Energy Materials

Metal nitride heterostructures capsulated in carbon nanospheres to accommodate lithium metal for constructing a stable composite anode

Section A. Experimental

Preparation of WN/Mo_2N@HCN: WN/Mo_2N@HCN was prepared through a one-pot aqueous pathway, where copolymerization reaction at micelle interfaces induced the condensation of metal salts inside the cavity. 105.9 mg ammonium molybdate tetrahydrate ($H_{24}Mo_7N_6O_{24}·4H_2O$) and 73.9 mg ammonium tungstate ($(NH_4)_6H_2W_{12}O_{40}·xH_2O$) were first dissolved in 60 mL deionized water. Then, 0.06 g Triton X-100, 0.38 mL pyrrole and 0.49 mL aniline were added under magnetic stirring and ultrasonication for 30 min each to form a uniform mixture. After that, 2.465 g ammonium persulfate dissolved in 5 mL deionized water was added quickly to the above-precooled mixture with stir for 30 s and then reacted for 10 h at 0 °C. Finally, the precipitates were vacuum filtrated, washed with deionized water and dried at 60 °C for overnight. The prepared samples were carbonized and nitrided at 800 °C for 3 h with a heating rate of 5 °C min^{-1} under an ammonia atmosphere to obtain WN/Mo_2N@HCN. The synthesis processes for WN@HCN, Mo_2N@HCN and HCN were almost the same except for the differences in the added metal salts.

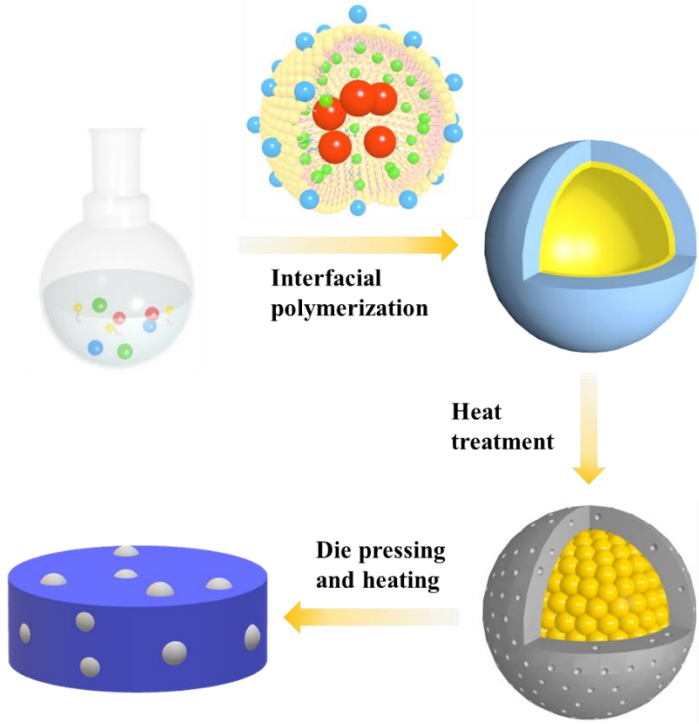
Preparation of composite anode: WN/Mo_2N@HCN and Li metal powder were added to a centrifuge tube with a mass ratio of 1:3 and stirred for 8 h. Subsequently, 40 mg of the mixture powder was pressed onto Cu foil of Φ12 mm at the pressure of 5 MPa, followed by heating at 200 °C for 5 min, and then cooled down naturally. For comparison, the Li metal foil anode was prepared with pure lithium powder using the same process. All the preparation of the anodes was conducted in an Ar-filled glove box with water and oxygen content less than 0.1 ppm.

Cell fabrication: CR2032 coin cells were fabricated in an argon-filled glovebox with the composite anode as the working electrode, commercial Li foil as the

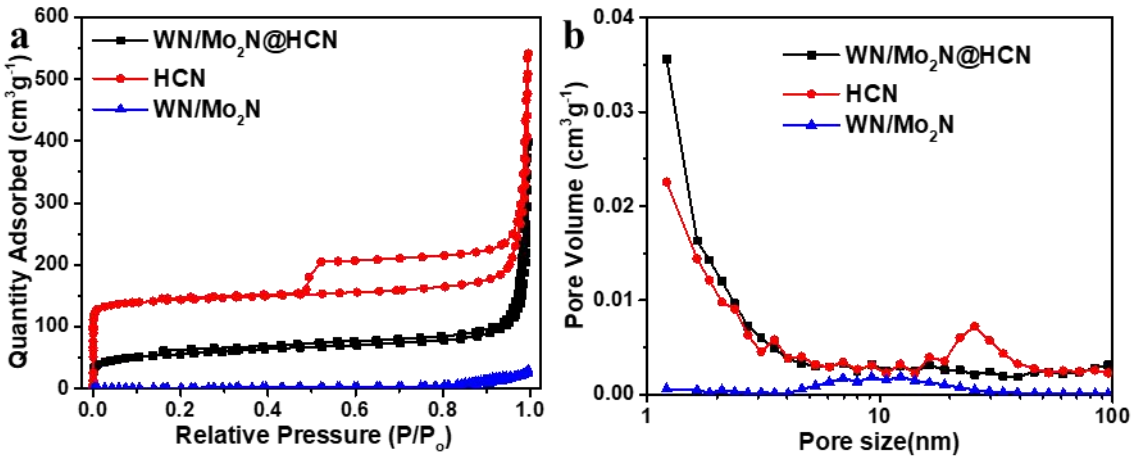
counter/reference electrode and polyethylene membrane (Celgard 2500) as the separator. The electrolyte used in the symmetric cells was comprised of 1 M lithium bistrifluoromethanesulphonylimide (LiTFSI) and 2 wt% lithium nitrate ($LiNO_3$) mixed with 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume ratio). The full cells were also assembled using the composite anode and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) cathode. The cathode electrodes were prepared by mixing active materials, carbon black, and polyvinylidene fluoride in a weight ratio 8:1:1 in N-Methyl pyrrolidone (NMP) solvent. Then the slurry was coated on an aluminum foil prior to magnetic stirring for 2 h. The slurry-coated aluminum foil was dried in a vacuum oven at 60 °C for 8 h to evaporate NMP. Finally, the electrodes were prepared by cutting the coated aluminum foil into round plates of Φ10 mm. The electrolyte used in the full cells was 1.0 M $LiPF_6$ dissolved in EC/EMC/DMC(1 : 1 : 1 in volume) in a potential window from 2.8 to 4.3 V. Electrochemical impedance spectroscopy (EIS) was recorded from 100 kHz to 1Hz using a Bio-Logic VMP3 multichannel electrochemical station.

Materials characterization: The morphology and structure of WN/Mo_2N@HCN were characterized with a field emission transmission electron microscope (TEM, FEI Tecnai G_2 F30). The surface and cross-sectional morphologies of the composite anode were observed with a scanning electron microscope (SEM, HITACHI SU8010) with an energy-dispersive X-ray spectrometer (EDS). X-ray photoelectron spectra (XPS) were conducted on a PHI 5000 VersaProbe II spectrometer using a monochromatic Al K(alpha) X-ray source. All XPS spectra were referenced using the C 1s peak at 284.8 eV for comparison. The surface properties of the anode were observed with a MDTC-EQ-M16-03 atomic force microscope (AFM, Bruker Dimensionicon, Germany) which was placed in a glove box. The nitrogen adsorption/desorption isotherms of the materials were obtained using an automated adsorption device (Micromeritics ASAP 2020) at 77 K and the specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation. Metallic elemental composition analysis and contact angle test were conducted using a inductively coupled plasma emission spectrometer (SPECTRO Arcos II) and a contact angle measuring device (KRUSS DSA30), respectively.

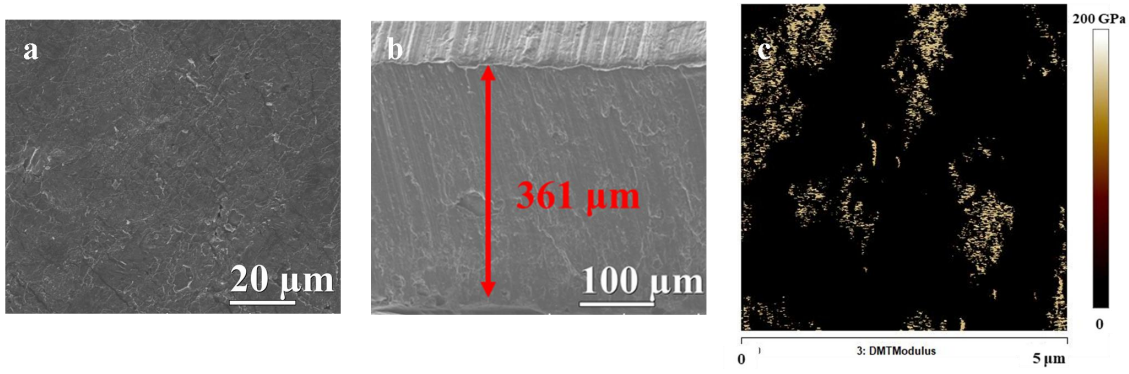
Section B. Supplementary Figures



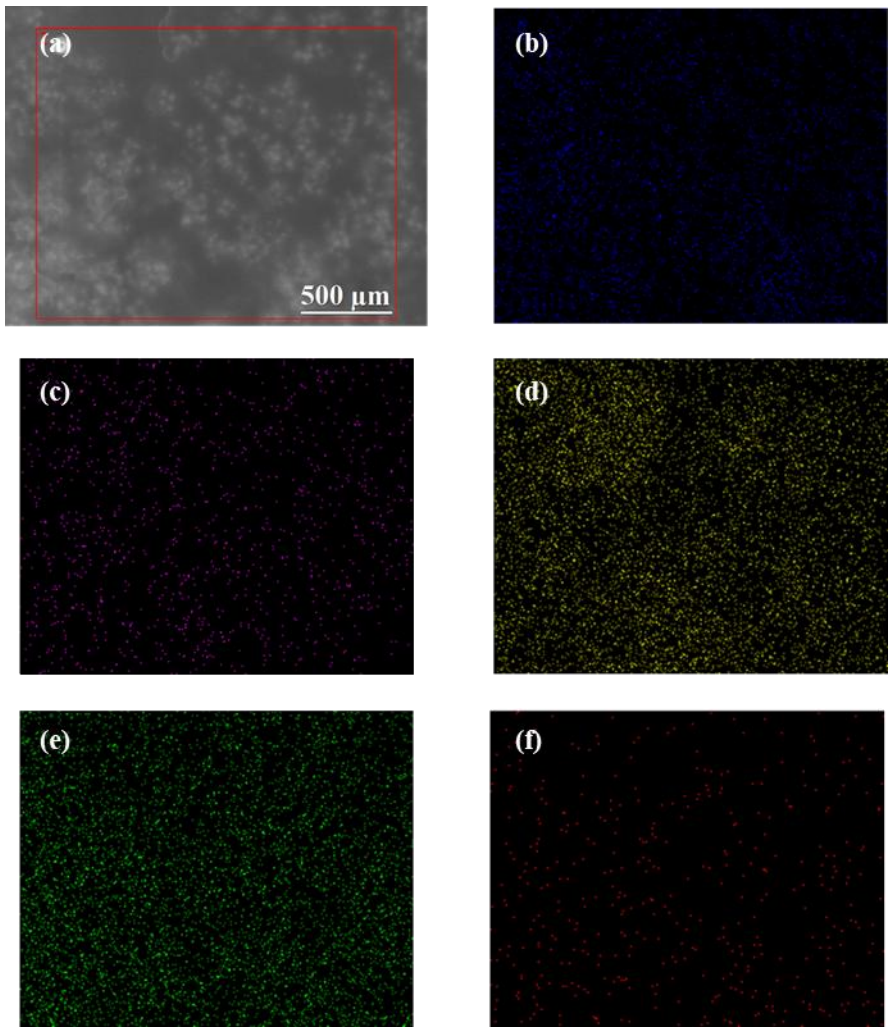
Supplementary Figure 1. Schematic illustration of the preparation of the composite Li anode.



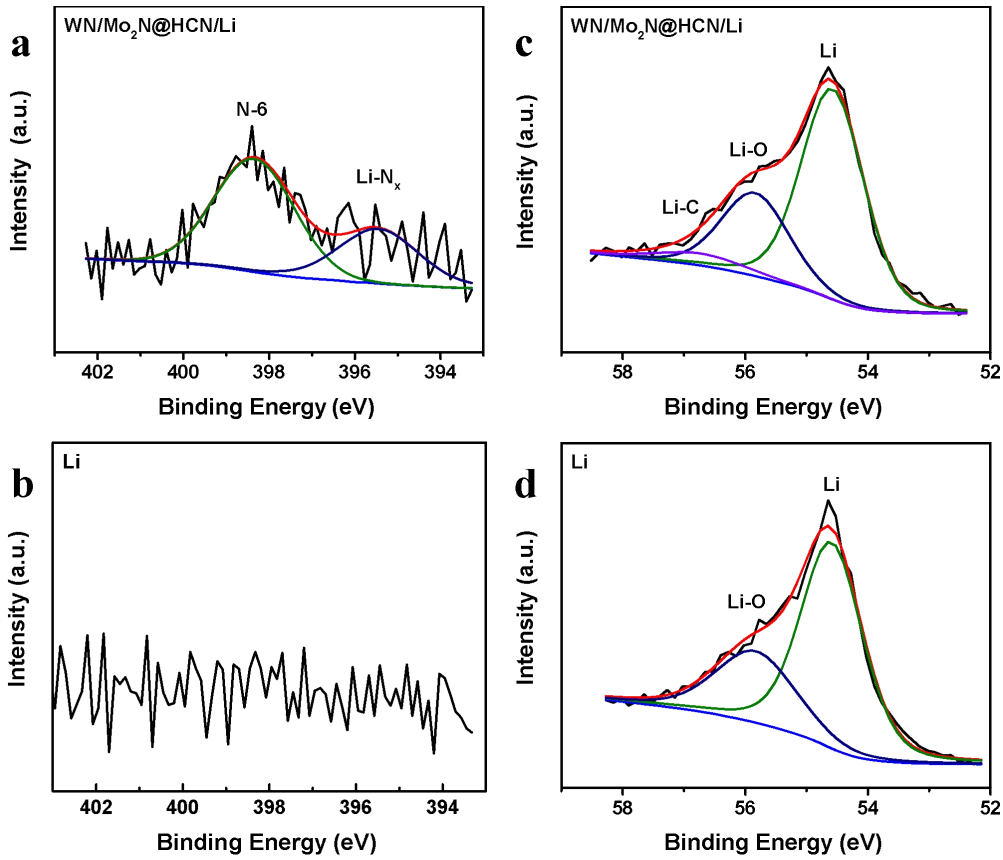
Supplementary Figure 2. (a) N_2 adsorption-desorption isotherms and(b) pore size distribution curves of the WN/Mo_2N@HCN, HCN and WN/Mo_2N.



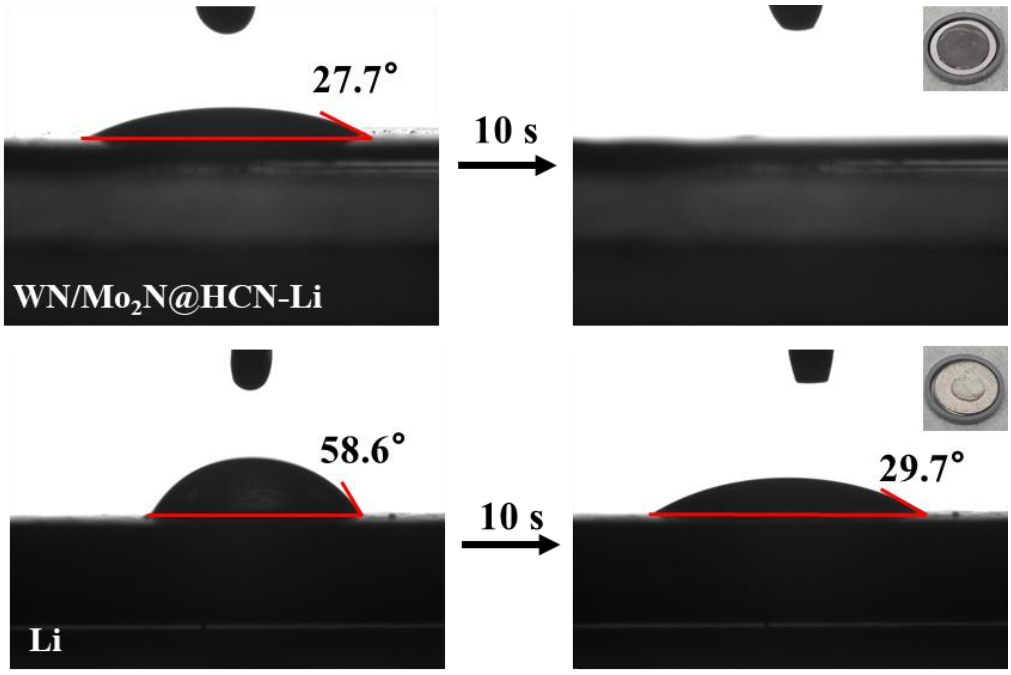
Supplementary Figure 3. (a,b) SEM images and (c) AFM image with Young's modulus mapping of pure Li metal anode.



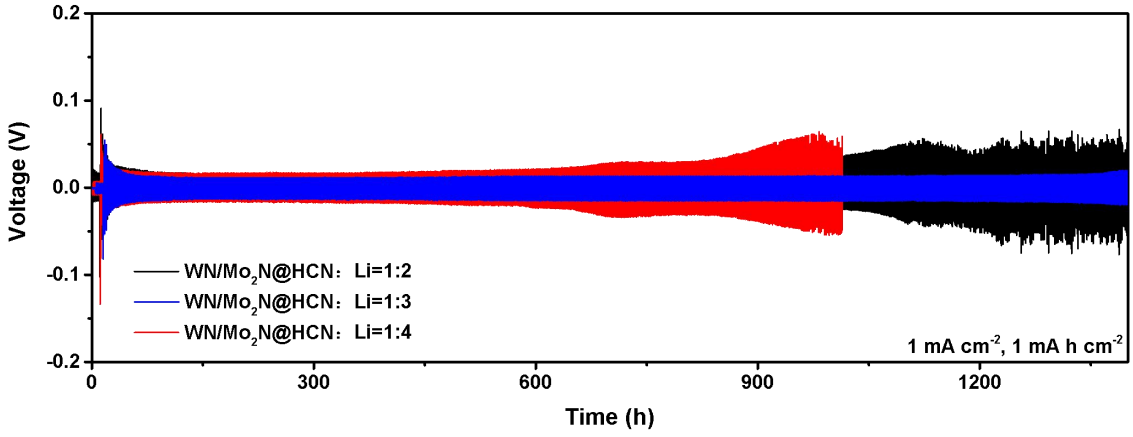
Supplementary Figure 4. (a) SEM image and element mappings of WN/Mo_2N@HCN/Li: (b)C; (c)N; (d) O; (e)Mo; (f)W.



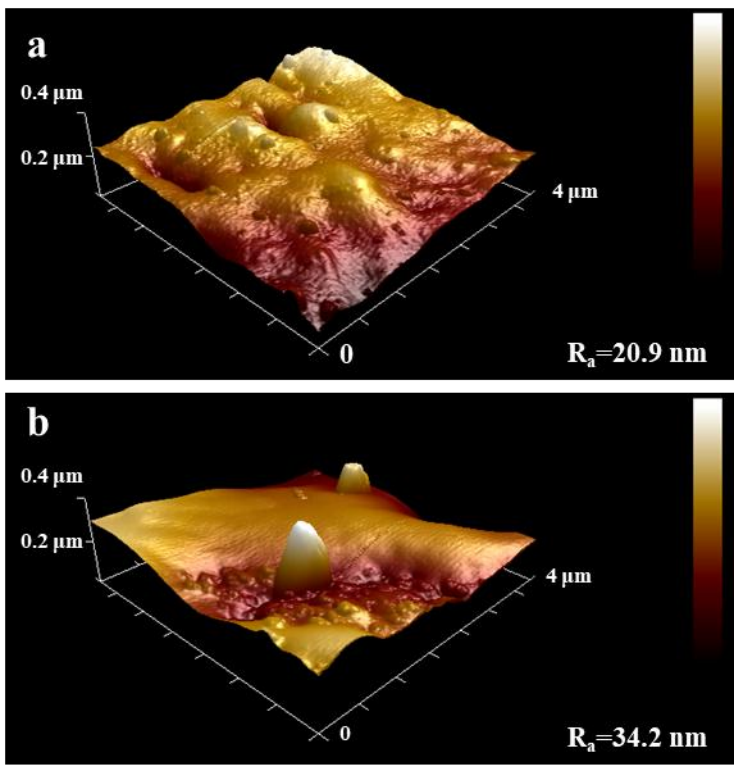
Supplementary Figure 5. High-resolution XPS spectra of (a,b) N 1s and (c,d) Li 1s for WN/Mo_2N@HCN/Li and pure Li metal anode.



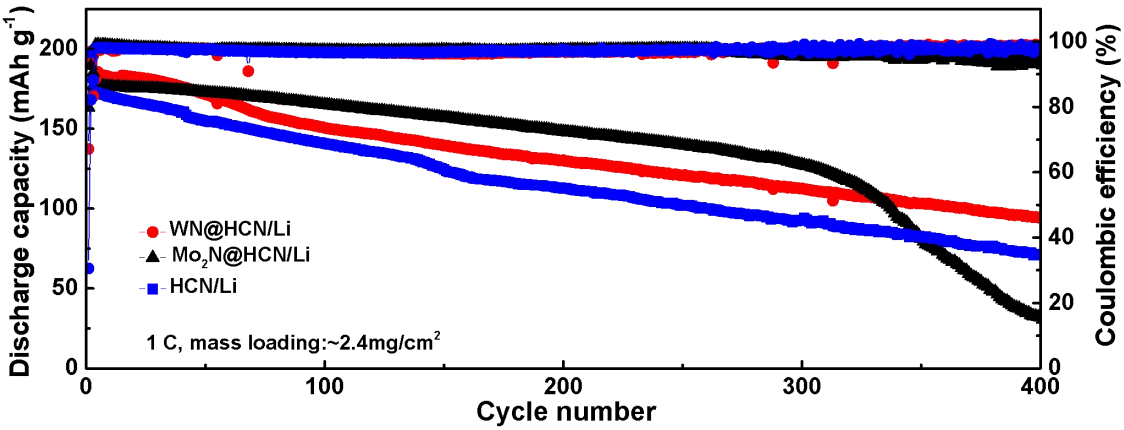
Supplementary Figure 6. Contact angle measurement of WN/Mo_2N@HCN/Li and pure Li metal anode.



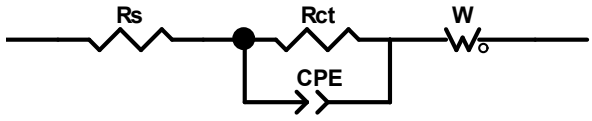
Supplementary Figure 7. Long-term plating/stripping profiles of WN/Mo_2N@HCN/Li anodes with different Li content in the symmetric cells at 1 mA cm^{-2} and 1 mA h cm^{-2}.



Supplementary Figure 8. Surface roughness of (a) WN/Mo_2N@HCN/Li and (b) pure Li metal anode by AFM.



Supplementary Figure 9 Cycling performance of full cells with WN@HCN/Li, Mo_2N@HCN/Li and HCN/Li.



Supplementary Figure 10 Equivalent circuit model for fitting.

Section C. Supplementary Tables

Supplementary Table 1. Summary of the pore parameters for different samples.

Sample	S_{BET} ($m^2 g^{-1}$)	S_{mic} ($m^2 g^{-1}$)	V_{mic}($cm^3 g^{-1}$)	V_{total}($cm^3 g^{-1}$)
WN/Mo_2N@HCN	206	74	0.29	0.35
HCN	569	63	0.34	0.54
WN/Mo_2N	6	6	0.04	0.04

Supplementary Table 2. Elemental composition of different samples.

Sample	W content（wt%）	Mo content（wt%）
WN/Mo_2N@HCN	13.03	12.13
WN@HCN	10.62	-
Mo_2N@HCN	-	19.79

Supplementary Table 3. The bulk densities of different Li.

Sample	Li powder	Li anode	WN/Mo_2N@HCN/Li
The bulk density (g/cm^3)	0.32	0.52	0.71

Supplementary Table 4 Fitting results of EIS data with the composite Li anode and pure Li metal anode.

Sample	R_s/Ω	R_{ct}/Ω
Li	1.15	222.70
WN/Mo_2N@HCN/Li	2.06	41.21