Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Designed TiS_2 nanosheets efficient for electrocatalytic reductive amination of biomass-derived furfurals

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1. Experimental procedures

1.1 Chemicals and Equipment. 5-hydroxymethylfurfural (HMF, 98%) were purchased from Alfa Aesar (China) Chemicals Co., Ltd. Sodium hydroxide (98%), ethanolamine (99%), furfural (FF, 99%), and 5-melthyfurfural (MF, 98%) were purchased from Shanghai Macklin Biochemical Co., Ltd. The nitric acid (HNO_3, 68%) and sulfuric acid (H_2SO_4, 95-98%) were manufactured by Guangzhou Chemical Reagent Factory. Carbon fiber paper (CFP, TGP-H-060) was purchased from Toray Industries, Inc (Japan). High purity argon (≥ 99.999%) was purchased from Dacheng (Guangzhou) Gas Co., LTd. All reagents were raw and used to experiment. Ultra-pure water (~18.25 MΩ×cm) was obtained by the reverse osmosis (RO) technology and ultra-purification system filtration (Ulupure, China) using for the whole experiment. The pH meter (Starter 3100) with a resolution ratio of 0.01 pH was purchased from OHAUS Laboratory (USA).

1.2 Controllable Synthesis of TiS_2 Nanosheets. The layer structure TiS_2 nanosheets were assembled over a solid-state reaction. The titanium powder (4.787 g, -325 mesh, 99.00%) and sulfur powder (6.734 g, 99.99%) were accurately obtain and homogeneously mixed in a mortar. After that, the powder was pressed into a plate under 30 MPa. Then, the plate was sealed in a vacuum vessel. Next, being calcined at 1000 °C for 14 d at a speed of 0.5 $°C\ min^{-1}$, the as-prepared gold-bronze powders were sharply cooled in mixed solution of water and ice. Subsequently, the material was dried in a vacuum oven at 60 °C overnight to obtain the TiS_2 powder of gold-like.

1.3 Characterization. The crystalline phase of the as-synthesized materials was carried out on a Rigaku Ultima IV (Janpan) X-ray diffractometer using Cu K^{α} target at a voltage of 40 kV and a current of 40 mA, using the scanning rage of theta (2θ) was from 5° to 70° at a scan rate of $10^{\circ}\ min^{-1}$. For the samples on carbon fiber paper, we used a scan rate of $5^{\circ}\ min^{-1}$. X-ray photoelectron spectroscopy (XPS) studies were tested through the Thermo ESCALab250 X-ray photoelectron spectrometer (USA) with pass energy of 20 eV and a monochromatized Al Kα as the excitation source at 150 W. Scanning electron microscopy (SEM) images were obtained by a Gemini500 scanning electron microscope operating at 15 kV with the distinguishability of 0.6 nm. Energy dispersive X-ray spectroscopy (EDX) mapping was performed on the catalysts equipped with an Aztec Xmax 50 EDS detector at 15 kV. The transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were taken on a FEI Tecnai G^2 F30 instrument operated at 200 kV to survey the material microstructure and lattice fringes. Atomic force microscope (AFM) was performed on a Nano ManVS instrument in tapping mode. The ex situ electron paramagnetic resonance (EPR) spectra were collected on a Bruker A300. The measurement of *In-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Nicolet iS50 FTIR spectrometer (Thermo Fisher, USA), equipped with a diffuse reflectance accessory coupling a specimen chamber with two ZnSe windows and one SiO_2 window. A reaction pool was connected to the specimen chamber, where the surface of the working electrode was faced to the DRITFS measurement interface. The surface changes of the working electrode were collected. For test, reaction pool with three electrodes and workstation were linked, with the catalyst added on a Pt plate as the work electrode. The signal acquisition and tests are consistent with the experimental system in the three-electrode system. Before the electrochemical reductive amination (ERA), the background spectrum of the Pt wok electrode without the catalyst loaded was collected. Then the working electrode was loaded with catalysts and the 10 mM FF and 0.7 M ethanolamine solution was added into the reaction pool before the potential is applied, as consistent with the experimental system in the routine three-electrode system. Then the DRIFTS spectra were collected at a resolution of 4 cm^{-1}, and average time is 32 over the ERA reaction performed at the constant potential of -0.6 V vs. RHE (V_{RHE}) for 6h. Additionally, the IR information of the FF substrate was measured using the Attenuated total reflection (ATR)-FTIR mode as reference.

1.4 Preparation of Electrolyte Solution. The pH environment of the buffer solution plays an important role for the aldimine formation, because the targeted product amines are substantially basic in aqueous solution, which can be protonated and dissociated in an acidic solution. The aldimine could also be hydrolyzed to the aldehyde in solution of $pH < 7.0$. Therefore, an unprotonated aqueous of 0.7 M ethanolamine ($pH = 11.0$ adjusting by 98 wt% H_2SO_4) was used as electrolyte solution.

2. Equations

Equation S1: $E_{RHE} = E^{\ominus}_{(Hg/HgO)} + 0.0596 \times pH + 0.114$.

Equation S2: $C_{dl} = \frac{1}{2}\frac{\Delta j}{\Delta v}$.

Where Δj denotes the cathodic charging current in CV curves obtained at different scan rates in a non-Faradaic region.

Equation S3: $ECSA = \frac{C_{dl}}{C_s}$.

Equation S4: $Mass\ activity = \frac{Current}{m_{catalyst}}$.

Equation S5: $TOF = \frac{1}{2} \times \frac{|j| \times A}{n \times F}$.

Where A, j, n and F are the area of the electrode, the current density, and the number of active sites (mol), the Faraday constant (96485 C mol^{-1}), respectively.

Equation S6: $Conversion\ (\%) = (1 - \frac{n'_{substrate}}{n_{substrate}}) \times 100\ \%$.

Equation S7: $Selectivity\ (\%) = \frac{n_{product}}{n_{substrate}} \times 100\ \%$.

Equation S8: $FE\ (\%) = \frac{n_{product}}{Total\ charge\ passed\ (C)/(F \times n)} \times 100\ \%$.

Where F is the Faraday constant (96485 C mol^{-1}) and n is the number of electrons required for the conversion of the aldimine to an amine, which is 2 for all substrates.

Equation S9: $TON = \frac{n_{product}}{n_{catalyst}}$.

Equation S10: $MASA = \frac{m_{product}}{ECSA}$.

3. Results and discussion

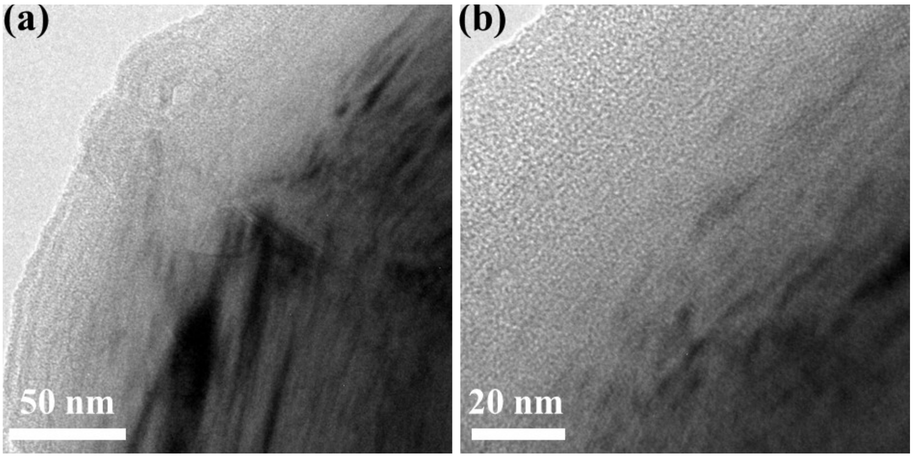

Fig. S1 TEM images of TiS_2.

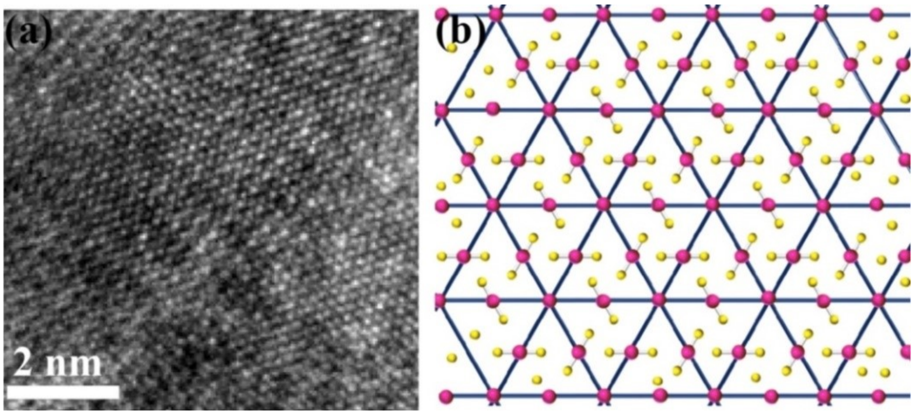

Fig. S2 HR-TEM image (a) and the schematic illustration (b) of the as-obtained TiS_2 microsphere (red: Ti, yellow: S).

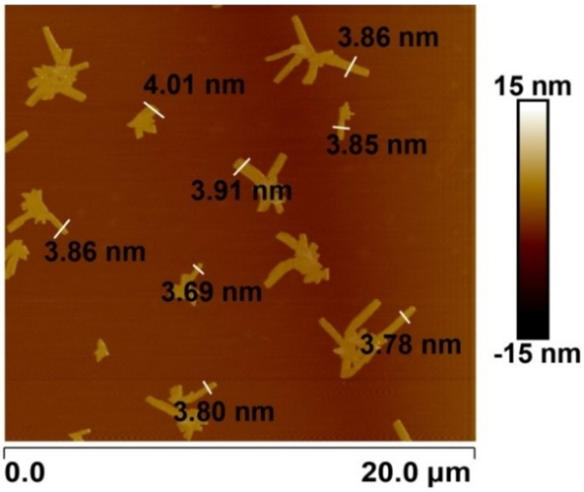

Fig. S3 AFM images of the as-prepared TiS_2.

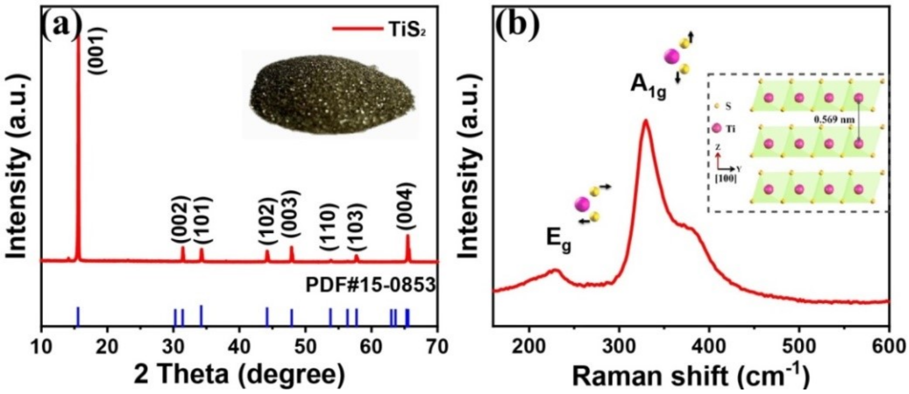

Fig. S4 (a) XRD patterns (Inset: the standard card of PDF#15-0853), (b) Raman shift of TiS_2 and corresponding crystalline structure of TiS_2 (Inset).

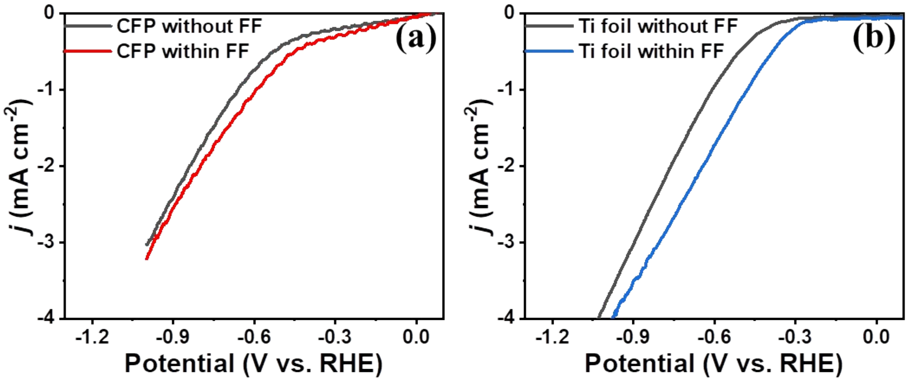

Fig. S5 LSV curves of CFP and Ti foil in 0.7 M ethanolamine electrolyte without FF and containing 5 mM FF at scan rate 5 mV s^{-1}.

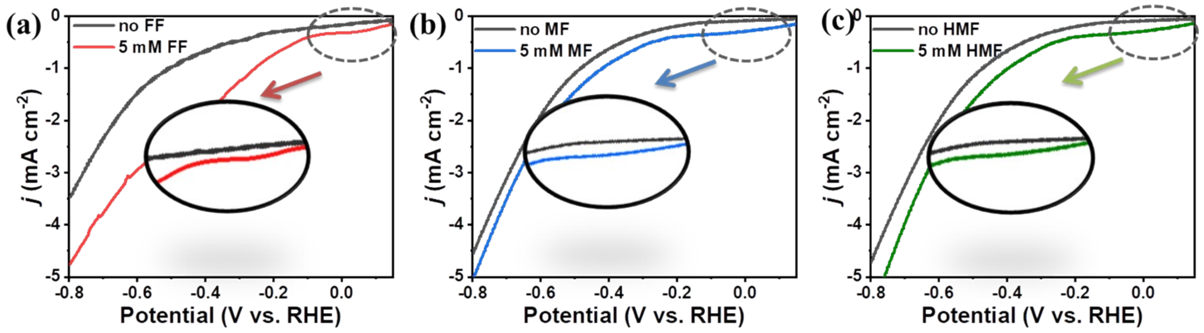

Fig. S6 (a) LSV curves of TiS_2 in 0.7 M ethanolamine electrolyte with and without FF at scan rate 2 mV s^{-1}; Likewise, (b) LSV curves in 5 mM HMF, and in 5 mM MF (c).

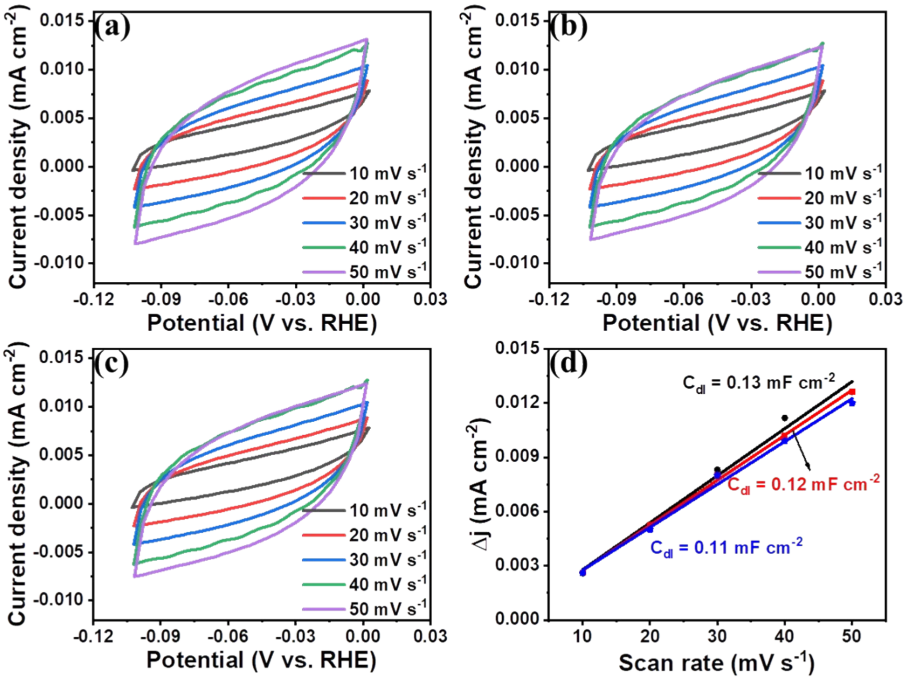

Fig. S7 The polarization curves of TiS_2 in 5 mM FF (a), MF (b), and HMF (c) solution at different scan rates from 10 to 50 mV s^{-1}. (d) Change of current density plotted against the scan rate at -0.05 V_{RHE}.

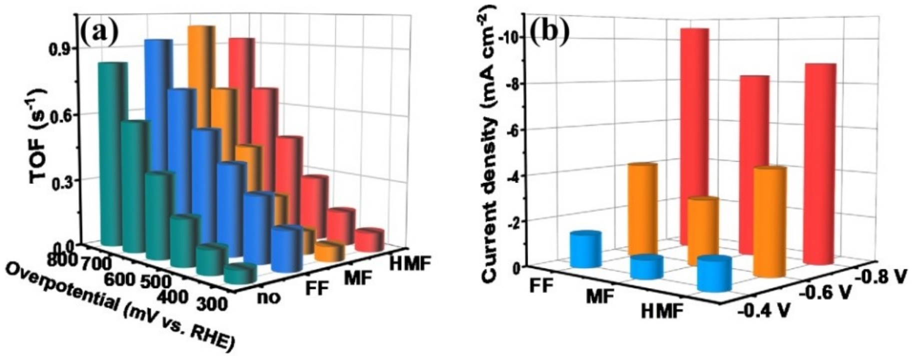

Fig. S8 (a) TOF of the TiS_2 electrode at overpotential of -300, -400, -500, -600, -700, -800 mV. (b) Average current density values (in FF, MF and HMF, respectively) at potentials of -0.4, -0.6, -0.8 V_{RHE} using chronoamperometric tests.

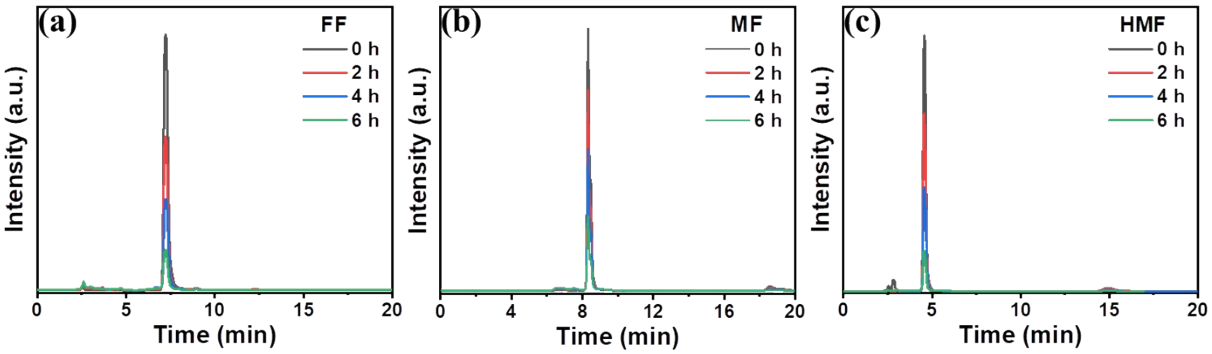

Fig. S9 HPLC chromatogram traces of the various products at different reaction times following ERA of (a) FF, (b) MF, and (c) HMF at -0.6 V_{RHE} (mobile phase solution, 5 mM ammonium formate (70 vol%) aqueous solution and methanol (30 vol%); flow rate, 1.0 mL min^{-1}; temperature: 35 °C).

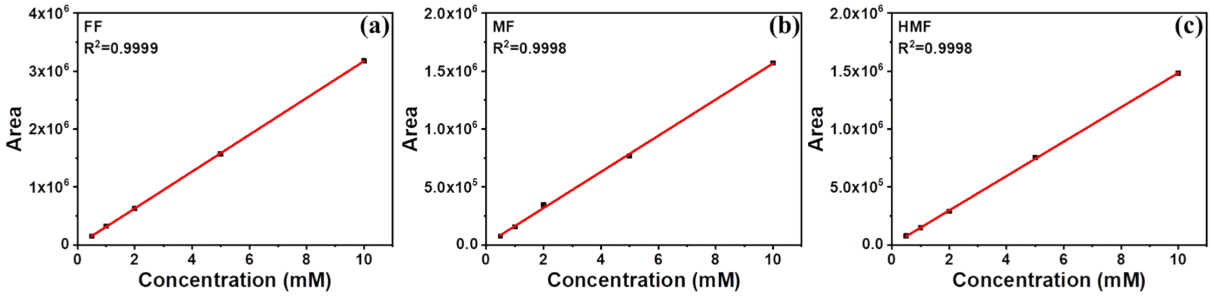

Fig. S10 Standard curves of FF (a), MF (b) and HMF (c) using HPLC.

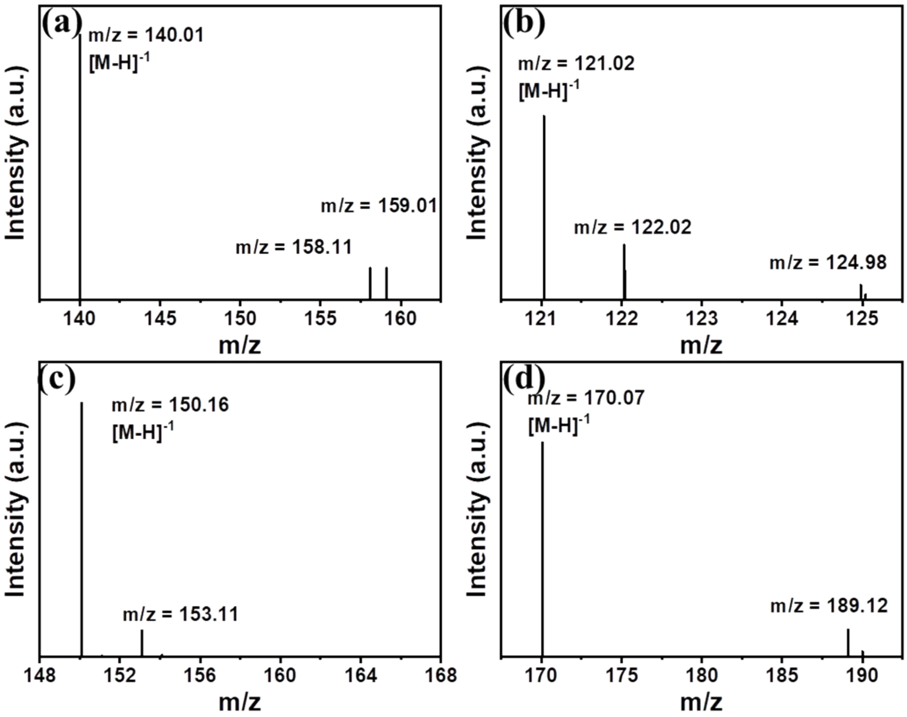

Fig. S11 The mass spectra of the products derived from FF (a, b), MF (c), and HMF (d) over the TiS_2 electrode.

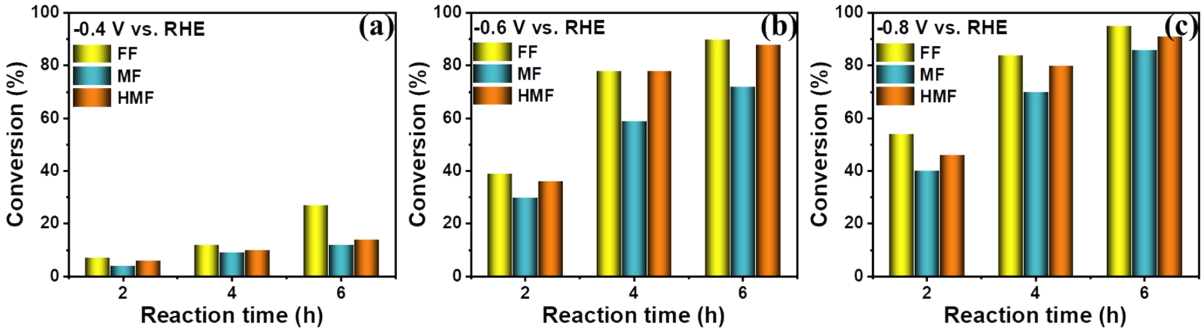

Fig. S12 Conversion of FF (a), MF (b) and HMF (c) over the reaction time at different constant potential influences on the surface of TiS_2 electrode.

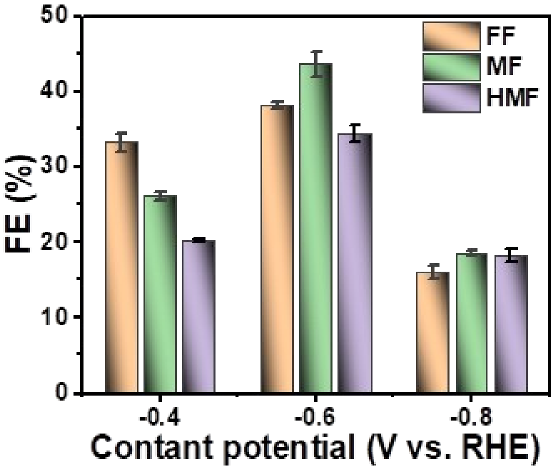

Fig. S13 FE of reductive amination for FF, MF, and HMF with a concentration of 5 mM at different potential over the TiS_2 electrode.

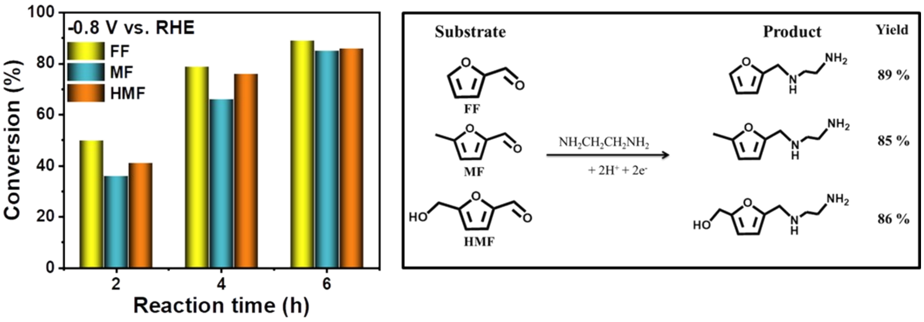

Fig. S14 Conversion (left) of FF, MF, and HMF using a nitrogen source of ethanediamine ($NH_2CH_2CH_2NH_2$) at a potential of -0.8 V_{RHE} on the TiS_2 electrode, and product of electrochemical reductive amination.

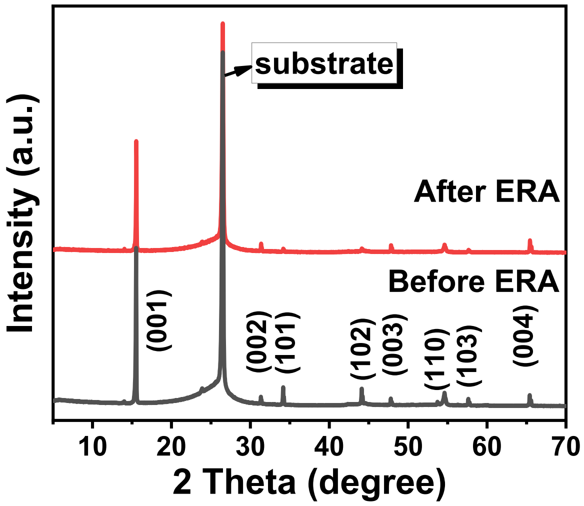

Fig. S15 XRD patterns of TiS_2 electrode before and after reductive amination.

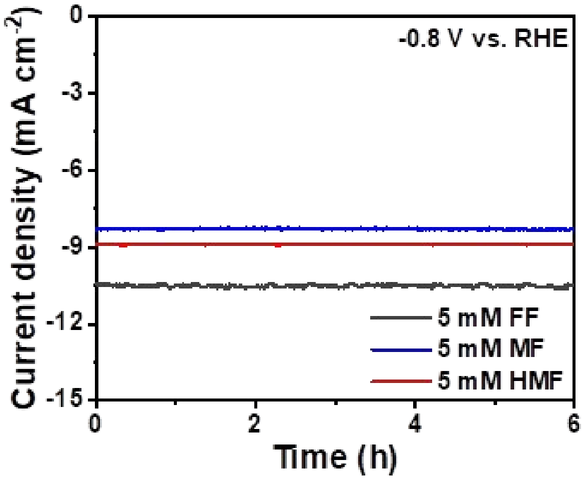

Fig. S16 Chronoamperometric curves (in 5 mM FF, 5 mM MF, 5 mM HMF, respectively) at a constant potential of -0.8 V_{RHE}.

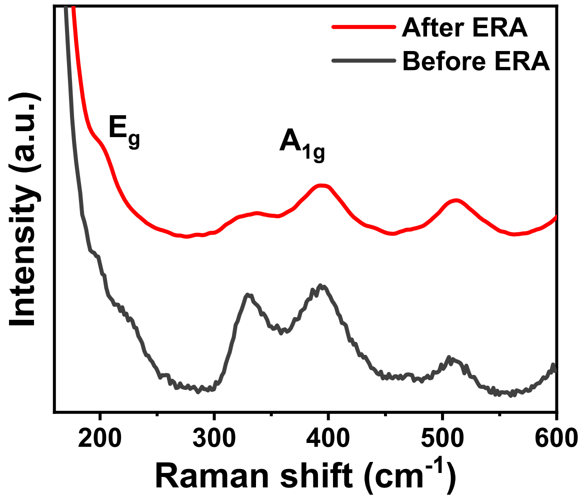

Fig. S17 Raman patterns of TiS_2 electrode before and after reductive amination.

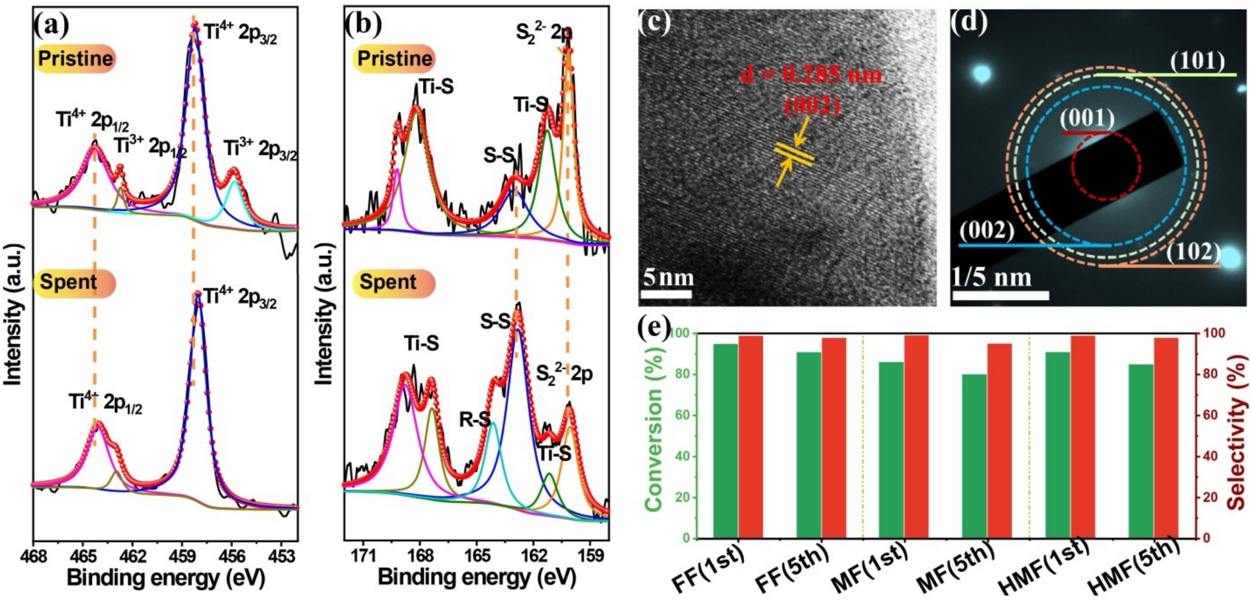

Fig. S18 (a) Ti 2p and (b) S 2p XPS spectra of pristine and spent TiS_2. After undergoing the ERA, XPS spectra were subsequently used to compare the structural changes of the pristine and spent TiS_2. (c, d) HR-TEM images of TiS_2 after the ERA and (e) catalytic performance TiS_2 in 0.7 M ethanolamine containing 5 mM FF, MF, HMF for the ERA. The catalytic performance for ERA-FA was executed using the recycled TiS_2 electrode. Over five cycles of FF, MF and HMF aminations, TiS_2 remained over 90% FF conversion and over 95% selectivity for EMF.

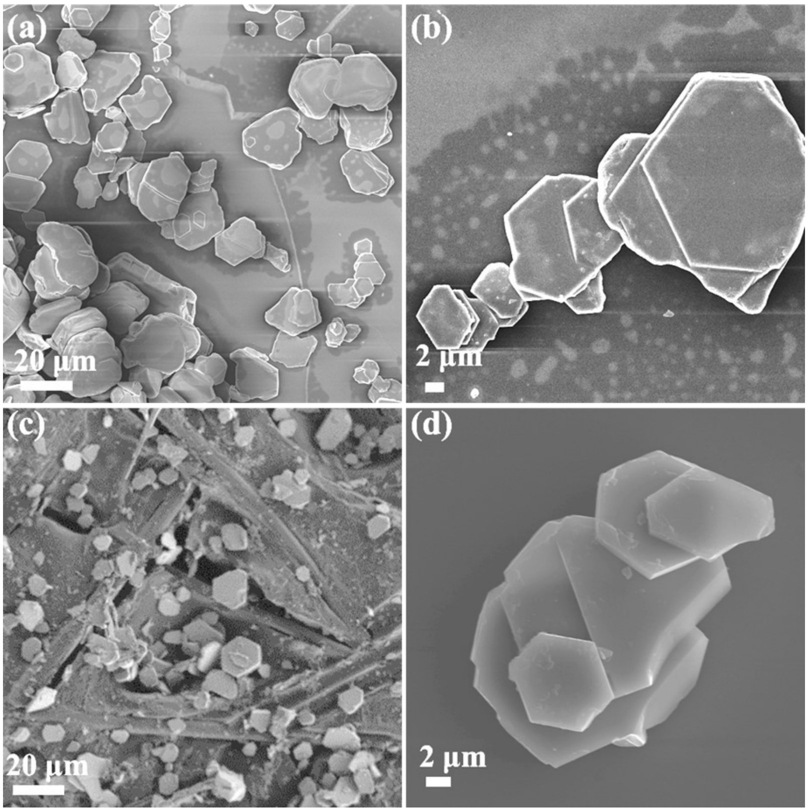

Fig. S19 SEM images of TiS_2 powder (a, b) before reductive amination and TiS_2 electrode (c, d) after reductive amination.

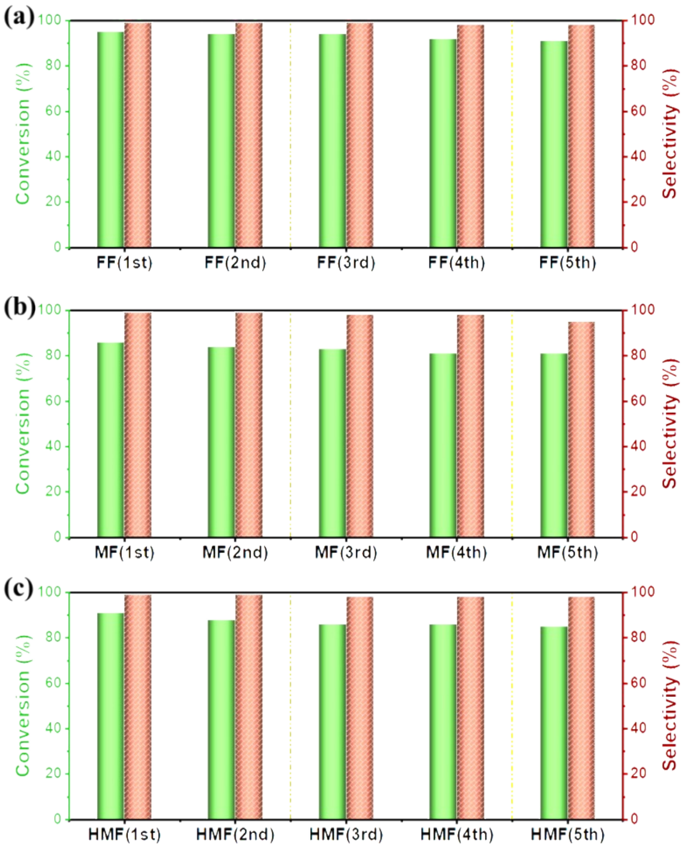

Fig. S20 Catalytic performance TiS_2 in 0.7 M ethanolamine containing 5 mM FF, MF, HMF for the ERA.

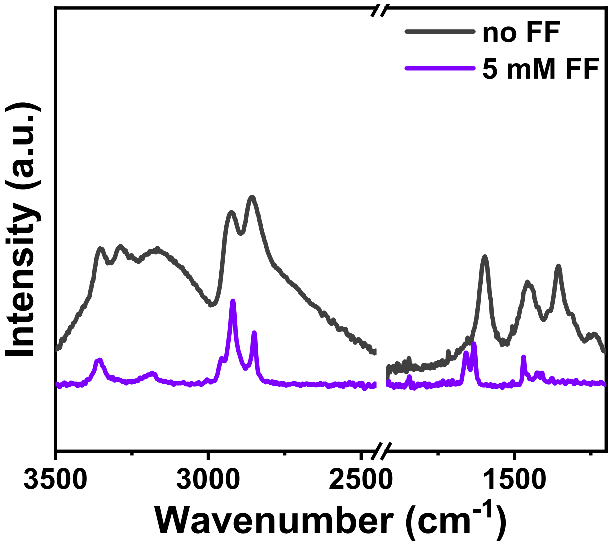

Fig. S21 FT-IR spectra for ethanolamine (no FF) and ethanolamine solution containing 5 mM FF.

Table S1 Local structure parameters around Ti estimated by EXAFS analysis.

Sample	**Absorber - Scatterer**	***N***	***R* (Å)**	**σ^2 (Å^2)**	**E_0 (eV)**	***R* factor**
TiS_2	Ti-S	3.1 (8)	2.43 (2)	0.004 (3)	5 (2)	0.03
TiS_2 standard	Ti-S	4.0 (1)	2.40 (2)	0.004 (3)	1 (3)	0.02

Note: Fitting parameters: S_0^2=0.707 calculated from the foil, fit range $3 < k(Å^{-2}) < 10.5$, $1.4 < R(Å) < 2.5$; number of independent points = 5.1.

Table S2 Results obtained from the electrochemical and traditional reductive amination under various conditions.

Catalysts	**Electrolyde/Atmosphere**	**Potential (V)**	***j* (mA cm^{-2})**	**T (°C)**	**Conv.**	**Sel.**	**MASA**	**Ref.**
Carbon-anode, Pt-cathode	substrate, TFA, H_2O, and n-Bu_4NPF_6 in acetonitrile	1.6 V vs SCE	/	room temperature	>81	/	/	[1]
Zn	0.7 M MEA (pH 11.0) & 0.02 M HMF	-1.3 V vs. AgCl	9.83	room temperature	/	85	/	[2]
Pt	$Et_3N\cdot3HF$ & cyclopropanes & $PhCF_3$	/	7.1	25	/	77	/	[3]
Raney Co catalyst	0.5 g HMF, 1 M H_2 & 0.35 M NH_3	/	/	120	100	99.5	/	[4]
graphite	DMSO-*d*$_6$, 0.3 mM benzaldehyde & 0.6 mM aniline	/	10	room temperature	>98	/	/	[5]
Pd/Al_2O_3 (10 mg)	FF (1.04 mM), $BuNH_2$,, 1 bar H_2, 12 h	/	/	25 °C	99	99	/	[6]
Co@CN-800 (40 mg)	2 mM benzaldehyde,; 1 mM nitrobenzene; 1 MPa N_2; 14 h	/	/	190 °C	100	91	/	[7]
TiS_2	0.7 M ethanolamine & 5 mM FF	-0.8 V vs. RHE	10.52	room temperature	95	> 99	206.9	**This work***
TiS_2	0.7 M ethanolamine & 10 mM FF	-0.8 V vs. RHE	11.32	room temperature	80	> 99	/	**This work***

* Reported values are averages obtained from three or more measurements. Reaction conditions: 0.7 M methylamine buffer (pH 11.0) containing FF at room temperature with 1.0 cm^2 electrodes (geometric area).

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