Electronic Supplementary Information

Hexagonally arranged arrays of urchin-like Ag-nanoparticles decorated ZnO-nanorods grafted on the PAN-nanopillars as surface-enhanced Raman scattering substrates

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Part S1: Fig. S1 to S9

Fig. S1 (a-c) SEM images of the Si mold with ordered nanohole arrays; (d-f) SEM images of as-fabricated PAN-nanopillar arrays.
Fig. S2 A photograph of ZnO-nanorods grafted on PAN-nanopillar array film fixed on a piece of glass.

Fig. S3 (a-h) SEM images of the ZnO-nanorods grafted on PAN-nanopillar arrays with different electrodeposition durations, a-b) 30 min; c-d) 60 min; e-f) 90 min; g-h) 120 min.
Fig. S4 SEM images of Ag-NPs sputtered PAN-nanopillar arrays without ZnO nanorods and substrate of Ag-NPs sputtered flat PAN film without nanostructures.

Fig. S5 Raman spectra of R6g obtained from the 30 random points on the substrate shown in Fig. 4g, exposure time 3s. f) The intensity of the peaks at 612 cm$^{-1}$ from random 30 spots on the substrate shown in Fig. 4g.

Part S2: Estimation of enhancement factor

The enhancement factor (EF) was calculated using the reported protocol. The EF can be calculated by:
\[
EF = \frac{I_{\text{SERS}} N_{\text{Ref}}}{I_{\text{Ref}} N_{\text{SERS}}}
\]

Where \(N_{\text{SERS}}\) and \(N_{\text{Ref}}\) are the number of molecules absorbed on the Ag-NPs@ZnO-nanorod/PAN-nanopillar arrays and on the flat silicon wafer, respectively. \(I_{\text{SERS}}\) and \(I_{\text{Ref}}\) correspond to SERS signal and the un-enhanced normal signals intensities, respectively. Herein, 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 Ag-NPs@ZnO-nanorod/PAN-nanopillar array substrate. For non-SERS Raman spectra, a certain volume \(V_{\text{Ref}}\) and concentration \(C_{\text{Ref}}\) p-ATP ethanol solution was dispersed to an area of \(S_{\text{Ref}}\) at a clean silicon wafer. Both the substrates were dried in the air. Considering the area of laser spot is the same, the foregoing equation thus becomes:

\[
EF = \frac{I_{\text{SERS}}}{I_{\text{Ref}}} \cdot \frac{C_{\text{Ref}} V_{\text{Ref}}}{C_{\text{SERS}} V_{\text{SERS}}} \cdot \frac{S_{\text{SERS}}}{S_{\text{Ref}}}
\]

In our experiment, 1 \(\mu\)L of \(1\times10^{-9}\) M p-ATP ethanol solution was dispersed to an area of 78.5 mm\(^2\) for the optimal Ag-NPs@ZnO-nanorod/PAN-nanopillar array substrate and 1 \(\mu\)L of \(1\times10^{-3}\) M p-ATP ethanol solution was dispersed to an area of 30 mm\(^2\) for the silicon wafer. For the band at 1078 cm\(^{-1}\), \(I_{\text{SERS}}/I_{\text{Ref}}\) was \(\frac{1773}{133}\) Therefore average enhancement factor for the band at 1078 cm\(^{-1}\) is calculated to be \(3.5\times10^7\).

**Figure for estimation of enhancement factor:**

(a) SERS spectrum of 1 \(\mu\)L \(10^{-9}\) M p-ATP ethanol solution dispersed on 78.5 mm\(^2\) optimal Ag-NPs@ZnO-nanorod/PAN-nanopillar arrays. (b) Raman spectrum of p-ATP obtained by dispersing 1 \(\mu\)L \(10^{-3}\) M p-ATP ethanol solution on 30 mm\(^2\) Si wafer. The exposure time was 30 s.