Electronic Supplementary Information

Ag-nanoparticles-decorated ZnO Porous-nanosheets  
Grafted on Carbon Fiber Cloth as Effective SERS Substrates

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The Supporting Information includes:

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Part S1. Characterization of ZnO-seeds@CFC.

Fig. S1. (a) Typical SEM images of ZnO-seeds@CFC; (b) Energy dispersive X-ray spectrum (EDS) performed on the ZnO-seeds@CFC.

Part S2. Lattice-resolved TEM image of ZnO-mesoporous-NS.

Fig. S2. Lattice-resolved TEM image of ZnO-mesoporous-NS.
Part S3. XRD patterns of ZnO-mesoporous-NSs@CFC and bare CFC.

![XRD patterns](image1)

**Fig. S3.** XRD patterns of I: ZnO-mesoporous-NSs@CFC; II: bare CFC.

Part S4. Adsorption capacity of different substrates.

As ZnO seeds have completely covered on the surface of CFC, it indeed formed a solid and nonporous ZnO film on the surface of CFC. Therefore ZnO-seeds@CFC were used as control experimental examples to examine the impact of porous structure. The same size of CFC, ZnO-seeds@CFC, ZnO-mesoporous-NSs@CFC substrates were put into same volume of $10^{-5}$ M R6G solution for 12 hours respectively and then their remnant concentration were examined through UV-vis spectroscopy. Fig. S4 shows that the absorbance of the R6G solution decreased significantly with ZnO-mesoporous-NSs@CFC dipped inside, indicating that ZnO-NSs@CFC with porous structure have the highest adsorption capacity.

**Fig. S4.** UV-vis spectra of I: original $10^{-5}$ M R6G solution; II: R6G solution with CFC; III: R6G solution with ZnO-seeds@CFC; IV: R6G solution with ZnO-mesoporous-NSs@CFC.
Part S5. The photos of each stage.

Fig. S5. The photo of (a) black CFC; (b) light-blue ZnO-seeds@CFC; (c) white ZnO-mesoporous-NSs@CFC; (d) gray Ag-NPs@ZnO-mesoporous-NSs@CFC.

Part S6. EDS characterization of Ag-NPs@ZnO-mesoporous-NSs@CFC.

Fig. S6. EDS performed on the optimal Ag-NPs@ZnO-mesoporous-NSs@CFC.
Part S7. Lattice-resolved TEM image of Ag-NPs@ZnO-mesoporous-NS.

Fig. S7. Lattice-resolved TEM image of Ag-NPs@ZnO-mesoporous-NS.

Part S8. UV-vis spectra.

Fig. S8. UV-vis spectra of I: The difference spectrum of Ag-NPs@ZnO-mesoporous-NSs@CFC and ZnO-mesoporous-NSs@CFC; II: Ag-NPs@ZnO-mesoporous-NSs@CFC; III: ZnO-mesoporous-NSs@CFC.
**Part S9. The enhancement contribution of ZnO.**

To evaluate the existence of chemical enhancements from ZnO, the SERS spectra of p-ATP with different concentrations adsorbed on the ZnO-mesoporous-NSs@CFC are shown in Fig. S9. For 10^{-3} M p-ATP, four fingerprint peaks of p-ATP at 1085 cm^{-1}, 1143 cm^{-1}, 1456 cm^{-1} and 1586 cm^{-1} can be clear seen in Fig. S9(a) curve I. While for 10^{-4} M p-ATP, the fingerprint peaks of p-ATP can still be distinguished, but not so obvious, as shown in Fig. S9(a) curve II. So we further design some indirect experiments to examine its existence according to a previous work\(^1\). In detail, CFC, ZnO-seeds@CFC, and Zn\(_4\)(CO\(_3\))(OH)\(_6\)·H\(_2\)O-NSs@CFC with the same Ag sputtering durations were used as experimental examples. Their SERS-activity to 10^{-4} M p-ATP are shown in Fig. S9(b). It is clear that Raman signal intensities of p-ATP adsorbed on the surface of Ag-NPs@ZnO-mesoporous-NSs@CFC are the largest. Although Raman signal of 10^{-4} M p-ATP adsorbed on pure ZnO-mesoporous-NSs@CFC is weak, as the Zn\(_4\)(CO\(_3\))(OH)\(_6\)·H\(_2\)O-NSs have similar sheet-like structures with that of ZnO-mesoporous-NSs, the larger SERS-activity of Ag-NPs@ZnO-mesoporous-NSs@CFC than that of Ag-NPs@Zn\(_4\)(CO\(_3\))(OH)\(_6\)·H\(_2\)O-NSs@CFC should be related to the contribution of ZnO.

**Fig. S9.** (a) SERS spectra of p-ATP with different concentrations adsorbed on the ZnO-mesoporous-NSs@CFC. I: 10^{-3} M p-ATP; II 10^{-4} M p-ATP. (b) SERS spectra of 10^{-4} M p-ATP by using I: Ag-NPs@ZnO-mesoporous-NSs@CFC; II: Ag-NPs@Zn\(_4\)(CO\(_3\))(OH)\(_6\)·H\(_2\)O-NSs@CFC; III: Ag-NPs@ZnO-seeds@CFC; IV: Ag-NPs@CFC.
Part S10. Calculation of the average enhancement factor (EF).

The EF can be calculated by

\[ EF = \frac{I_{\text{SERS}} / N_{\text{SERS}}}{I_{\text{Nor}} / N_{\text{Nor}}} \]

Where \( I_{\text{SERS}} \) and \( I_{\text{Nor}} \) represent the intensity of the 1600 cm\(^{-1}\) band in the Raman spectrum of p-ATP and normal Raman spectrum, under the same experimental conditions (laser wavelength, laser power, microscope objective/lenses, accumulation time), respectively. \( N_{\text{SERS}} \) and \( N_{\text{Nor}} \) represent the corresponding number of molecules in the focused incident laser spot. Herein, for SERS experiment, a certain volume \( (V_{\text{SERS}}) \) and concentration \( (C_{\text{SERS}}) \) p-ATP ethanol solution was dispersed to an area of \( S_{\text{SERS}} \) at the as-fabricated substrate. Similarly, for normal Raman experiment, a certain volume \( (V_{\text{Nor}}) \) and concentration \( (C_{\text{Nor}}) \) p-ATP ethanol solution was dispersed to an area of \( S_{\text{Nor}} \) at a clean glass substrate. Both the substrates were dried in air. Thus the foregoing equation can be rewritten as follows:

\[ EF = \frac{I_{\text{SERS}}}{I_{\text{Nor}}} \cdot \frac{S_{\text{SERS}} V_{\text{Nor}} C_{\text{Nor}}}{S_{\text{Nor}} V_{\text{SERS}} C_{\text{SERS}}} \]

In our experiments, 70 µL 10\(^{-3}\) M p-ATP ethanol solution was dispersed to an area of about 50 mm\(^2\) on a glass substrate. 40 µL 10\(^{-9}\) M p-ATP ethanol solution was dispersed to an area of about 60 mm\(^2\) for the Ag-NPs@ZnO-mesoporous-NSs@CFC and 40 µL 10\(^{-7}\) M p-ATP ethanol solution was dispersed to an area of about 70 mm\(^2\) for the Ag-NPs@ZnO-seeds@CFC. Fig. S10(a) and S10(b) show the Raman spectrum of p-ATP from the above-mentioned substrates. For the band at 1600 cm\(^{-1}\), \( I_{\text{SERS}}/I_{\text{Nor}} \) is about 2.66 and 1.66. Hence the average enhancement factor for Ag-
NPs@ZnO-mesoporous-NSs@CFC and Ag-NPs@ZnO-seeds@CFC are calculated to be $5.58 \times 10^6$ and $4.06 \times 10^4$.

**Fig. S10.** (a) I: Raman spectrum of p-ATP obtained using dried 70 µL $10^{-3}$ M PATP ethanol solution dispersed on 50 mm$^2$ glass substrate. II: SERS spectrum of 40 µL $10^{-9}$ M p-ATP ethanol solution dispersed on 60 mm$^2$ Ag-NPs@ZnO-mesoporous-NSs@CFC (b) I: Raman spectrum of p-ATP obtained using dried 70 µL $10^{-3}$ M PATP ethanol solution dispersed on 50 mm$^2$ glass substrate. II: SERS spectrum of 40 µL $10^{-7}$ M p-ATP ethanol solution dispersed on 70 mm$^2$ Ag-NPs@ZnO-seeds@CFC.

**Part S11.** SERS-signal uniformity of Ag-NPs@ZnO-mesoporous-NSs@CFC.

**Fig. S11.** SERS spectra of R6G obtained from ten random carbon fibers of as-prepared optimal SERS substrate. Data acquisition time 5 s, [R6G] = $1.0 \times 10^{-7}$ M.
Part S12. Raman spectrum of CFC.

Fig. S12. Raman spectrum of CFC.

References