<tr>
<td>CdTe nanoparticles</td>
<td>4-Mpy</td>
<td>10$^4$</td>
<td>514.5</td>
<td>Y. F. Wang et al.[3]</td>
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<tr>
<td>W$<em>{18}$O$</em>{49}$ nanowires</td>
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<td>532.8</td>
<td>S. Cong et al.[4]</td>
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<tr>
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<td>514.5</td>
<td>Y. Wang et al.[5]</td>
</tr>
<tr>
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<td>Y. F. Wang et al.[6]</td>
</tr>
<tr>
<td>Cu$_2$O superstructure</td>
<td>R6G</td>
<td>8×10$^5$</td>
<td>674</td>
<td>J. Lin et al.[7]</td>
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<td>Fe$_3$O$_5$ nanoparticles</td>
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<td>X. Q. Fu et al.[8]</td>
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<tr>
<td>Au–CdSe nanowires</td>
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<td>Colloidal ZnO</td>
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<td>H. Wen et al.[10]</td>
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<td>3.4×10$^3$</td>
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<td>Mehmet Yilmaz et al.[11]</td>
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<td>TiO$_2$</td>
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<td>488</td>
<td>Teguh et. al.[12]</td>
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<td>InAs/GaAs quantum dots</td>
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<td>Quagliano et. al.[14]</td>
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<td>H-Si nanowire</td>
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<td>532</td>
<td>Wang et. al.[15]</td>
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<td>Graphene</td>
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<td>2-17</td>
<td>632.8</td>
<td>Ling et. al.[16]</td>
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\begin{table}[h]
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\begin{tabular}{|c|c|c|c|}
\hline
         &      &     &                        \\
\hline
GaP     & CuPc & 700 & 514.5                  \\
\hline
WO\textsubscript{2} & R6G & 1.3×10\textsuperscript{6} & 532                    \\
\hline
\end{tabular}
\caption{Summary of experimental data.}
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