Figure S1. XRD patterns of three different substrates.
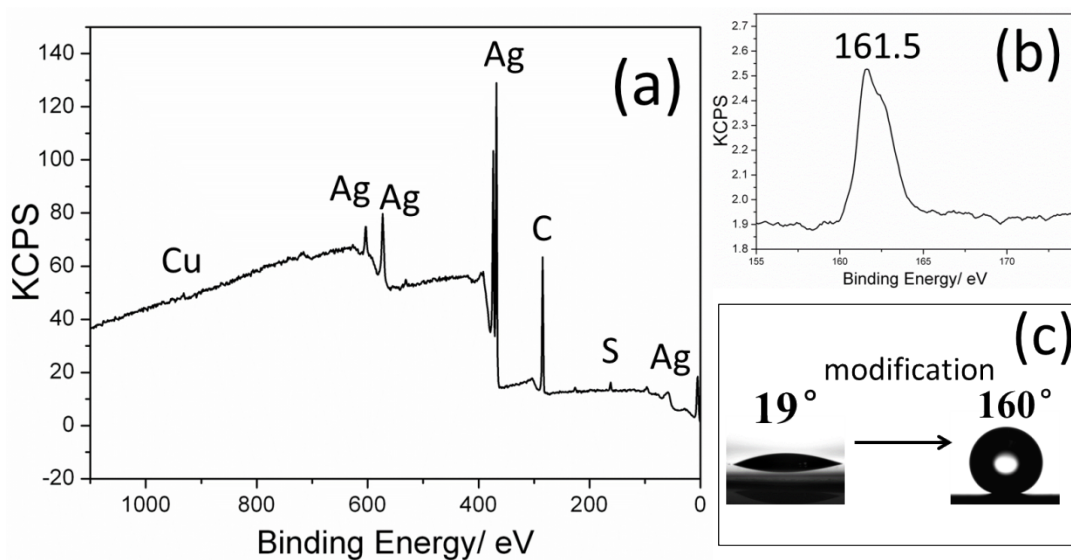

Figure S2. XPS spectra after surface modification. (a) survey spectra; (b) XPS S 2p spectra. (c) Shapes of water droplets (4 μL) on MN surface before and after modification.

The peak located in 161.5 eV is attributed to the S of the n- hexadecanethiol (S1 2b). After modification, the products' surface wettability changed from superhydrophilic to superhydrophobic (Figure 2c).

Two classic states are used to depict the contact condition between the water drop

and the superhydrophobic surface. One is the Wenzel state, based on which the water drop is stick to the surface and could hardly roll off. So we suggest the MN substrate contact condition to be the Cassie state, which assumes that air pockets are entrapped inside the rough grooves between the microballs, as well as the air sheets entrapped among the nanosheets underneath the liquid, leading to a heterogeneous interface. The contact model is illustrated in Fig. 5. The relationship between the water on a smooth surface and a rough surface composed of a solid and air is depicted in equation 1, which is proposed by Cassie[28].

$$\cos\theta r = f_1 \cos\theta - f_2 \qquad (1)$$

Here f1 is the fraction of the solid surface in contact with water, and f_2 is the fraction of air in contact with water, θr and θ are the CAs on the rough and smooth surface, respectively. Since we already know that f1+f2=1, θr =160° and θ = 116 °, f_2 was calculated to be about 0.91. The high fraction of air pocket on the rough surface is responsible for the superhydrophobic property.
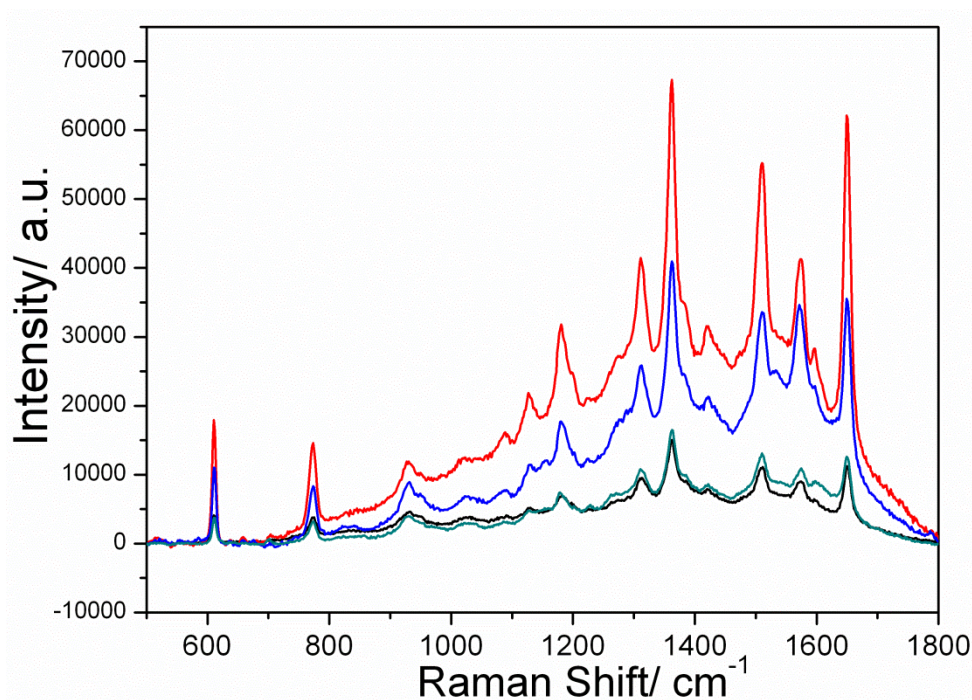

Figure S3. Raman spectra collected from five different points by dropping 25μL 10^{-6} R6G on 1 cm^2 NP substrate.
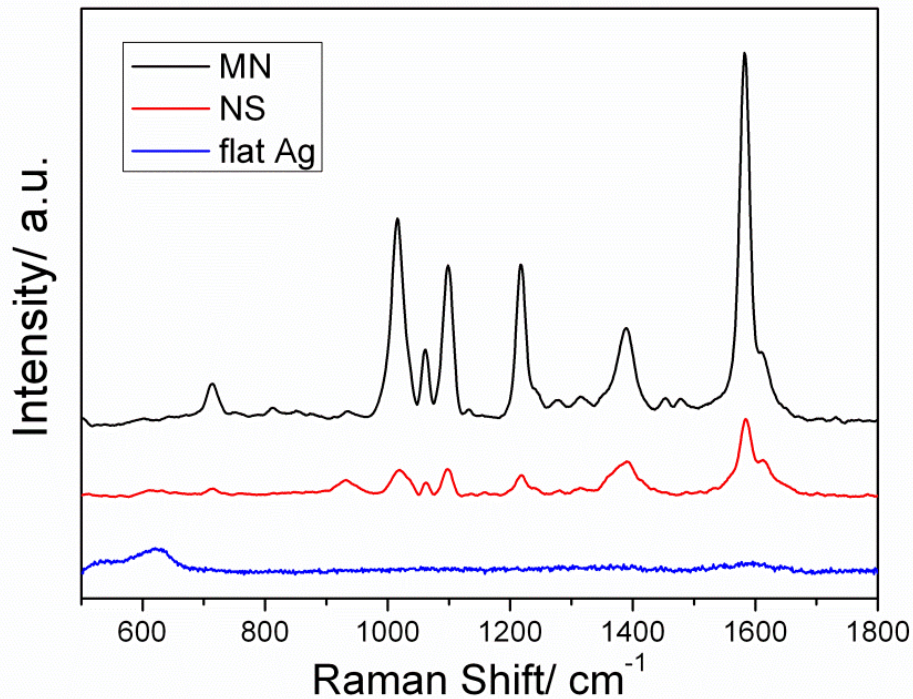
Figure S4. SERS spectra of 1μM 4-Mpy absorbed on different substrates: (a) MN sbustrate; (b) NS substrate; (c) flat silver.

25μL 1μM 4-Mpy ethanol solution was drop-coated onto these substrates and dried in air to collect SERS spectrum. It is believed that the 4-Mpy may be adsorbed on silver surface by S atom.[34] The SERS spectra of 4-Mpy on MN substrate in Figure 6a clearly show intrinsic peaks of 4-Mpy, such as the peaks located at 1586, 1221,1102 and 710 cm^{-1}.[34-35]The most prominent peak around 1586 cm^{-1} is attributed to the C-C ring breathing mode. The peak at 1221 cm-1 is associated with C-O stretching vibrations. The peak at 1102 cm^{-1} is assigned to the C-N stretching vibrations. [35] In Figure 7, curve a and b represents Ag MN and NSs respectively. Compared with curve c, the particular morphology of NS and MN can both amplify the Raman signal of 4-Mpy. Raman enhancement of the Ag MNs is better than Ag NSs. In particular, the Ag NSs exhibits quite weak Raman peak, which would probably due to its lack of hot spots.
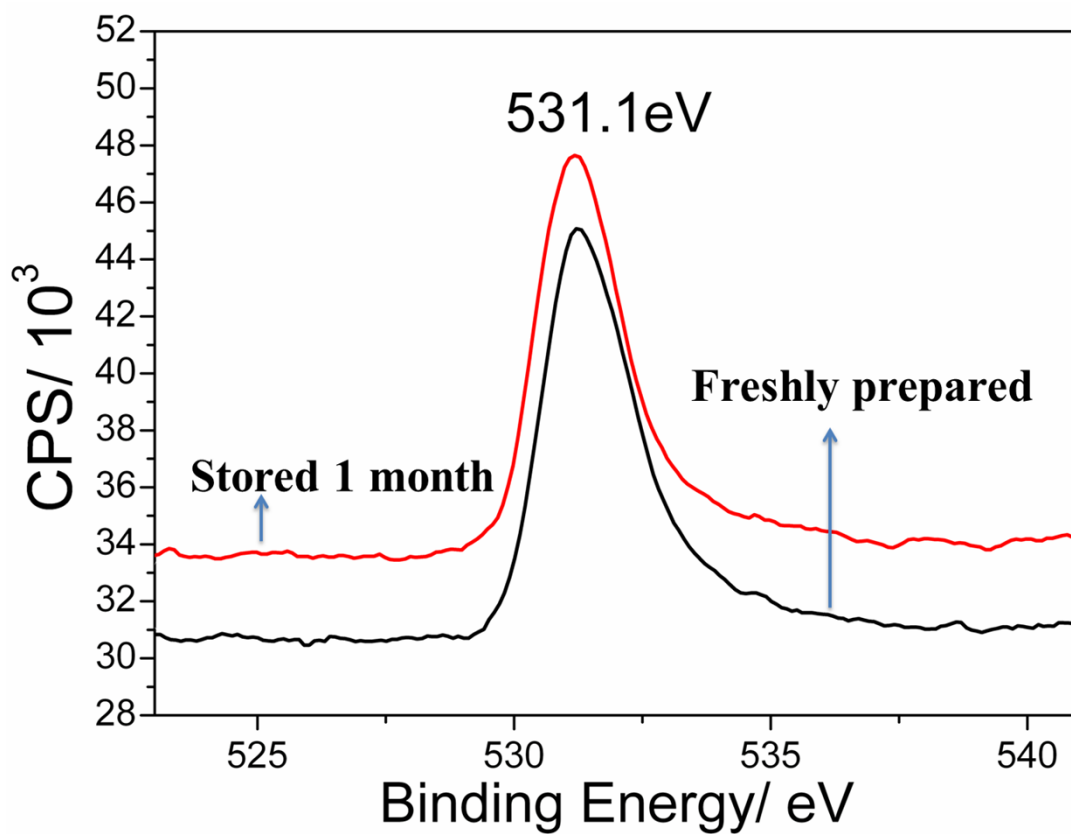
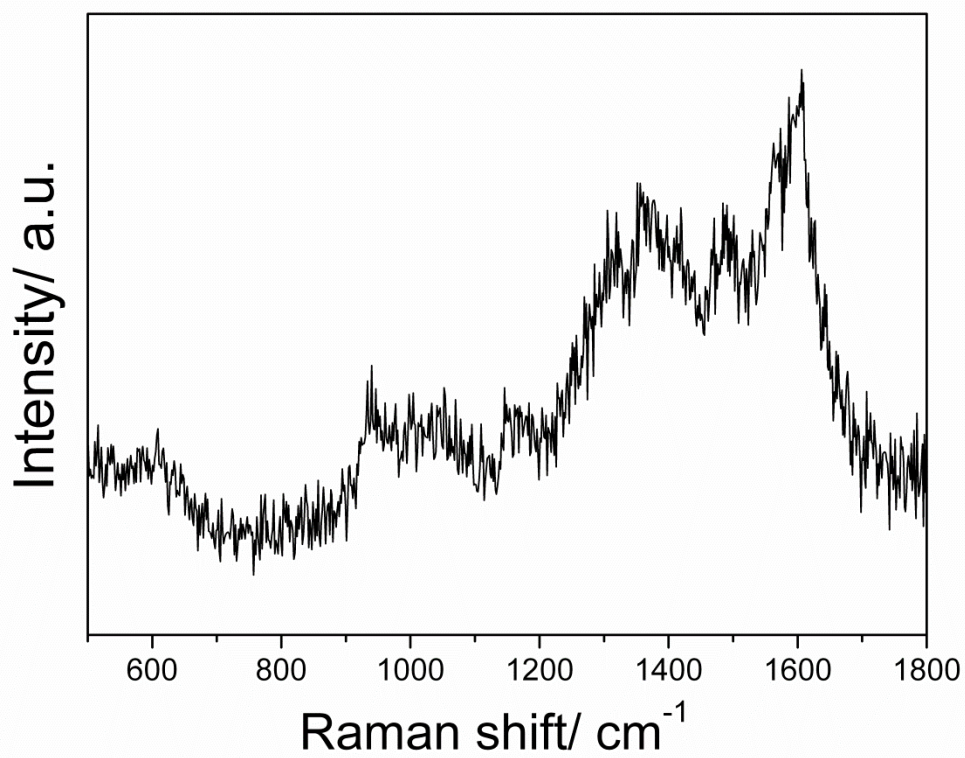**Figure S5.** XPS O 1s spectra of the MN surface before and after 1 month's storage.

Figure S6. SERS spectra of 4μL 10^{-12} R6G absorbed on the freshly prepared MN substrate.
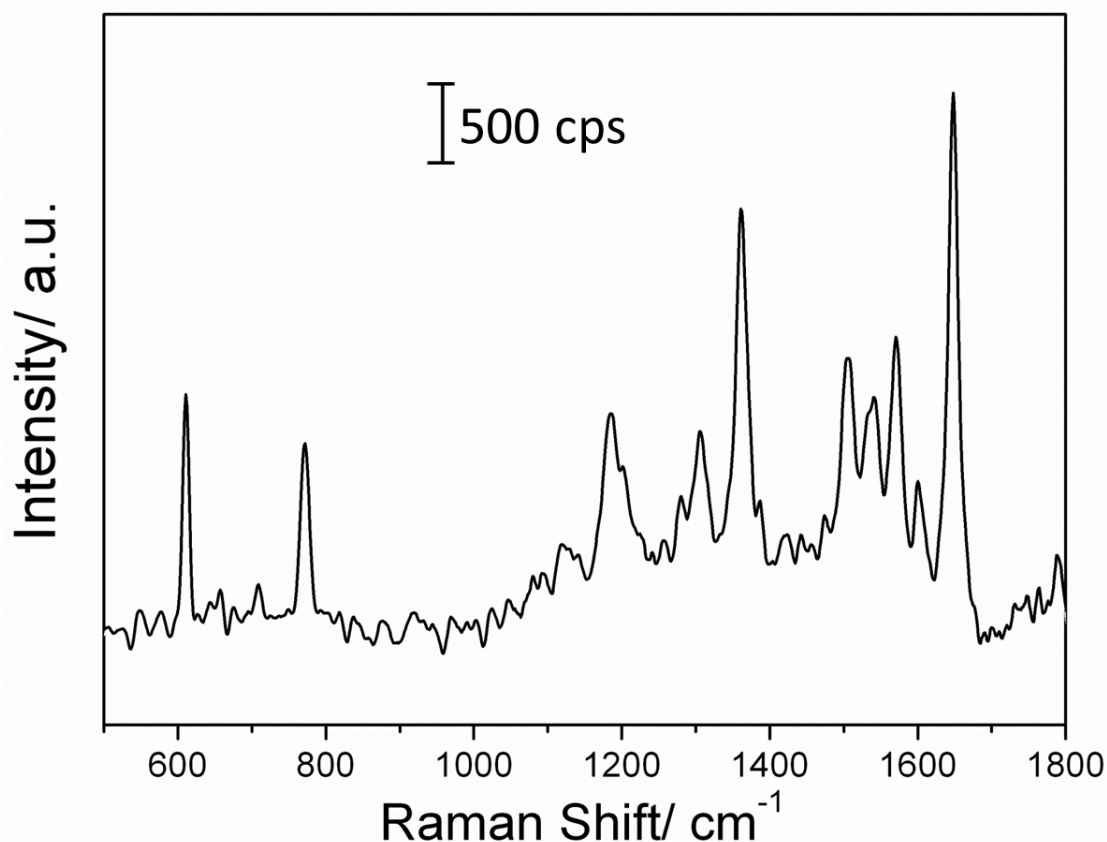

Figure S7. Raman spectra of the solid R6G.

The 1650cm^{-1} peak was employed to estimate the enhancement factor (EF) of the MN substrate before and after oxidation.

The EF can be calculated by the following equation:

$$EF = (I_{SERS}/I_{bulk})(N_{bulk}/N_{SERS})$$

N_{bulk} is the molecule number of the solid R6G in the laser illumination volume. In our experiment, the laser spot of 1 μm diameter and the penetration depth ($\sim$2 μm) of the focused laser beam are used. Taking the density of the solid R6G (0.99 g/cm3) into account, N_{bulk} was calculated to be about 1.97×10^9 within the illuminated laser light. The oxidized sample has a contact area of 0.503 mm^2 after a month's storage. So the total number of surface adsorbed molecules (N_{SERS}) within the illuminated laser spot can then be calculated.

$$N_{SERS}= N_A \times 0.25\pi\mu m^2 \times (4\mu L \times 10^{-12}M)/(0.503mm^2)=3.8$$

The Intensity of the normal Raman spectra (I_{bulk}) of solid R6G is 3349 counts (S4). The 1560 cm^{-1} peak intensities in the SERS spectra (I_{SERS}) were measured to be 865 counts Thus, the EF of the MN substrate can be calculated to be 4.57×10^{10} at 514nm excitation. Thus, we can calculated the EF=1.4×10^8.
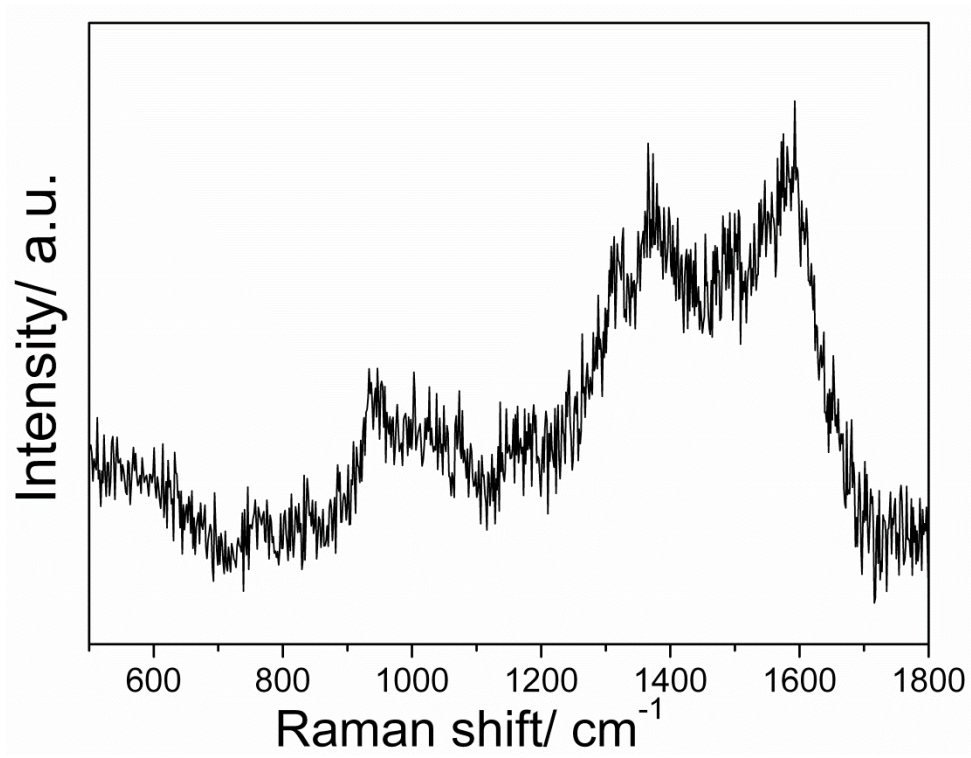
Figure S8. SERS spectra obtained on the surface of the oxidized MN substrate after rinsing by deionized water.