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Supporting Information

Designed 3D heterostructure by 0D/1D/2D hierarchy for low-frequency microwave absorption in the S-band

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Experimental

Synthesis of ZIF-67

Typically, 6 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 24 mmol 2-methylimidazole were dissolved in 50 mL methanol, respectively. Secondly, the 2-methylimidazole solution was quickly added to the Co^{2+} solution, and the solution was stirred for 10 minutes. Thirdly, the above mixture was aged at 20°C for 24h. Finally, the precipitate was washed three times by absolute ethanol, and dried under vacuum at 60°C for 12h.

Synthesis of Co-Ni LDH

Firstly, 80 mg of as-prepared ZIF-67 was dissolved in methanol solution (80 mL). Herein, 160 mg $Ni(NO_3)_2 \cdot 6H_2O$ was contained in methanol solution. Secondly, the solution was continuously stirred for 1h at room temperature. Finally, the product was collected by centrifugation and washed, and dried under vacuum at 60°C for 12 h.

Synthesis of CoNi/N-CNT

Representatively, 100 mg Co-Ni LDH and 1.0 g dicyandiamide (DCTA) were placed in two separate ceramic boats with DCDA at the upstream side of the furnace in a N_2 atmosphere. Then, the boat was kept at 430°C for 8 h in the first stage, and then continue maintained at 700°C for another 2h at a heating rate of 5°C/min.

Synthesis of $Ti_3C_2T_x$ MXene

Typically, 2g LiF was added to 40 mL of 9M HCl solution under stirring for 2h at 40°C. Secondly, 1g Ti_3AlC_2 was slowly added to the above solution. Thirdly, the mixed solution was stirred at 40°C for 32h. Fourthly, the precipitate after the reaction was collected by centrifugation and washed with deionized water until the pH=6 or so.

Fifthly, the mixed solution was sonicated for 1.5h in an ultrasonic instrument with ice packs. Then, the above solution was centrifuged at 3500 rpm for 30 min. Finally, the product was collected by suction filtration and freeze-dried.

Synthesis of $Ti_3C_2T_x$ MXene/ CoNi/N-CNT 3D superstructure nanocomposites

Firstly, configure the MXene aqueous solution. Specifically, 40 mg MXene was dissolved in deionized water (80 mL). Secondly, the MXene aqueous solution was sonicated for 30 minutes and stirred for 15 minutes, respectively. Thirdly, 80 mg CoNi/N-CNT were added to the CTAB solution (1 mg mL^{-1}) and further immersed in MXene solution. After this, the mixed solution were sonicated and stirred for 30 and 15 min, respectively. Importantly, the whole process is carried out in N_2 atmosphere. Finally, the product is obtained by suction filtration and freeze-dried.

Characterization

The phase of the sample was analyzed by XRD (Bruker D8 Advance, Germany) at 5-80°. Raman spectra were obtained using a Raman spectrometer (LabRAM HR Evolution, HORIBA JobinYvon, France) at room temperature using the 532 nm line as the excitation source. XPS measurements were carried out on an ESCALAB 250Xi spectrometer (Thermo Scientific, USA) equipped with a pass energy of 30 eV with a power of 100 W (10 kV and 10 mA). The microstructure was observed and analyzed by FESEM (FEI Quanta 400Feg, USA), TEM and HRTEM (JEM 2100F, Japan). The adsorption-desorption isotherm is obtained by the specific surface area analyzer (Micromeritics ASAP 2460, USA). Magnetization was measured by using a vibrating sample magnetometer (Quantum Design Lakeshore7404, USA) at room temperature.

The Zeta-potentials in deionized water of the samples were measured with a Malvern zeta analyzer (Zetasizer Nano, Malvern Instrument, UK).

Electromagnetic parameters

The absorption parameters of the sample were obtained by the network analyzer (AV3672B-S, China) at the frequency (2-18 GHz). The sample preparation is divided into three steps. First, evenly mix the sample with molten paraffin. To obtain the samples for microwave measurement, the powders were uniformly mixed with molten paraffin, with a paraffin-powder mass ratio of 7:3. Then, natural curing. Finally, the mixtures were pressed into a cylindrical shape with a mold, with an inner diameter of 3.04 mm, an outer diameter of 7 mm and thicknesses of 2-3 mm.

Results and Discussion

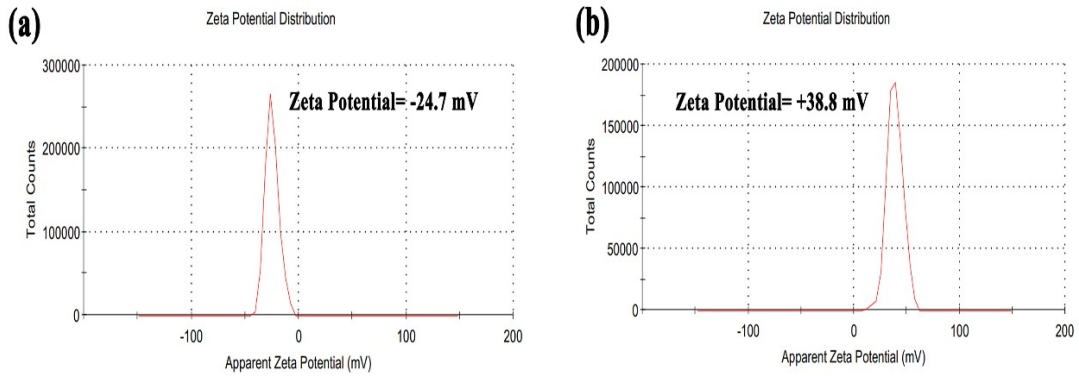

Fig. S1. Zeta potential of MXene aqueous solution (a) and (b) CoNi/N-CNTs modified by CTAB.

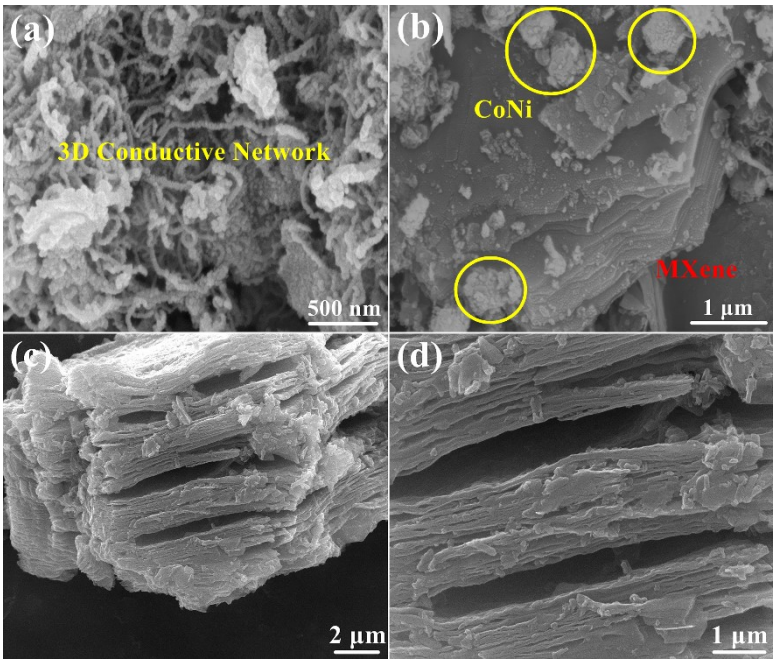

Fig. S2. FESEM images with different magnifications of samples: (a-b) S1 and (c-d) $Ti_3C_2T_x$.

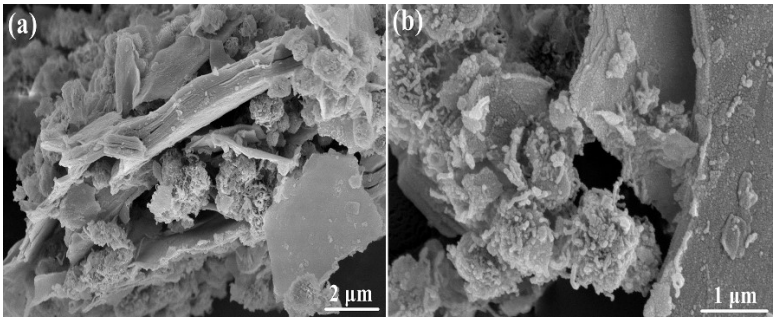

Fig. S3. FESEM images with different magnifications of samples: (a-b) S2 and (c-d) S3.

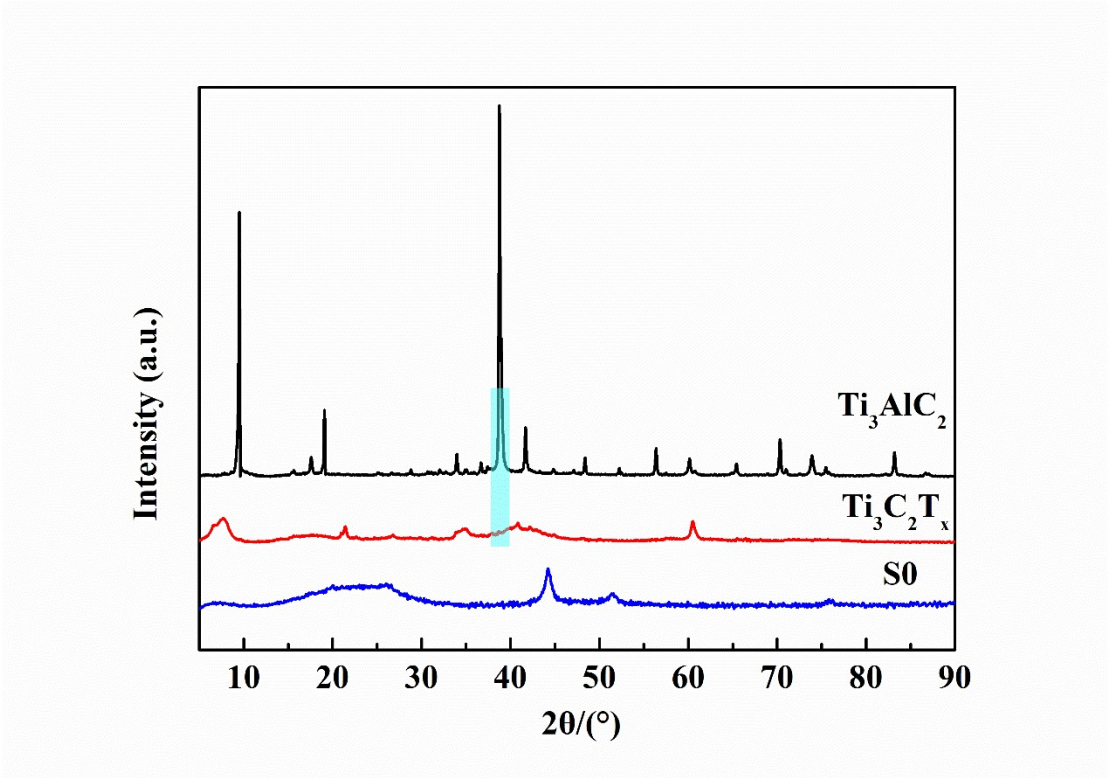

Fig. S4. XRD patterns of samples.

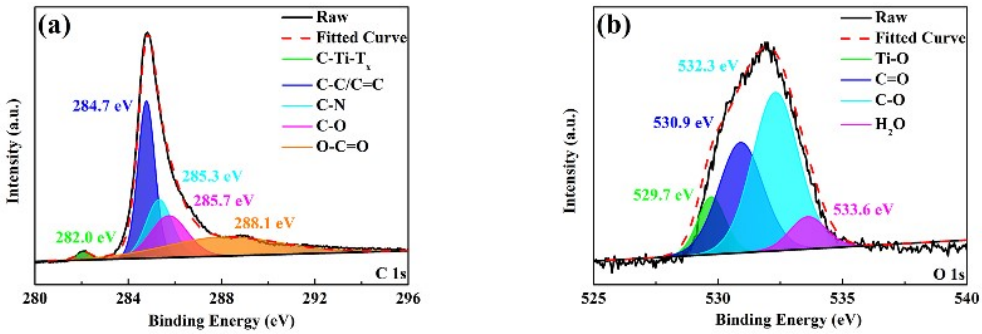

Fig. S5. XPS spectra of (a) C 1s and (b) O 1s.

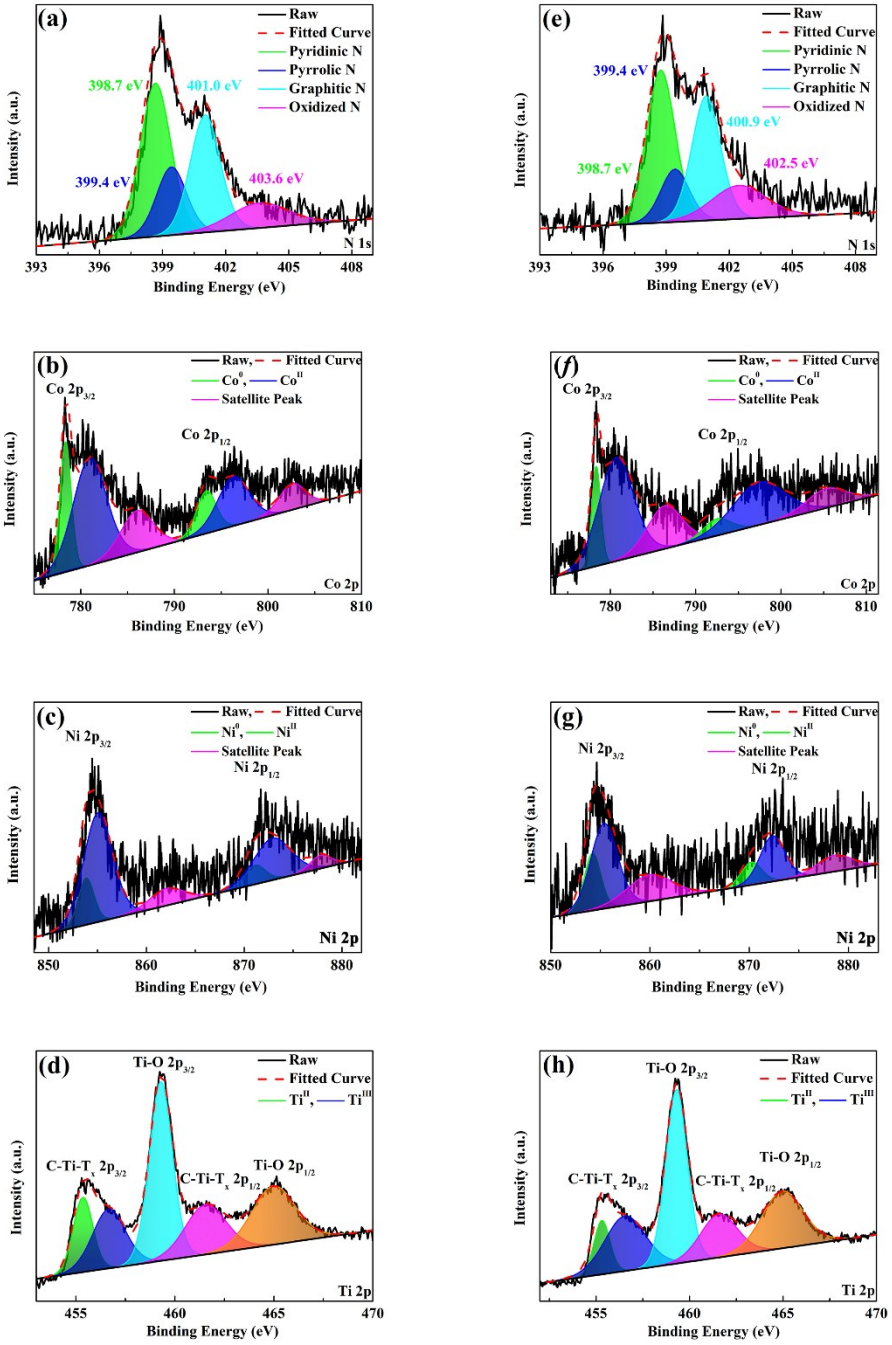

Fig. S6. XPS spectra of N 1s, Co 2p, Ni 2p and Ti 2p of S2 (a-d) and S3 (e-h).

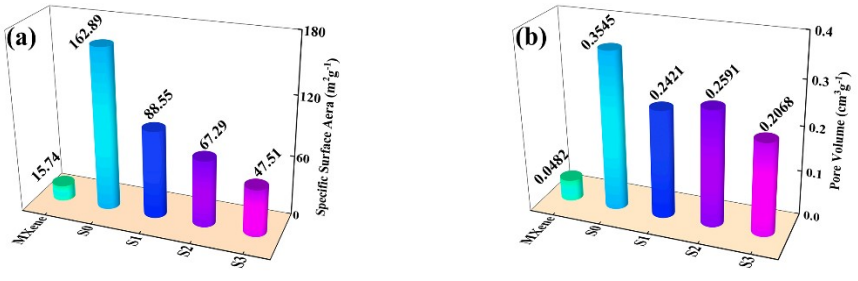

Fig. S7. The specific surface area (a) and pore volume (b) of the as-prepared samples.

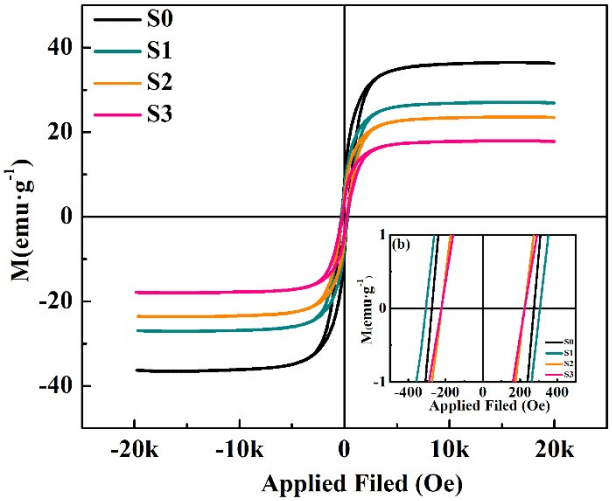

Fig. S8. Hysteresis loops of the samples, with the insets showing enlarged view.

Table S1 Magnetic parameters of the samples.

Samples	S0	S1	S2	S3
Ms (emu/g)	36.36	26.95	23.47	17.83
Mr (emu/g)	8.46	7.09	4.90	3.75
Hc (Oe)	283.07	311.96	230.53	227.41

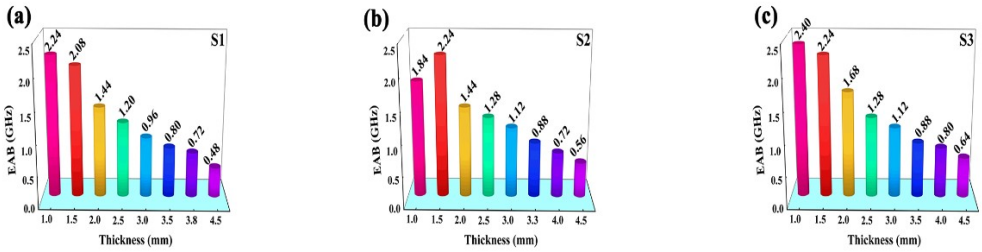

Fig. S9. Effective absorption bandwidth for samples: (a) S1, (b) S2 and (c) S3.

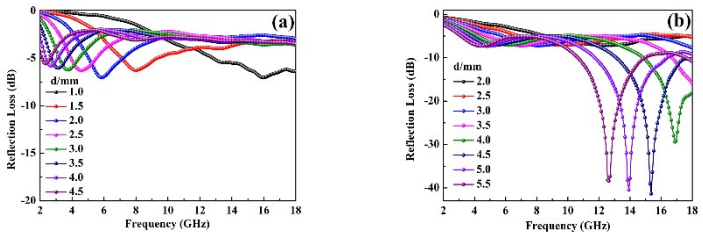

Fig. S10. Reflection loss curves of the samples at different thicknesses: (a) MXene and (b) S0.

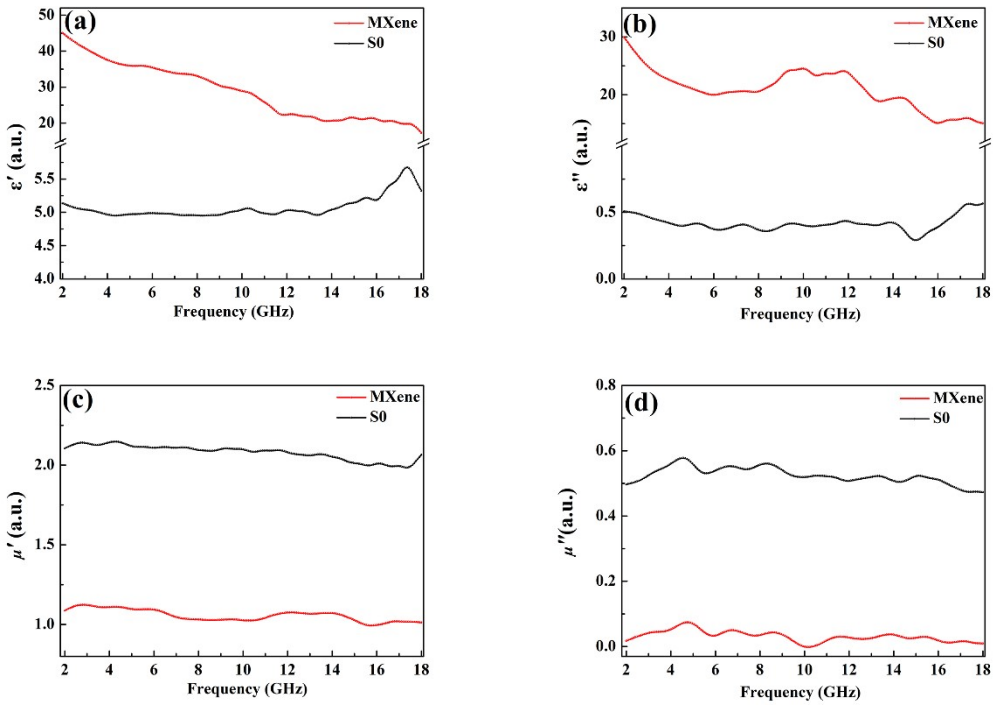

Fig. S11. Frequency dependence of (a) real permittivity (ε′), (b) imaginary permittivity (ε″), (c) real permeability (μ') and (d) imaginary permeability (μ″).

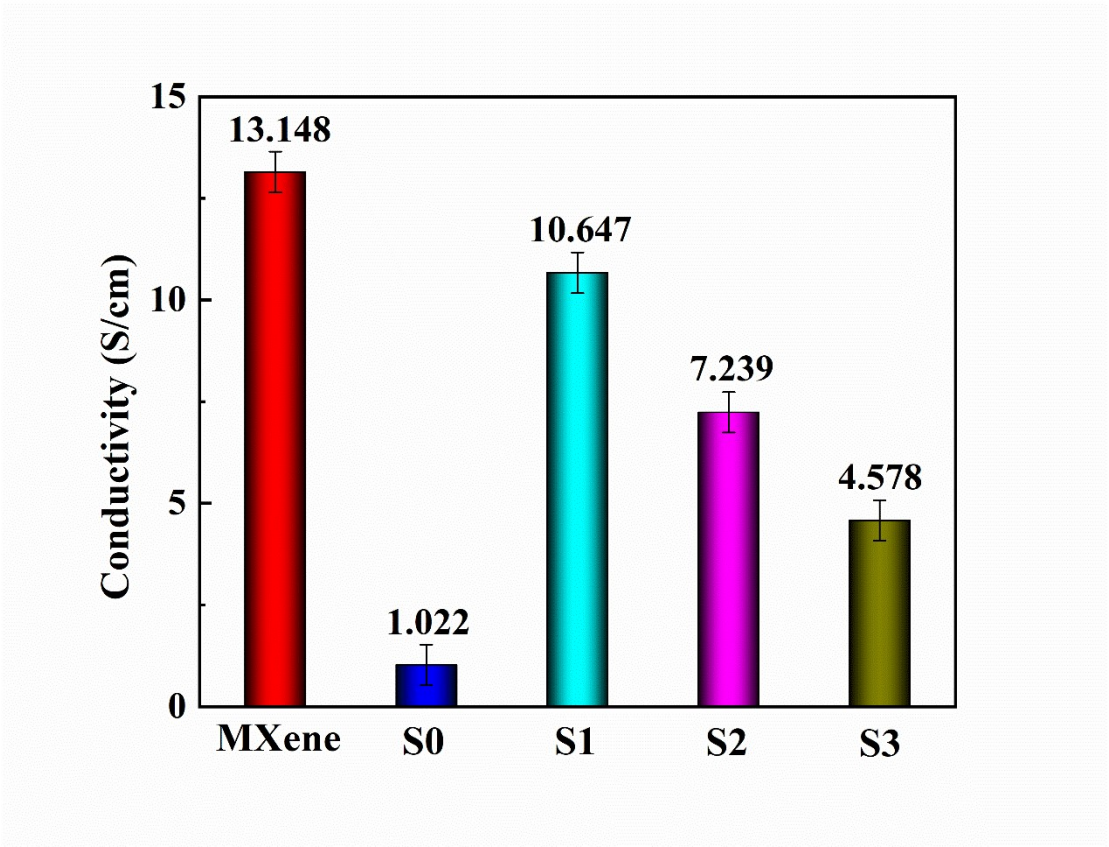

Fig. S12. (a) Statistics of electrical conductivity for different sample.

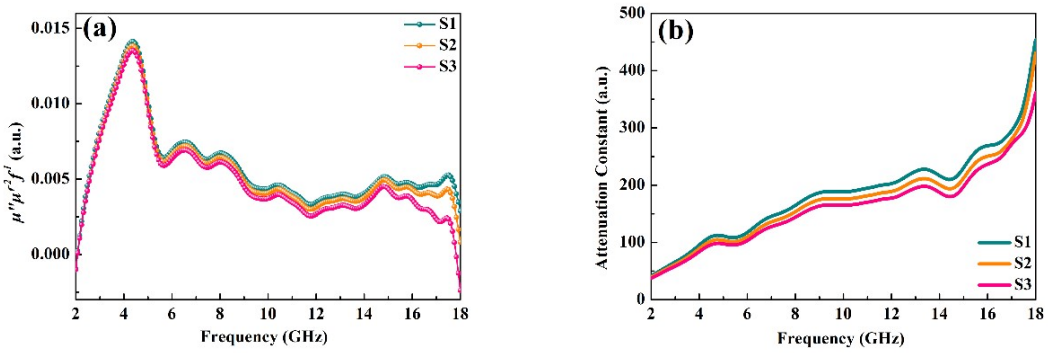

Fig. S13. (a) Plots of $f^{1}(\mu')^{-2}\mu''$ and (b) attenuation constant α of the samples.

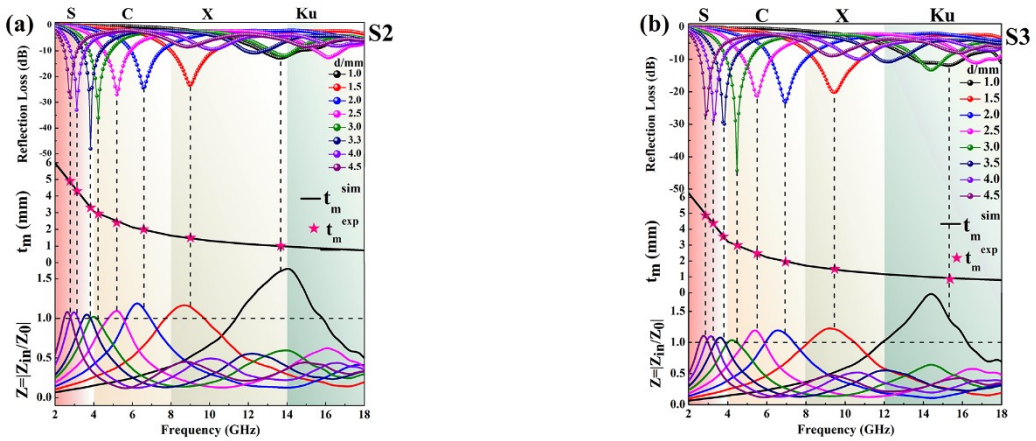

Fig. S14. Dependence of RL on frequency at 1/4λ thicknesses and the Z for the sample: (a) S2 and (S3).