
Supporting Information

Intermetallic PtTe metallene for formic acid oxidation assisted electrocatalytic nitrate reduction

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Experimental Section

Physical characterization

The morphology and composition of the samples were characterized by SU-8020 scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscope (TEM) and selected area electron diffraction (SAED) were tested with TECNAI G2 F20 instrument. A DX-2700 power X-ray diffractometer was used to obtain powder X-ray diffraction (XRD) patterns. X-ray photoelectron spectroscopy (XPS) was conducted on AXIS ULTRA spectrometer. The binding energies achieved in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.5 eV. The ultraviolet-visible (UV-vis) spectroscopy measurements were performed at Shimadzu UV-3600U instrument.

Electrochemical measurement

The electrochemical measurements were performed on a CHI 660D electrochemical analyzer. All potentials mentioned in the work correspond to the reversible hydrogen electrode potential (RHE), where $E_{RHE} = E_{SCE} + 0.242 + 0.059\text{pH}$. The working electrode was obtained as follows: 2 mg of electrocatalyst was dispersed into a mixture of 0.8 mL of water, 0.2 mL of isopropyl alcohol and 10 μL of Nafion to prepare the electrocatalyst ink, and 4 μL of electrocatalyst ink was taken in drops on a glassy carbon electrode. In three electrode system, a saturated glycerol electrode (SCE) serves as the reference electrode and a carbon rod serves as the counter electrode. In two electrode system, Nitrate reduction was tested in an H-type electrolytic cell separated by an N-117 Nafion membrane at room temperature. 0.5 M H_2SO_4 electrolyte (60 mL) was uniformly distributed between the cathode and anode. 50 mmol of KNO_3 was added to the cathode chamber for the electrical reduction of KNO_3 . The LSV curves for nitrate reduction reaction of all the electrocatalysts are iR -corrected at a ratio of 95% by setting the corresponding parameters for real-time compensation on the electrochemical workstation.

Detection of NH_3

The Faradaic efficiency of NO_3^- -ERR and NH_3 yield

The chronoamperometry tests of NO_3^- -ERR were performed at a two-compartment cell with Ar-purged 0.5 M H_2SO_4 +0.05 M KNO_3 solution and 0.5 M H_2SO_4 solution (30 mL in each cell). The faradaic efficiency for NH_4^+ production was defined as charge converted to NH_4^+ divided by the total charge passed through the electrodes during the electrolysis (Q), which was calculated according to the following formula:

$$\text{Faradaic efficiency} = \frac{8F \cdot c_{\text{NH}_3} \cdot V}{M_{\text{NH}_3} \cdot Q}$$

The NH_4^+ yield was calculated by following formula:

$$\text{Yield}_{\text{NH}_3} = \frac{c_{\text{NH}_3} \cdot V}{m \cdot t}$$

where C_{NH_3} was the mass concentration of $\text{NH}_3(\text{aq})$, V was the volume of electrolyte in the cathode compartment (30 mL), M_{NH_3} was the molar mass of NH_3 , t was the electrolysis time (3 h), F was the Faradaic constant (96485 C mol^{-1}), Q was the total charge passing the electrode. m and t were the electrocatalyst mass and the reduction reaction time, respectively.

Determination of NH_4^+

Phenolhypochlorite method was used to detect the NH_3 concentration. Firstly, the corresponding calibration curve was obtained by UV-vis curves for known concentration of NH_4^+ in 0.05 M H_2SO_4 . After running chronoamperometry test for 3 h, 1 mL were taken from the electrolyte and put it into the centrifuge tube and diluted to 10 mL with water. Then Stock reagents were added in solution and stand for 3 h. Finally, NH_4^+ -N concentration was calculated according to the UV-vis curve and calibration curve.

DFT Calculation

Density functional theory (DFT) calculations of Pt(111) and PtTe(111) surfaces were obtained by using Material studio 2019 through the local density approximation (LDA). An additional Coulomb potential ($U_{\text{Pt}} = 3.0 \text{ eV}$) and GGA+U functional was applied to states of 3d-orbit. Norm-conserving pseudopotentials were used altogether with a 400

eV of plane-wave energy cut off. The Brillouin zone was sampled with a $2 \times 2 \times 1$ Monkhorst-Pack grid. The force on each atom of the structure was fully optimized less than 10^{-4} eV/Å. A vacuum layer of 20 Å was incorporated into the slabs to avoid periodic interaction. The free energy (G) was computed using formula: $G=E+ZPE-T\Delta S$, where E was the total energy, ZPE was the zero-point energy, the entropy (ΔS) of each adsorbed state were carried out from DFT calculation, the thermodynamic corrections for gas molecules were obtained from standard tables. For calculating the free energies of all electrochemical reaction steps, $H^+ + e^-$ was described by the gas phase energy of hydrogen seizing the equilibrium between $H^+ + e^-$ in aqueous media and the gas phase hydrogen.

For the reaction energy calculations, the reaction processes below were considered (Equations S1-S8):

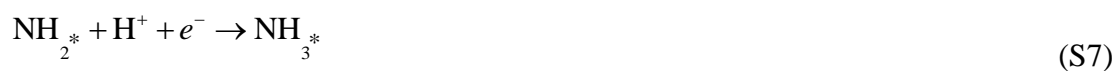
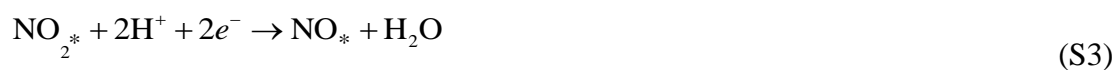
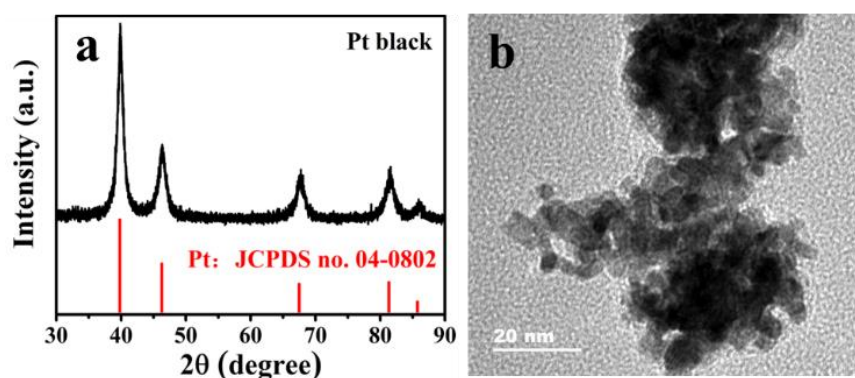


Table S1. The zero-point energies for each of the adsorption states

		zero-point energy (kcal/mol)
PtTe-ML	PtTe	41.617
	PtTe-NO ₃ [*]	51.383
	PtTe-NO ₂ [*]	47.893
	PtTe-NO [*]	45.045
	PtTe-HNO [*]	51.193
	PtTe-NH [*]	48.901
	PtTe-NH ₂ [*]	57.073
	PtTe-NH ₃ [*]	64.384
Pt-black		zero-point energy (kcal/mol)
	Pt	24.397
	Pt-NO ₃ [*]	33.149
	Pt-NO ₂ [*]	30.256
	Pt-NO [*]	28.279
	Pt-HNO [*]	34.656
	Pt-NH [*]	32.462
	Pt-NH ₂ [*]	39.462
Pt-NH ₃ [*]	46.814	

- **Figures**

**Figure S1.** (a) XRD pattern and (b) TEM image of commercial Pt black

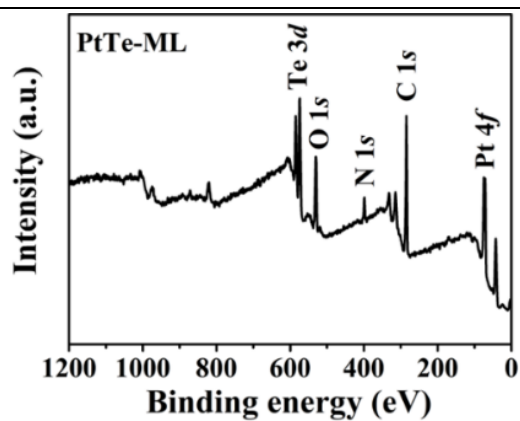


Figure S2. XPS survey spectrum of PtTe-ML.

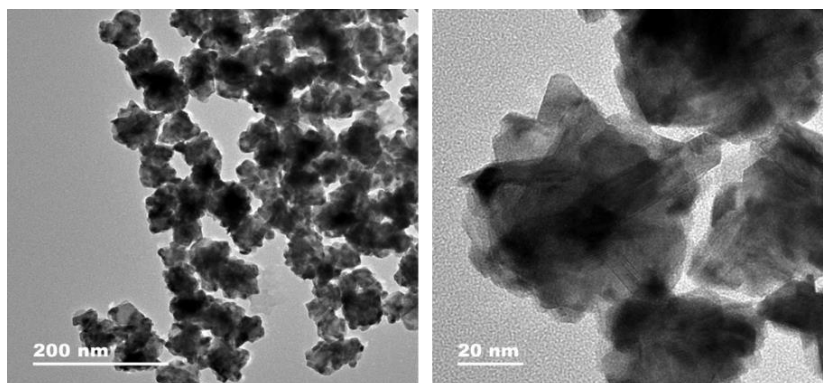


Figure S3. TEM image of PtTe nanomaterials in the absence of PVP.

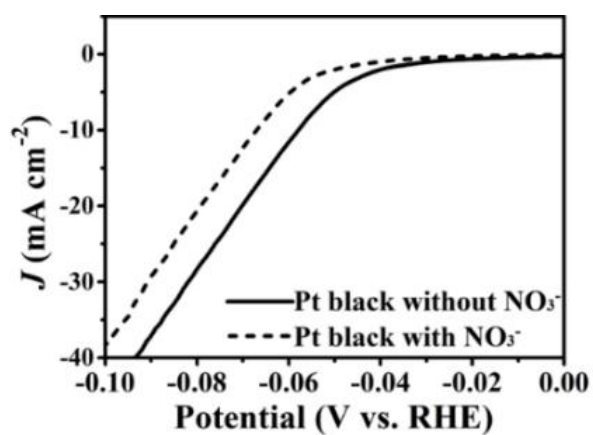


Figure S4. LSV curves of commercial Pt black in 0.5 M H₂SO₄ electrolyte with and without 50 mM KNO₃ at 50 mV s⁻¹.

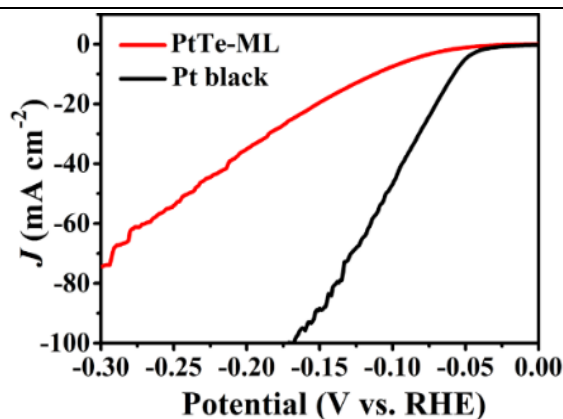


Figure S5. LSV curves of PtTe-ML and commercial Pt black in 0.5 M H₂SO₄ electrolyte at 50 mV s⁻¹.

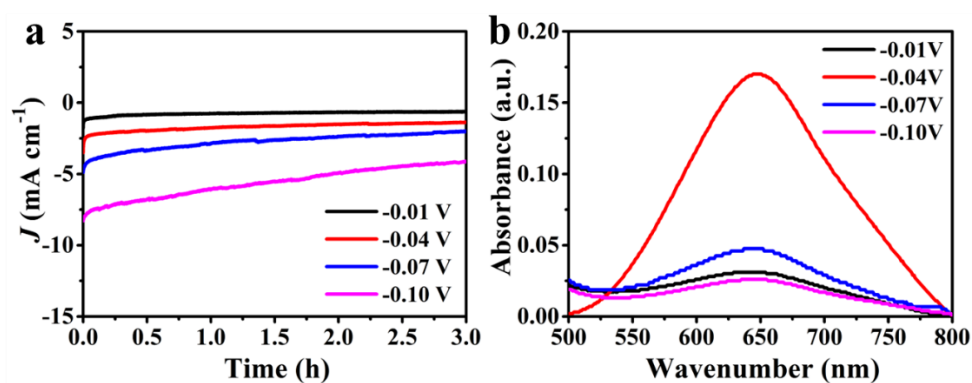


Figure S6. (a) Chronoamperometric curves and (b) the UV-vis spectra of PtTe-ML between -0.01 V and -0.10 V in 0.5 M H₂SO₄ and 50 mM KNO₃ electrolyte at the corresponding potentials.

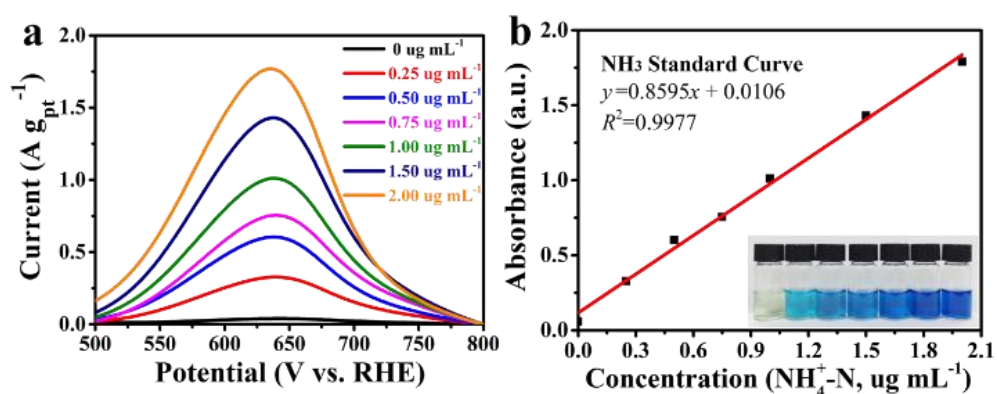


Figure S7. Absolute calibration of the phenate method using ammonium solutions of known concentration as standards. (a) UV-vis curves of phenate assays after in darkness for 3 h at room temperature and (b) calibration curve used for estimation of NH₃ by NH₄⁺-N ion concentration.

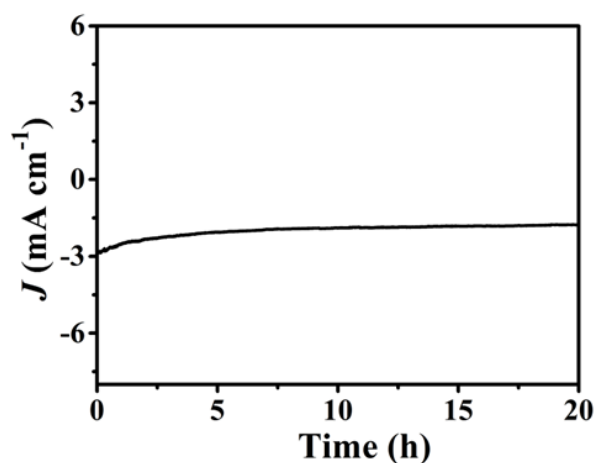


Figure S8. Chronoamperometry curve of PtTe-ML at -0.04 V for 20 h in 0.5 M H₂SO₄ and 50 mM KNO₃ electrolyte.

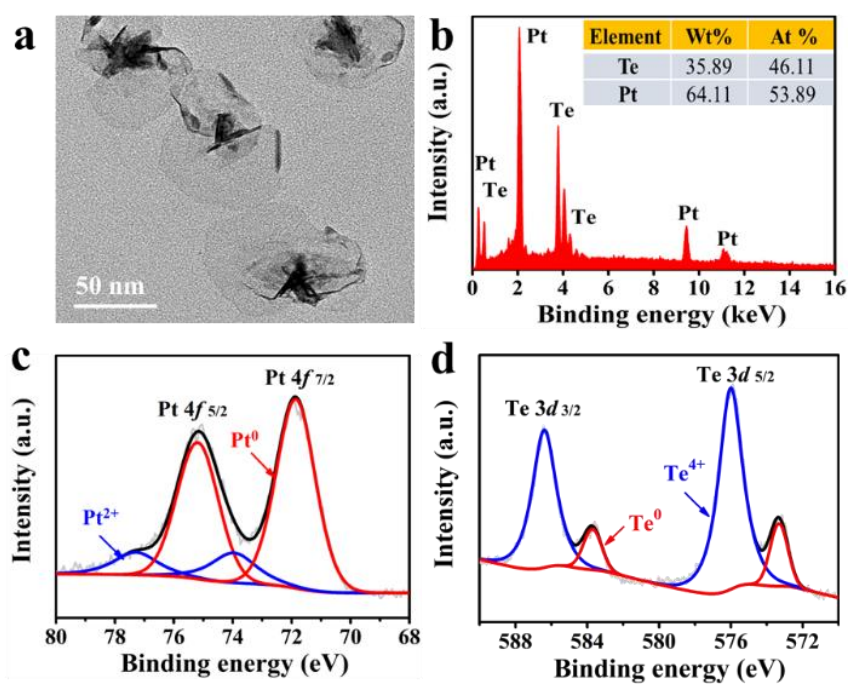


Figure S9. (a) TEM image, (b) EDX spectrum and (c) Pt 4*f* and (d) Te 3*d* XPS spectra of PtTe-ML after chronoamperometry test.

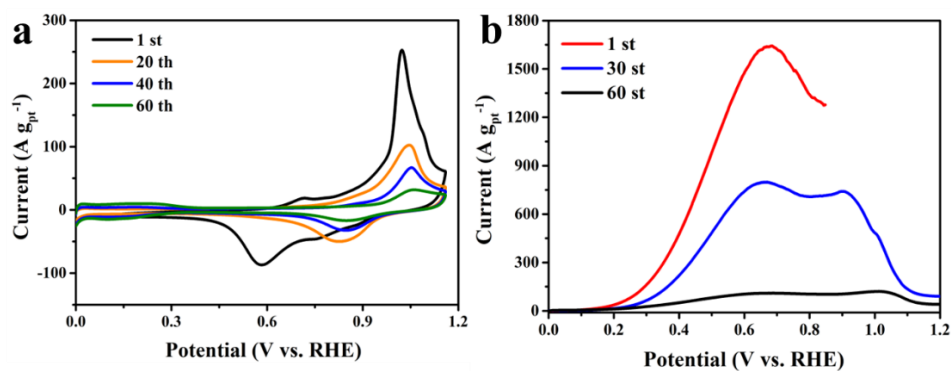


Figure S10. CV curves of PtTe A-ML at the different number of scanning turns at high potential.

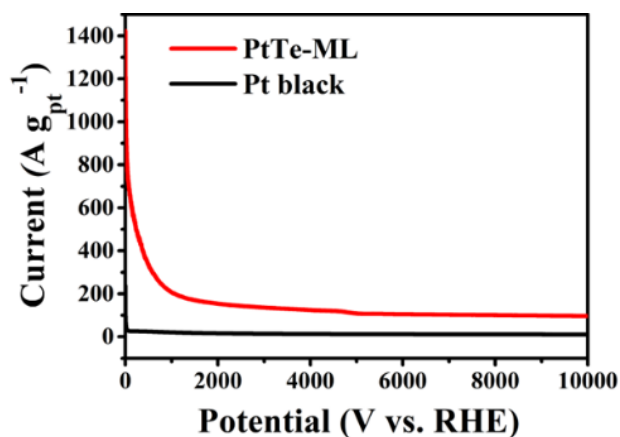


Figure S11. Amperometric *i-t* curves of PtTe-ML and commercial Pt black at 0.6 V potential in Ar-saturated 0.5 M H₂SO₄ and 0.5 M HCOOH solution.

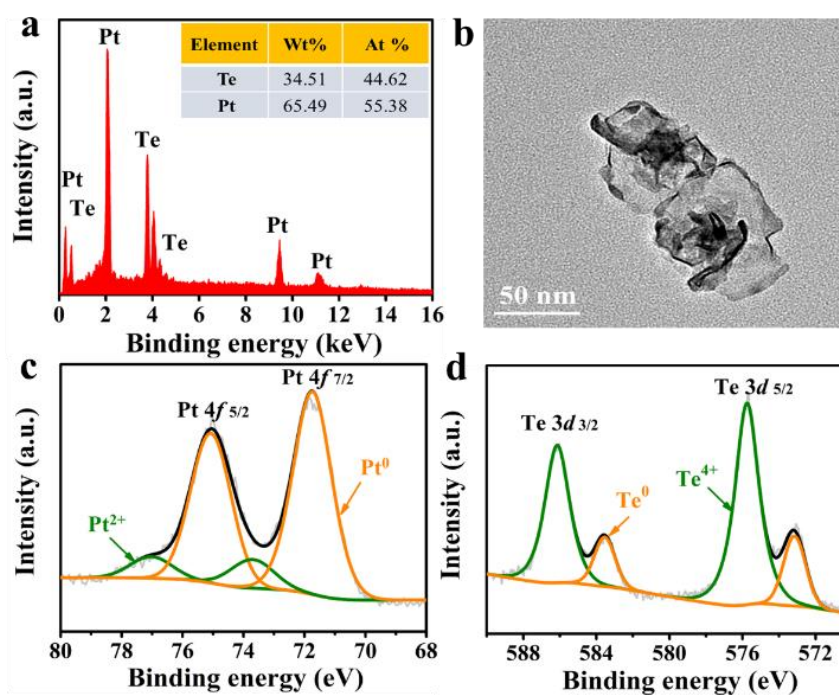


Figure S12. (a) EDX spectrum TEM image, (b) TEM image and (c) Pt 4f and (d) Te 3d XPS spectra of PtTe-ML after chronoamperometry test.