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# Stabilizing Atomically Dispersed Catalytic Sites on Tellurium Nanosheets with Strong Metal–Support Interaction Boosts Photocatalysis

Li Shi, Xiaohui Ren, Qi Wang, Yunxiang Li, Fumihiko Ichihara, Hongwei Zhang, Yasuo Izumi, Long Ren, Wei Zhou, Yang Yang, and Jinhua Ye\*

The utilization of appropriate supports for constructing single-atom-catalysts is of vital importance to achieve high catalytic performances, as the strong mutual interactions between the atomically dispersed metal atoms and supports significantly influence their electronic properties. Herein, it is reported that atomic cobalt species (ACS) anchored 2D tellurium nanosheets (Te NS) can act as a highly active single-atom cocatalyst for boosting photocatalytic H<sub>2</sub> production and CO<sub>2</sub> reduction reactions under visible light irradiation, wherein Te NS serves as the ideal support material to bridge the light absorbers and ACS catalytic sites for efficient electron transfer. X-ray absorption near-edge structure spectroscopy reveals that the ACS are built by a Co center coordinated with five Co-O bonding, which are anchored on Te NS through one Co-Te bonding. The strong mutual interaction between the Te NS and ACS alters the electronic structure of Te NS, inducing the introduction of intermediate energy states, which act as trap sites to accommodate the photogenerated electrons for promoting photocatalytic reactions. This work may inspire further capability in designing other Te-based single-atom-catalysts for highly efficient solar energy conversion.

#### 1. Introduction

The conversion of abundant and renewable solar energy into valuable chemical fuels is highly desirable to meet current and future energy demand.<sup>[1]</sup> As a promising strategy to harvest and convert solar energy, photocatalysis has attracted considerable attention, because it can produce clean and sustainable fuels in an energy-saving way.<sup>[2,3]</sup> The exploration of appropriate materials as photocatalysts historically guided the development of photocatalysis. Although significant progress has been achieved during the past decades, it still remains challenging to construct highly efficient materials for photocatalysis, largely because of the main intrinsic limitation: fast recombination of photogenerated charge carriers.<sup>[4,5]</sup> The photocatalytic performances can be greatly improved with the assistance of cocatalysts via lowering the overpotential or activation

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energy of the targeted reactions and retarding the recombination of electron-hole pairs.<sup>[6,7]</sup> Noble-metals, such as Au, Pt, and Ru, are extensively investigated as effective cocatalysts to boost photocatalysis, however, their large-scale energy production is greatly limited by their scarcity and high cost.<sup>[8,9]</sup> In recent decades, transition metal-based materials, particularly cobalt and its derivative oxide, phosphide, sulfide, and boride have been proposed as efficient and nonprecious cocatalysts alternative to noble-metals.<sup>[6,7]</sup> The high activity of cobalt-based cocatalysts can be due to their intrinsic catalytic active sites that can lower the overpotential of photocatalytic reactions, as well as the strong interfacial interactions between the semiconductor and the cocatalyst that expedite the charge transfer.<sup>[6]</sup> Reducing the size and dimension of cocatalysts to clusters or even single atoms provides an effective way to further boost the photocatalytic performances by maximizing the amount of exposed active sites, which is emerging as a new research frontier.<sup>[10-14]</sup> The atomically dispersed single metal atoms have high surface energy and are easy to mobile and aggregate during the preparation process, thus an appropriate support material with available anchor sites is required to coordinate/stabilize them.<sup>[15,16]</sup>

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From a perspective of fully exploiting the performances of single atom cocatalysts, two prime factors are of vital importance: i) the efficiency of electron transfer from photocatalysts to atomically dispersed catalytic sites and ii) the mutual metal-support interactions between atomically dispersed metals and supports.<sup>[10,17]</sup> The strong metal-support interactions have significant influences on the electronic structure of single-atom-catalysts, guarantee the charge transfer, and finally improve the catalytic activities and the stability.<sup>[18,19]</sup> Thus, the selection of supports that can produce strong metal-support interactions and facilitate the electron transfer between the photocatalysts and atomically dispersed catalytic sites is significant for achieving efficient photocatalysis. An ideal support material for constructing single atom cocatalysts owns two main features: i) flexible surface and available coordination sites to stabilize atomically dispersed metals and ii) high carrier mobility to guarantee the charge transportation.<sup>[15]</sup> Metal oxide, metal sulfide, graphene, metal-organic frameworks, and g-C<sub>3</sub>N<sub>4</sub> have been intensively investigated as appropriate support materials for anchoring single metal atoms based on M-O, M-S, M-C, and M-N bonding interactions (M refers to metal), which strengthen the stability and improve the catalytic performances.<sup>[10]</sup> However, the recently developed supports cannot fulfill the entire requirements of catalysis community. The exploration of novel supports for producing strong metalsupport interactions and the systematic study of the related mechanism are of vital importance to the practical applications of single-atom-catalysts but remain challenging.

Tellurium (Te) has received tremendous attention as an emerging material because of its intriguing properties, including high carrier mobility, excellent thermo/piezoelectricity, high electronic conductivity, and fast photoresponse.<sup>[20,21]</sup> Those properties guarantee enormous potential applications of Te in electronic devices.<sup>[22]</sup> Te displays a typical chiral-chain-like crystalline structure, which is built with helical Te chains along the direction of the *c*-axis. Every Te atom is covalently bonded with two Te atoms in the same chain, while individual chains are bound together via van der Waals' force into a 2D hexagonal

elementary cell.<sup>[20]</sup> Due to its unique crystal structure, 2D hexagonal Te nanosheets were reported to be obtained via either hydrothermal process or liquid-phase exfoliation method.<sup>[23,24]</sup> In sharp contrast to phosphorene and other environmentsensitive 2D materials, Te exhibits pronounced stability, which renders it more attractive in practical applications.<sup>[25]</sup> Recent studies have revealed that 2D Te displays p-type semiconducting property with tunable bandgaps from 0.35 eV in bulk state to 1 eV in a monolayer.<sup>[21]</sup> The thickness-dependent bandgap and high photoconductivity enable 2D Te promising application in optoelectronics. In addition, 2D Te with abundant surface Te sites is a promising support to readily immobilize other elements, such as transition metals, to form functionalized 2D Te materials. The utilization of 2D Te or its functionalized materials as cocatalysts in photocatalysis is promising but has not been explored yet.

Herein, we demonstrate a facile method to stabilize the atomic cobalt species (ACS) on the Te NS, and apply it as a novel and highly active cocatalyst for boosting photocatalytic H<sub>2</sub> production and CO<sub>2</sub> reduction reactions. The extended X-ray absorption fine structure (EXAFS) spectra confirm the homogeneous dispersion of ACS on the Te NS. The coordination between the Te NS support and ACS can not only strongly immobilize monodispersed ACS but also affect the electronic structure of Te NS. The functionalization of Te NS by ACS introduces intermediate energy states below the conduction band position of Te NS, which act as trap sites to accommodate the photogenerated electrons, and promote charge separation and transfer. The photocatalytic performance evaluations indicate that ACS functionalized Te NS (Te NS-ACS) shows a dramatically enhanced visible-light photocatalytic H<sub>2</sub> production rate of 130.8  $\mu$ mol h<sup>-1</sup> in the presence of Eosin Y (EY) as light absorber, and CO production rate of 52.3 µmol h<sup>-1</sup> in the presence of Tris(2,2'-bipyridyl)dichlororuthenium(II) ([Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>) as light absorber, representing the state-ofthe-art noble-metal-free cocatalyst.

#### 2. Results and Discussion

The rationale for the proposed concept of using 2D Te as a support material is that the abundant surface Te sites can coordinate readily with the Co atom through Co-Te bonding in order to prevent the ACS aggregation. Moreover, Te with high electronic conductivity (2 × 10<sup>2</sup> S m<sup>-1</sup>)<sup>[26]</sup> can serve as an electron relay to facilitate the electron transfer between ACS catalytic sites and light absorbers, which fulfils the criteria for ideal supports. Figure 1a illustrates the synthetic process of Te NS-ACS. First of all, the Te NS was prepared from the liquid exfoliation of bulk Te in 1-methyl-2-pyrrolidinone (NMP) solution. As characterized by atomic force microscopy (AFM, Figure S1, Supporting Information), the measured 2D Te NS has size distributions in a broad range from around 20 to 70 nm. Much smaller Te NS with lateral dimensions in several nanometers is also observed. The measured thickness of Te NS varies from 2.0 to 8.2 nm. The transmission electron microscopy (TEM) image in Figure S2a of the Supporting Information further confirms the nanoscale size of Te NS. The high-resolution transmission electron microscopy (HRTEM) image in Figure S2b of

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Figure 1. a) The illustration of the process to fabricate Te NS-ACS. b) AFM and the corresponding thickness distribution of randomly measured Te NS-ACS. c) TEM and HRTEM images of Te NS-ACS. d) XRD patterns, e) Raman spectra, and f) UV-vis absorption spectra of bulk Te, Te NS, and Te NS-ACS.

the Supporting Information shows a lattice spacing of 0.32 nm, which is ascribed to the (101) plane of Te.<sup>[24]</sup> Then, the Te NS reacted with  $CoCl_2 \cdot 6H_2O$  to obtain Te NS-ACS. The loading amount of Co on Te NS is 1.5 wt% measured by ICP-AES. Figure 1b shows the AFM image and its corresponding thickness distribution of six randomly measured Te NS-ACS. It can be seen that the randomly measured thickness of nanosheets varies from 1.5 to 7.3 nm, which is similar to the pristine Te NS, indicating the thickness of Te NS remains almost unchanged after ACS functionalization. The as-obtained Te NS-ACS shows a diameter of tens of nanometers, and the lattice spacing of 0.32 nm can be attributed to the (101) plane of Te (Figure 1c; Figure S3, Supporting Information).

X-ray diffraction (XRD) patterns were measured to investigate the crystal structures of samples. As shown in Figure 1d, bulk Te shows a standard hexagonal crystalline structure, matching well with the references.<sup>[24,27]</sup> The as-prepared 2D Te NS and Te NS-ACS exhibit the same hexagonal structure, confirming that the crystal structure of 2D Te is unchanged after exfoliation and ACS functionalization. No peaks corresponding to CoO or Co are observed. The Raman spectra in Figure 1e show that the bulk Te exhibits vibration peaks centered at 119.2 and 145.1 cm<sup>-1</sup>, ascribing to the A<sup>1</sup> and E<sub>2</sub> phonon modes, respectively.<sup>[28]</sup> Te NS shows red-shift of E<sub>2</sub> and blue-shift of A<sup>1</sup> compared with bulk Te, reaching 140.7 and 122.1 cm<sup>-1</sup>, respectively. The red-shift of the E<sub>2</sub> mode is attributed to the length elongation of the covalent bond between two adjacent Te atoms and weakening of the interatomic interactions, while the blue-shift of A<sup>1</sup> is caused by the equilateral triangle projection increasing on basal plane, which is perpendicular to the *c*-axis of the Te chain.<sup>[28]</sup> For the Te NS-ACS, the A<sup>1</sup> and E<sub>2</sub> peaks, located at 122.2 and 141.9 cm<sup>-1</sup>, respectively, exhibit minor blueshifts as compared to the pristine Te NS, further confirming that the hexagonal crystalline structure of 2D Te is unchanged after ACS functionalization. The optical properties of samples were recorded by ultraviolet-visible (UV-vis) diffuse reflectance spectra. As shown in Figure 1f, bulk Te exhibits a very broad absorption from the UV to near-infrared (NIR) region with a typical absorption peak located at 250.9 nm, which is due to the p-bonding to p-antibonding bands interband transitions.<sup>[29]</sup> The Te NS shows an improved light absorption ability than its bulk phase, with a very strong absorption tail from the visible to NIR region, which is due to the weaker electronic band dispersion of Te NS than that of bulk Te.<sup>[29]</sup> The bandgaps of samples were calculated according to transformed Kubelka-Munk function as shown in Figure S4 of the Supporting Information. The bandgap of bulk Te is 0.37 eV, which is similar to the reported value of bulk Te.<sup>[21]</sup> The bandgap of Te NS increases to 0.71 eV, which is ascribed to the quantum confinement effect induced by reducing the layer numbers in Te.<sup>[21]</sup> The calculated bandgap of Te NS-ACS decreases to 0.61 eV as compared to the Te NS, owing to the increase in the carrier concentration by the introduction of ACS and the creation of energy levels in the bandgap. The flat-band (FB) potentials for Te NS and Te NS-ACS are +0.22 V versus NHE and +0.13 V versus NHE, respectively (Figure S5, Supporting Information). Considering



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**Figure 2.** a) Co K-edge XANES spectra and b) the associated Fourier transform  $k^3$ -weighted EXAFS spectra for Co metal, CoO, CoTe<sub>2</sub>, and Te NS-ACS. Best-fit results in k- and R-space of c) Co–O and d) Co–Te for Fourier-filtered EXAFS data of Te NS-ACS.

the small difference between the FB potential and the higher valence band edge for p-type semiconductor, the estimated band positions of Te NS with and without ACS functionalization are shown in Figure S5 of the Supporting Information, which indicates that the conduction band minimum potentials of Te NS and Te NS-ACS can reach the  $H_2$  evolution energy level.

To probe the chemical environment of Co element in the Te NS-ACS, the Co K-edge EXAFS and X-ray absorption near-edge structure (XANES) spectroscopies were measured. Figure 2a shows the normalized XANES spectra collected at Co K-edge for Co metal, CoO, CoTe<sub>2</sub>, and Te NS-ACS. The Co K-edge of Te NS-ACS sample displays a similar near edge structure to that of CoO, indicating the presence of bivalent Co. The detailed coordination environment of Co was further investigated by the Fourier transform of EXAFS spectra. The first major peak in the EXAFS spectra of Te NS-ACS (Figure 2b) shows that Co atoms are coordinated with O nearest neighboring shell locates at 1.57 Å, referring to the peak of Co-O bonding in CoO. The second major peak can be attributed to Co-Te bonding that Co atoms are coordinated by Te nearest neighboring shell at 2.37 Å, which is well consistent with data for CoTe<sub>2</sub> reference sample, indicating that Co atoms interact with Te NS through Co-Te bonding. As compared to the EXAFS spectra of Co metal foil, the signal at 2.19 Å is absent in Te NS-ACS, which excludes the existence of Co-Co coordination bonding. Moreover, comparing with CoO, the Co-O-Co coordination bonding is also absent in the Te NS-ACS sample, demonstrating that the Co atom exists as the single-atom structure to bond with O and Te. The coordination numbers of the nearest-neighbor O and Te atoms surrounding the single Co atom are estimated to be 4.8 and 0.92, respectively, according to the EXAFS curve fitting analysis (Figure 2c,d; Table S1, Supporting Information). Based on above information, the atomic geometry structure of Te NS-ACS is built by the density functional theory (DFT) simulation, in which the Co center is coordinated with five Co–O bonding and one Co–Te bonding, and the optimized atomic structure model is described in **Figure 3**a.

DFT calculations were further performed to reveal the influence of ACS functionalization on the electronic structure of Te NS. Figure 3a,b shows the calculated density of states (DOS) of Te NS-ACS and Te NS, respectively. It can be seen that the total DOS of Te NS-ACS exhibit an upward shift of valence band minimum (0.08 eV) toward the Fermi level with respect to that of Te NS, leading to a narrower bandgap and easier excitation of charge carriers. The ACS are anchored on Te NS through Co-Te bonding, and due to the low orbital level of ACS, the orbital hybridization between the ACS and Te atoms would result in new intermediate energy states in the bandgap of Te NS. As shown in Figure 3a, intermediate energy states composed of Te 5p, Co 3d, and O 2p orbits appear below the conduction band (CB) of Te NS-ACS. The intermediate energy states act as trap sites to accommodate the photogenerated electrons, promoting charge separation and transfer. The charge density distributions of Te NS-ACS interface are shown in Figure 3c,d. ACS and Co-Te bonding exhibit stronger charge density than

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Figure 3. a) The optimized atomic structure model for Te NS-ACS, and the corresponding calculated DOS. b) The single-layer model structure of Te, and the corresponding calculated DOS. c) 3D and d) 2D charge density distributions of Te NS-ACS.

Te NS, indicating the strong mutual interaction between ACS and Te NS, and the generated Co—Te bonding induces the efficient charge transfer from Te NS to ACS. Figure S6 of the Supporting Information shows the electrochemical impedance spectrum of Te NS and Te NS-ACS, which experimentally proves the decreased electron transfer resistance of Te NS after ACS functionalization.

The photocatalytic performances of Te NS with and without ACS functionalization were first investigated for H<sub>2</sub> evolution under visible light irradiation using EY light absorber and triethanolamine (TEOA) sacrificial agent. As shown in Figure 4a,b, the H<sub>2</sub> evolution is not observed for pure Te NS with and without ACS functionalization in the absence of EY under visible light. Pure EY shows a very moderate H<sub>2</sub> evolution rate of 10.1  $\mu$ mol h<sup>-1</sup>, while the H<sub>2</sub> evolution activity is enhanced upon adding Te NS into the reaction system, suggesting the cocatalytic effect of Te NS for photocatalytic H<sub>2</sub> evolution. Te NS is a more effective cocatalyst than bulk Te for promoting photocatalytic H<sub>2</sub> evolution in the presence of EY (Figure S7, Supporting Information). When using Te NS-ACS as a cocatalyst in the system, the photocatalytic H<sub>2</sub> evolution activity can be significantly improved to an evolution rate of 130.8 µmol h<sup>-1</sup>. In addition, Te NS-ACS is much more effective than Te NS-Co<sup>2+</sup> for promoting photocatalytic H<sub>2</sub> evolution (Figure S8, Supporting Information). These results indicate that the ACS play a dominant role for improving the photocatalytic H<sub>2</sub> evolution. The measured CB position of Te NS-ACS is slightly above the potential required for H<sub>2</sub> evolution, thus the electrons on the CB position of Te NS-ACS have very weak reduction ability to produce  $H_2$ , and the high activity of Te NS-ACS is mainly ascribed to the atomic cobalt species active sites, which can accumulate electrons to promote  $H_2$  evolution. The obtained photocatalytic  $H_2$  evolution rate by Te NS-ACS cocatalyst is superior to those of the majority of reported noblemetal-free cocatalysts in EY sensitized photocatalytic reaction systems (Table S2, Supporting Information).<sup>[30–35]</sup> The photocatalytic stability of Te NS-ACS for  $H_2$  evolution was also examined. As shown in Figure 4c, continuous  $H_2$  production is observed with no obvious decrease in the subsequent runs, indicating that the Te NS-ACS acts as a stable cocatalyst for photocatalytic  $H_2$  evolution.

Noting that the charge transfer is a crucial fact that contributes to the improvement of the photocatalytic performance, photoluminescence (PL) spectroscopy is first utilized to reveal the charge transfer kinetics. As shown in Figure S9 of the Supporting Information, EY in aqueous solution shows a strong emission peak at 580.3 nm upon excitation at 400 nm. After dispersing Te NS and Te NS-ACS into EY solution, the PL is significantly quenched, indicating a promoted electron transfer from photoexcited EY to Te NS and Te NS-ACS. The PL intensity follows the order: pure EY > EY/Te NS > EY/Te NS-ACS, revealing that the electron transfer from EY to Te NS-ACS is more efficient than that from EY to Te NS. The time-resolved PL decay measurements were further employed to study the electron transfer kinetics. The decay spectra together with the corresponding lifetime calculated by the biexponential analysis





**Figure 4.** a) Time-dependent  $H_2$  evolution and b) comparison of  $H_2$  evolution activities under different conditions. c) Cycling test of EY/Te NS-ACS for photocatalytic  $H_2$  evolution. d) Proposed mechanism of EY/Te NS-ACS for photocatalytic  $H_2$  evolution.

are shown in Figure S10 of the Supporting Information. The PL lifetime follows in the order: pure EY > EY/Te NS > EY/Te NS-ACS. A shortened average lifetime is observed for EY in the presence of Te NS and Te NS-ACS, demonstrating the electron transfer from excited EY to Te NS and Te NS-ACS. It also indicates that the electron transfer from EY to Te NS-ACS is more efficient than that from EY to Te NS, as EY/Te NS-ACS shows the shortest PL lifetime. The improved electron transfer efficiency is largely due to the fact that the ACS sites can serve as trap sites to capture electrons from photoexcited EY. The mechanism of photocatalytic H<sub>2</sub> production for the EY-photosensitized Te NS-ACS system is shown in Figure 4d based on the above results and previous reports of EY-sensitized systems.<sup>[34,35]</sup> Under visible light irradiation, the EY can be excited to produce EY1\* (singlet excited state), followed to generate the EY<sup>3\*</sup> (lowest-lying triplet excited state) through an intersystem crossing process, yielding (EY+• EY--) radical pairs. Then, EY+• is reductively quenched back to EY by electron donor TEOA. The redox potential of EY<sup>1\*</sup>/EY<sup>+•</sup> is -1.1 V versus NHE,<sup>[36]</sup> which is much higher than the CB potential of Te NS-ACS, enabling the electrons transfer from photoexcited EY to the CB and the ACS intermediate energy level of Te NS-ACS, and finally initiate the H<sub>2</sub> evolution.

In an attempt to extend the applications of the constructed Te NS-ACS cocatalyst to other photocatalytic reactions, the photocatalytic  $CO_2$  reduction reactions were evaluated. The reactions were conducted under mild reaction conditions (ambient temperature and pressure), and a typical visible-light-active photosensitizer [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> was chosen as the light absorber and charge generator.<sup>[37,38]</sup> The setup of the system is shown in Figure S11 of the Supporting Information. The main products

detected in this system are CO and H<sub>2</sub>, and no CH<sub>4</sub> or liquid products evolution is observed, which is the same with the previously reported systems.<sup>[38]</sup> The time-dependent photocatalytic activity of Te NS-ACS photosensitized by [Ru(bpy)3] Cl<sub>2</sub> is shown in Figure S12 of the Supporting Information. The evolution rates for CO and H<sub>2</sub> decrease after 1 h continuous testing, which is largely ascribed to the photobleaching of the [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> photosensitizer.<sup>[37-39]</sup> Figure 5a summarizes the CO and H<sub>2</sub> evolution performances from photocatalytic CO2 reduction under various reaction conditions for 2 h. The bare [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> only exhibits the CO evolution amount of 4.5  $\mu$ mol and H<sub>2</sub> evolution amount of 6.7  $\mu$ mol, and the bare Te NS is inactive in photocatalytic CO<sub>2</sub> reduction reaction. When Te NS was added into the system, the evolution amount of H<sub>2</sub> slightly increased while the generation of CO was suppressed. This result indicates that the Te NS is not a promising cocatalyst for photocatalytic CO2 reduction, largely due to the low CB position (-0.49 V vs NHE, pH = 7) that cannot trigger the  $CO_2$  to CO conversion reaction ( $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ ,  $E_{redox}^0 = -0.53$  V vs NHE at pH 7). Interestingly, when Te NS-ACS was introduced into the system, dramatically improved CO and H<sub>2</sub> evolutions were observed, reaching 104.5 and 84.9 µmol within 2 h, respectively. The obtained CO evolution rate outperforms the state-of-the-art catalysts under comparable conditions (Table S3, Supporting Information).[37-43] The CO and H<sub>2</sub> evolutions are completely terminated in the absence of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, indicating the cocatalytic effect of Te NS-ACS in the photocatalytic  $CO_2$  reduction reaction. Apparently, it is the ACS that acts as the active site for superior CO and H<sub>2</sub> evolution. Even though the reduction potential of the CO formation is as negative as -0.53 V versus NHE at pH 7, which is

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**Figure 5.** a) CO and H<sub>2</sub> evolution from photocatalytic CO<sub>2</sub> reduction under different conditions (the reaction time is 2 h). b) Cycling test of  $[Ru(bpy)_3]$ Cl<sub>2</sub>/Te NS-ACS for photocatalytic CO<sub>2</sub> reduction, and each cycle is conducted for 2 h. c) GC-MS of <sup>13</sup>CO generated in the photocatalytic reduction of <sup>13</sup>CO<sub>2</sub> over  $[Ru(bpy)_3]Cl_2/Te$  NS-ACS. d) Proposed mechanism for photocatalytic CO<sub>2</sub> reduction over  $[Ru(bpy)_3]Cl_2/Te$  NS-ACS.

not energetically accessible for Te NS-ACS (CB position locates at -0.48 V vs NHE at pH 7), we propose that the ACS intermediate energy states with abundant localized electrons transferred from [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> are beneficial for lowering the energy barrier to activate CO<sub>2</sub> molecules. Similar mechanisms were reported in other photocatalyst systems such as TiO<sub>2</sub>, WO<sub>3</sub>, and Bi-based semiconductors with defective energy states for the reduction of CO<sub>2</sub> and N<sub>2</sub>.<sup>[44-46]</sup>

To reveal the photocatalytic  $CO_2$  reduction process in  $[Ru(bpy)_3]Cl_2/Te$  NS-ACS system, in situ Fourier transform infrared spectroscopy (FTIR) was employed. As is known to all, photocatalytic reduction of  $CO_2$  to CO proceeds through the generation of a formate intermediate (COOH\*) via the

reaction equation  $CO_2^* + H^+ + e^- \rightarrow COOH^{*,[40]}$  As shown in Figure S13a of the Supporting Information, the strong peak located at 2331 cm<sup>-1</sup> is attributed to the absorbed  $CO_2^{,[47]}$  The broad absorption peak centered at 1520 cm<sup>-1</sup> corresponds to the carbonate-type species, which are derived from the adsorbed formate (COOH\*) intermediate.<sup>[47]</sup> In addition, the broad absorption peak centered at 1725 cm<sup>-1</sup> is ascribed to the asymmetric stretching of O–C=O, which is also derived from the formate species.<sup>[48]</sup> The intensities of these peaks gradually increase with the increase of light irradiation time, demonstrating the generation of formate intermediate over the [Ru(bpy)\_3]Cl\_2/Te NS-ACS photocatalytic CO<sub>2</sub> reduction system. The formate intermediate originates from the CO<sub>2</sub> activation

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during photocatalytic CO<sub>2</sub> reduction reaction. The COOH\* intermediate is then converted to CO\* according to the reaction equation COOH\* +H<sup>+</sup> + e<sup>-</sup>  $\rightarrow$  CO\* + H<sub>2</sub>O, and the final product CO is produced from the dissociation of the CO\*.<sup>[40]</sup> In sharp contrast, when Te NS is used as cocatalyst in the reaction system, no obvious peaks correspond to the formate intermediate are observed (Figure S13b, Supporting Information). The in situ FTIR characterization clearly demonstrates that the intermediate energy states induced by ACS can lower the energy barrier for activating CO<sub>2</sub> molecules.

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The stability of Te NS-ACS for photocatalytic CO<sub>2</sub> reduction was then evaluated. As shown in Figure 5b, the recycled Te NS-ACS cocatalyst retains 93.3% of the original activity after four runs, indicating the good stability for photocatalytic CO<sub>2</sub> reduction. The XRD pattern of Te NS-ACS after photocatalytic CO<sub>2</sub> reduction is also recorded, which shows no obvious change of crystal structure (Figure S14, Supporting Information). The evolution of CO is not detected under either Ar or without light, showing that the CO product indeed comes from the photocatalytic CO<sub>2</sub> reduction. To validate the carbon source of the generated CO, isotopic experiment was conducted in the [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>/Te NS-ACS system by using <sup>13</sup>CO<sub>2</sub>. The generated gas products were analyzed by gas chromatogram (GC) and mass spectra (MS). As shown in Figure 5c, the CO product is detected at the GC retention time of 6.15 min, and the other two peaks before CO in GC spectrum are proved to be O2 and N2, which come from the remained air in the sampling needle. The analysis of CO product gets the m/z = 29 in MS, which is ascribed to the <sup>13</sup>CO, clearly confirming that the CO generates from CO<sub>2</sub> conversion. The proposed mechanism for the [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> related photocatalytic CO<sub>2</sub> reduction process is shown in Figure 5d. Under visible light irradiation, the light absorber [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> is promoted to the excited state [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>\*, which is then directly quenched to produce electrons and  $[Ru(bpy)_3]^{3+}$ . The generated electrons can be transferred to the CB and the ACS intermediate energy level of Te NS-ACS due to the high redox potential of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>  $(E^{0}[Ru(bpy)_{3}]Cl_{2}^{*}/[Ru(bpy)_{3}]^{3+} = -1.33 V \text{ vs SCE}).^{[49]}$  Then, the CO2 molecules and H<sup>+</sup> absorbed on the surface of Te NS-ACS are reduced to CO and H<sub>2</sub>. The oxidized state of the  $[Ru(bpy)_3]^{3+}$ is simultaneously reduced back to [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> by the sacrificial electron donor (TEOA).

#### 3. Conclusion

In summary, Te NS-ACS was rationally prepared and investigated as a novel and efficient noble-metal-free cocatalyst to boost the photocatalytic H<sub>2</sub> evolution and CO<sub>2</sub> reduction performances. Specifically, a stable and high photocatalytic H<sub>2</sub> production rate of 130.8  $\mu$ mol h<sup>-1</sup> was achieved by applying Te NS-ACS as cocatalyst and EY as light absorber, outperforming that of the majority of reported noble-metal-free cocatalysts in a similar system. Besides, the newly developed Te NS-ACS can also be applied as an effective cocatalyst to promote the photocatalytic CO<sub>2</sub> reduction reaction in the presence of [Ru(bpy)<sub>3</sub>] Cl<sub>2</sub> as light absorber with a CO evolution rate of 52.3  $\mu$ mol h<sup>-1</sup>, outperforming that of the state-of-the-art catalysts under comparable conditions. The high performance of Te NS-ACS

can be ascribed to the fact that the strong mutual interaction between the Te NS support and ACS alters the electronic structure of Te NS, leading to the introduction of intermediate energy states, which act as trap sites to accommodate the photogenerated electrons, promoting charge separation and transfer. This study adds a new class of 2D Te-based nanomaterials into the large family of noble-metal-free cocatalysts, and opens up new possibilities in the emerging field of solar energy conversion.

#### 4. Experimental Section

Preparation of Te Nanosheets: Te nanosheets were prepared by using a liquid exfoliation method. Typically, 0.5 g of bulk Te (purchased from Sigma-Aldrich) was added into 50 mL NMP solution. The exfoliation process was carried out on microtip probe ultrasonication (Branson Sonifier advanced 250) at an output power level 5 and duty cycle 50% cooled by ice water. After exfoliation for 2 h, the Te nanosheets solution was obtained after being centrifuged at 4000 rpm for 5 min in order to remove the residual bulk Te. After that, Te nanosheets were obtained by further centrifugation at 18 000 rpm for 10 min. The obtained Te nanosheets were washed with ethanol for three times, and dried in vacuum at 50 °C.

Preparation of Te NS-ACS: The obtained Te nanosheets were mixed with CoCl<sub>2</sub>·6H<sub>2</sub>O (5 wt% Co) directly in 5 mL of ethanol. The mixture was ground in agate mortar until dried, then the Te nanosheets CoCl<sub>2</sub>·6H<sub>2</sub>O precursor sample was put into a quartz boat and heated in the quartz tube furnace at 300 °C for 2 h in Ar. The final samples were collected after cooling down to room temperature and washed with water for several times to remove the unreacted CoCl<sub>2</sub>·6H<sub>2</sub>O, and dried in vacuum at 50 °C. The loading amount of Co on Te NS was 1.5 wt% measured by ICP-AES.

Photocatalytic  $H_2$  Evolution: 10 mg of Te NS or Te NS-ACS cocatalysts, 30 mg of EY, and 280 mL aqueous solution with 30 mL of triethanolamine were added in a glass reaction cell, and then the reaction cell was connected to a glass-closed reaction system. During the photocatalytic reaction, a gas circulation pump was utilized to cycle the gas in the reaction system. Before light irradiation, the air in the reaction solution was completely removed by evacuation. The visible light source was applied by a 300 W Xe lamp coupled with a UV-light cutoff filter (L42,  $\lambda > 420$  nm). The amount of  $H_2$  was determined by using a gas chromatograph (GC-8A, Shimadzu Co., Japan) with pure Ar carrier gas. The cycling experiment was carried out as follows. The used Te NS-ACS cocatalyst was obtained by centrifugation and then washing with water for three times, followed by redispersing in a fresh reaction solution (30 mg of EY, 280 mL solution containing 30 mL of triethanolamine) for the next cycling test until a total of 4 cycles.

Photocatalytic CO2 Reduction: The photocatalytic CO2 reduction reactions were conducted in a liquid-solid reaction mode in a 100 mL quartz reactor under ambient conditions, and the setup of the experiment is shown in Figure S11 of the Supporting Information. Typically, 10 mg of Te NS or Te NS-ACS cocatalysts, 30 mg of Tris(2,2'bipyridyl)dichlororuthenium(II) (commercially obtained from Sigma-Aldrich), 6 mL of water, 18 mL of acetonitrile (MeCN), and 6 mL of triethanolamine were dispersed in a guartz reactor. The reaction solution was sonicated for a while to obtain well-dispersed solution. Then the reactor was connected to a glass-closed reaction system, followed by evacuating completely (no O2 or N2 can be detected). After that, the airtight system was filled with about 101 kPa pure CO<sub>2</sub> gas. The visible light source was applied with a 300 W Xe lamp coupled with a UV cutoff filter (L42 filter,  $\lambda$  > 420 nm), and a cooling water filter was set between light and reactor. The evolved amount of H<sub>2</sub> and CO gas products were detected and analyzed by using gas chromatography (GC-8A, Shimadzu Co., Japan) and (GC-14B, Shimadzu Co., Japan), respectively. The isotope-labeled experiment was carried out by using  $^{13}\text{CO}_2$  instead

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of  ${}^{12}\text{CO}_2$ , while keeping other conditions unchanged, and the products were detected and analyzed by GC-MS (JEOL-GCQMS, JMS-K9, and 6890N Network GC). The cycling experiment was carried out as follows. The used Te NS-ACS cocatalyst was obtained by centrifugation and then washing with MeCN for three times, followed by redispersing in a fresh reaction solution (30 mg of Tris(2,2'-bipyridyl)dichlororuthenium(II), 6 mL of water, 18 mL of MeCN, and 6 mL of TEOA) for the next cycling test until a total of 4 cycles.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

### Keywords

cocatalysts, photocatalysis, single-atom-catalysts, tellurium nanosheets

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