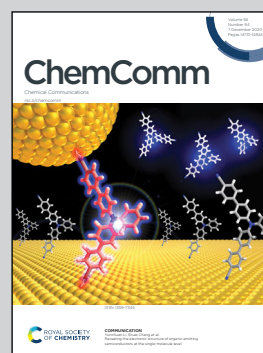


Showcasing research from Professor Li Wang's group at Dalian Maritime University, China and Professor Xin Tu's group at the University of Liverpool, UK

Plasma-enhanced direct conversion of CO_2 to CO over oxygen-deficient Mo-doped CeO_2

Plasma-catalytic direct splitting of CO_2 to CO over oxygen-deficient Mo-doped CeO_2 at ambient conditions was achieved. Developing new catalytic technologies involving plasma opens the door to unlocking the potential of using captured CO_2 to make valuable chemicals under mild conditions.

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Plasma-enhanced direct conversion of CO₂ to CO over oxygen-deficient Mo-doped CeO₂†

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Plasma CO₂ splitting to CO over oxygen-deficient Mo-doped CeO₂ under mild conditions was investigated for the first time, showing ~20 times higher CO₂ conversion compared to pure CeO₂, which can be attributed to the increased oxygen vacancies (V_O) and the formation of Ce³⁺–V_O–Mo on the catalyst surface. Importantly, V_O sites showed excellent catalytic stability.

Converting CO₂ to value-added fuels and chemicals has been considered as a promising route in CO₂ utilization. Significant efforts have been devoted to the chemical transformation of CO₂, including thermal catalysis,¹ photocatalysis,^{2,3} electrocatalysis,^{4,5} and plasma catalysis.^{6,7} Direct splitting of CO₂ to CO without using any reductant is attractive for CO₂ conversion, as CO is an important chemical feedstock for the synthesis of a range of chemicals and fuels. However, this reaction has to overcome a strong thermodynamic barrier (CO₂ → CO + 1/2O₂, ΔH_{298K} = 280 kJ mol^{−1} = 2.9 eV molecule^{−1}) to break the C=O bond, since CO₂ is very stable. Ultrahigh temperatures (2000 K) are often required to activate CO₂ (Fig. S1, ESI†).

In recent years, using non-thermal plasmas (NTPs) for the activation of inert molecules with strong chemical bonds (e.g., CO₂, CH₄ and N₂) under mild conditions has attracted significant interest, including CO₂ reforming with CH₄ to oxygenates,^{8,9} CO₂ hydrogenation to methanol,¹⁰ and ammonia synthesis.¹¹ NTP is rich in energetic electrons with a typical energy of 1–10 eV, which is sufficient to activate reactants into chemically reactive species, enabling thermodynamically unfavorable reactions (e.g. CO₂ splitting) to proceed at ambient conditions.

Up until now, studies on plasma CO₂ splitting to CO mainly focused on the optimization of operating parameters,^{12–16} and

only a few catalysts (e.g., Ni/SiO₂, NiO/TiO₂ and Rh/TiO₂) have been evaluated (Table S1, ESI†).^{17–20} Recently, surface oxygen vacancies (V_O) have been suggested to be the active sites in plasma-catalytic CO₂ splitting to CO. Mei *et al.* reported that higher CO₂ conversion was achieved when coupling plasma with BaTiO₃, which can be explained by the formation of more V_O sites on the surfaces of BaTiO₃ compared with TiO₂.²⁰ Chen *et al.* found the V_O on Ni/TiO₂ contributed to the enhanced CO₂ dissociation.¹⁸ In fact, the coupling of catalysts and plasma is a promising strategy to improve CO₂ conversion and energy efficiency. However, the knowledge in selection of appropriate catalysts for highly efficient CO₂ splitting to CO using NTP was still very limited until now.

Herein, CO₂ splitting to CO over M-doped CeO₂ catalysts (M = Fe, Co, Ni, Cu, Cr, V, Mn or Mo) has been carried out in a dielectric barrier discharge (DBD) reactor (Fig. S2–S5, ESI†). CeO₂ not only serves as a support to anchor and disperse the metal oxide particles but also generates V_O active sites through the interaction with metal oxides. Significant differences were observed among the M-doped CeO₂ catalysts in terms of CO₂ conversion, and the Mo-doped CeO₂ exhibited the best activity in CO₂ conversion (Fig. S3, ESI†). Therefore, Mo-doped CeO₂ has been selected for further studies.

Comprehensive catalyst characterization was carried out to understand the physicochemical properties of Mo-doped CeO₂. As shown in Fig. 1, the X-ray diffraction (XRD) pattern of CeO₂ exhibits characteristic peaks of a cubic fluorite phase (JCPDS, 34-0394). For Mo-doped CeO₂, small peaks of α-MoO₃ (JCPDS, 05-0508) and Mo₄O₁₁ (JCPDS, 05-0337) are observed, revealing the coexistence of Mo(vi) and Mo(v) species. Notably, the characteristic peaks of CeO₂ downshift compared to pure CeO₂, which suggests that Mo doping leads to the expansion of the CeO₂ unit cell. Usually, inserting Mo ions into CeO₂ induces shrinkage of the CeO₂ unit cell since the radius of Mo ions is much smaller than that of Ce ions, resulting in upshifting of CeO₂ peaks, rather than downshifting. Thus, Mo ions do not insert into the CeO₂ unit cell, and there might be other reasons responsible for this downshift. X-ray photoelectron spectroscopy

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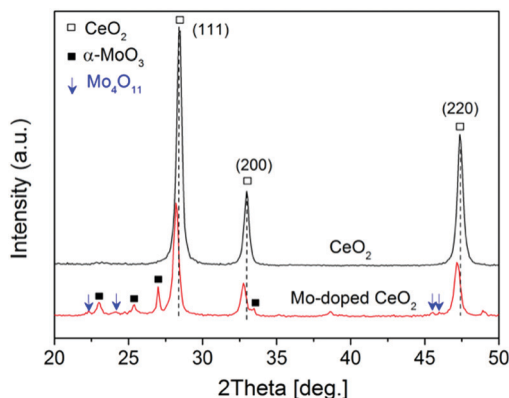


Fig. 1 XRD patterns of CeO₂ and as-prepared Mo-doped CeO₂.

(XPS) was employed to analyze surface properties of Mo-doped CeO₂. The deconvoluted Ce 3d XPS spectra are presented in Fig. 2(a). The peaks labeled as v, v', v'' and u, u', u'' are assigned to 3d_{5/2} and 3d_{3/2} electrons of Ce⁴⁺, respectively, while the peaks of v', u' and v_o, u_o correspond to 3d_{5/2} and 3d_{3/2} electrons of Ce³⁺, respectively.²¹ Clearly, Ce³⁺ exists in CeO₂ and Mo-doped CeO₂, suggesting the formation of V_O in both samples. More importantly, the proportion of Ce³⁺ in Mo-doped CeO₂ is 40.2%, higher than that in CeO₂ (30.0%) (Fig. S6 and S7, ESI†). This finding suggests that Mo doping induces partial transformation of Ce⁴⁺ to Ce³⁺ and creates more V_O on Mo-doped CeO₂. As reconfirmed by the O 1s XPS spectra in Fig. 2(b) and Fig. S6 (ESI†), a higher surface V_O (30.4%) is achieved in the Mo-doped CeO₂ in comparison to pure CeO₂ (21.0%). Furthermore, the transformation of Ce⁴⁺ to Ce³⁺ leads to the expansion of the CeO₂ unit cell since the ion radius of Ce³⁺ (1.23 Å) is higher than that of Ce⁴⁺ (0.97 Å),²² which explains the reason for the downshifting of CeO₂ peaks in Fig. 1. More interestingly, the

binding energies of Ce 3d shift significantly towards higher values after Mo doping, revealing that the electron density of the surface CeO₂ species is lower in Mo-doped CeO₂ compared with pure CeO₂, which might be induced by the electron transfer from Ce to Mo, due to the higher electronegativity of Mo. These results suggest different properties of V_O sites in the form of Ce³⁺-V_O in CeO₂ and Ce³⁺-V_O-Mo in Mo-doped CeO₂, as well as the strong interaction between Mo and CeO₂, which agrees with the results of H₂-temperature programmed reduction (H₂-TPR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. S8–S11, ESI†). Fig. 2(c) shows the deconvoluted Mo 3d spectra, in which the Mo-doped CeO₂ sample exhibits typical doublet peaks of Mo⁶⁺ with an energy gap of ca. 3.1 eV, indicating the formation of MoO₃ in Mo-doped CeO₂.²³ The two smaller peaks observed, however, are identified to be 3d_{3/2} and 3d_{5/2} electrons of Mo(v), demonstrating the formation of the non-stoichiometric MoO_{3-x},²³ which is consistent with the Mo₄O₁₁ species confirmed by the XRD analysis (Fig. 1). Fig. 2(d) shows the Raman spectra of CeO₂ and Mo-doped CeO₂. For pure CeO₂, the intense band at 465 cm⁻¹ is well-indexed to the typical F2g modes of a cubic CeO₂ fluorite structure, and the weak bands at 262, 597 and 1171 cm⁻¹ are assigned to V_O, reconfirming the XPS results in Fig. 2(a and b).²³ For Mo-doped CeO₂, the emerging Raman bands at 673, 824 and 997 cm⁻¹ are assigned to MoO₃ crystallites.²⁴ However, the band at 955 cm⁻¹ is associated with Mo suboxides (MoO_{3-x}).^{24,25} These results indicate that the valence state of Mo in suboxides is Mo⁵⁺. Moreover, the presence of Mo⁵⁺ and Ce³⁺ indicates that more V_O sites are created through the strong interaction between Mo and CeO₂, as well as the calcining atmosphere with deficient oxygen and rich energetic Ar species, which agrees with the results reported by Chen *et al.*¹⁸

Fig. 3 shows the effect of different operating conditions on CO₂ conversion. Clearly, no reaction occurred without plasma (catalyst only, 400 °C). The conversion of CO₂ was 3.8% in the plasma reaction without a catalyst (plasma only). In the plasma reaction coupled with pure CeO₂, the CO₂ conversion dropped to 1.2%, which suggests that pure CeO₂ is unfavorable for CO₂ splitting to CO despite CeO₂ being O-deficient. Using Mo-doped

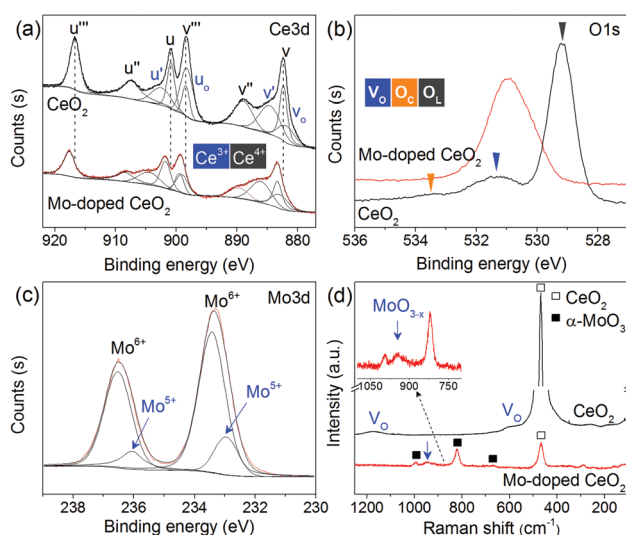


Fig. 2 XPS and Raman spectra of CeO₂ and as-prepared Mo-doped CeO₂ (a) Ce 3d, (b) O 1s, (c) Mo 3d and (d) Raman spectra (V_O, O_C and O_L represent oxygen vacancy, chemisorbed oxygen species and oxygen lattice, respectively).

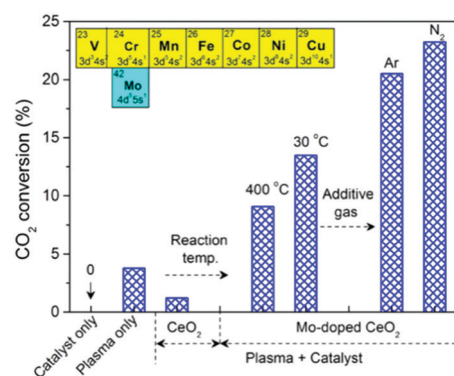


Fig. 3 Effect of reaction temperature and additive gas on CO₂ conversion (CO₂ flow rate 40 ml min⁻¹, SEI 20 kJ L⁻¹, molar ratio 4 : 1 and 30 °C for CO₂/Ar and CO₂/N₂; catalyst only 400 °C).



CeO₂ instead of CeO₂, however, results in a significant increase of CO₂ conversion by a factor of 9 at 400 °C. In addition, the Mo-doped CeO₂ showed stable CO₂ conversion for at least 10 h (Fig. S12, ESI†). Interestingly, the reaction performance can be further improved by using a lower reaction temperature (30 °C) and an additive gas (Ar or N₂). This promotional effect was more pronounced when adding N₂. The highest CO₂ conversion of 23.2% and energy efficiency of 14.3% were achieved in the plasma splitting of CO₂ with N₂ addition over Mo-doped CeO₂ at 30 °C (Table S1, ESI†), while the corresponding formation rate of CO and O₂ was 24.9 mmol h⁻¹ and 12.4 mmol h⁻¹, respectively (Table S2, ESI†). The optimal energy efficiency achieved in this study is comparable to that reported in previous works (Table S1, ESI†).

Regarding surface reactions, the improved activity over Mo-doped CeO₂, on one hand, is mainly attributed to the increased formation of V_O (Fig. 2 and Fig. S6, ESI†), since V_O serve as adsorption centers for CO₂ dissociative adsorption,^{17,26} i.e., CO₂ + V_O → O_L/O_C + CO. On the other hand, the promoted performance originates from the different properties of V_O in the forms of Ce³⁺-V_O and Ce³⁺-V_O-Mo due to strong interaction between Mo and CeO₂ and the higher electronegativity of Mo compared with Ce (Fig. 1, 2 and Fig. S8, ESI†), which leads to a stronger binding strength of CO₂ with the V_O of Ce³⁺-V_O-Mo. As discussed above, V_O is the active site for CO₂ activation; thus, the stability of V_O greatly influences the subsequent catalytic cycle. It is well recognized that oxygen can be produced in plasma CO₂ splitting, and the produced O species could poison the catalyst through filling V_O sites to form stable lattice oxygen species, resulting in termination of the catalytic cycle.

Therefore, the spent Mo-doped CeO₂ catalysts were further characterized by XPS, Raman, XRD and H₂-TPR (Fig. 4). Interestingly, compared with the fresh catalyst, the spent Mo-doped CeO₂ catalysts show an increased amount of Ce³⁺ and MoO_{3-x}, which can be confirmed by the higher intensities of Ce³⁺ peaks

and the Raman band at ~950 cm⁻¹ in Fig. 4(a and b), respectively. The enhancement effect is more pronounced for the catalyst used at 400 °C. Correspondingly, more V_O sites were created in the high-temperature reaction (Table S3, ESI†). In addition, the color of the catalyst changed from gray/blue (MoO_{3-x}) to yellow (MoO_{3-y}) with $x > y$ after the reaction at 30 °C, while no visible changes were observed on the phase structure of Mo-doped CeO₂ before and after the reaction (30 °C), as shown in Fig. 4(c). These results indicate that some O atoms from CO₂ splitting are adsorbed onto the catalyst, as seen by the slightly increased H₂ consumption in Fig. 4(d). Even so, the V_O concentration of Mo-doped CeO₂ used at 30 °C remained at a similar level with that of the fresh sample (Table S3, ESI†). These findings suggest that V_O-rich Mo-doped CeO₂ is stable after the plasma reaction, and high-temperature reactions facilitate the formation and recovery of V_O sites, resulting from accelerating recombinative desorption of adsorbed O atoms.²⁷

In addition to surface reactions, gas-phase reactions also play a crucial role in the plasma-catalytic process. In a pure CO₂ DBD, CO₂ splitting to CO mainly proceeds through the electron impact dissociation of CO₂ (CO₂ + e → CO + O + e), which can be confirmed by plasma chemical kinetic modeling,²⁸ as well as the formation of CO bands and O atomic lines detected by optical emission spectra of CO₂ DBD (Fig. 5(a)). As shown in Fig. 5(a), the presence of strong N₂ (C³Π_u → B³Π_g, B³Π_g → A³Σ_u⁺) molecular bands and Ar atomic lines suggests the formation of excited nitrogen species (N₂^{*}) and metastable Ar species (Ar^{*}).^{29,30} These species create an additional reaction route for CO₂ dissociation (N₂^{*} (or Ar^{*}) + CO₂ → CO + O + N₂ (or Ar)), supported by the increased intensity of O atomic lines and CO bands when adding N₂ or Ar, which contributes to the enhanced CO₂ conversion. Furthermore, 150 ppm NO_x was detected by Fourier transform infrared (FTIR) in the case of N₂ addition (Fig. S13, ESI†), revealing that N₂ can be regarded as an alternative scavenger of O species.¹² The elimination of partial O species can effectively limit the reverse reaction, i.e., O + CO + M → CO₂ + M, and thus enhance the CO₂ conversion. This could explain why adding N₂ has a stronger promotion on the CO₂ conversion compared with Ar.

Interaction between reactive species in the gas phase and catalyst is also crucial in plasma-catalytic reactions.³¹ Compared to plasma only, packing Mo-doped CeO₂ into the

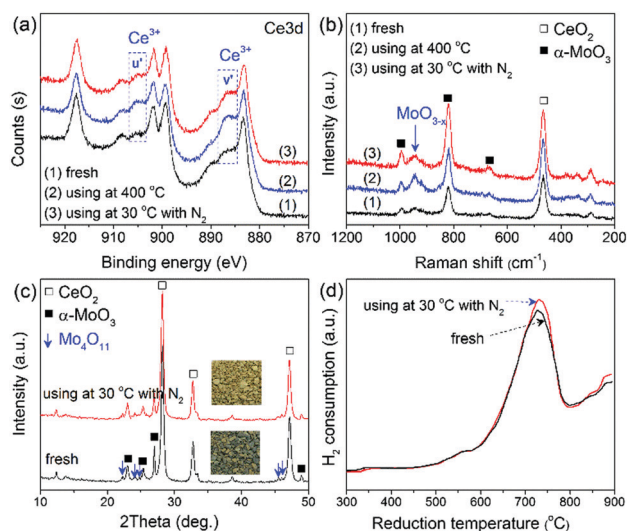


Fig. 4 (a) XPS spectra, (b) Raman spectra, (c) XRD patterns, (d) H₂-TPR profiles of Mo-doped CeO₂ before and after reaction.

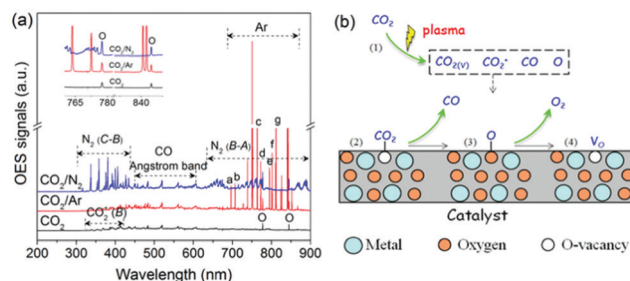


Fig. 5 (a) Emission spectra of CO₂ plasma, (b) possible pathways of plasma-catalytic CO₂ splitting over V_O-rich catalyst.



discharge zone decreased the current (Fig. S14, ESI[†]), lowering the contribution of the gas-phase reactions. In this case, the CO₂ conversion, however, was still improved, which might be attributed to the interaction between active species and V_O-rich Mo-doped CeO₂, accelerating V_O recovery. Therefore, a possible reaction mechanism is proposed in Fig. 5(b). Firstly, CO₂ is activated to species of CO₂⁺, CO_{2(v)}, CO and O radicals as shown in Fig. 5(a) (step 1). Then, the energetic CO₂-species are adsorbed on the V_O sites to decrease their internal energy (step 2). After that, the V_O sites have the potential to grasp the O atom of the adsorbed CO₂ molecule, which weakens the C=O bond, producing adsorbed CO and O (step 3). Subsequently, the adsorbed CO desorbs as the final CO product. While the adsorbed O mainly desorbs from V_O sites in the form of O₂ through reacting with the active O radicals produced in the gas phase (O_g + O_{ad}-V_O → O_{2,g} + V_O), i.e., Eley-Rideal (E-R) mechanism. Meanwhile, V_O sites recover completing the catalytic cycle (step 4). Using isotope trace analysis, we demonstrated the desorption of N_{ad} through an E-R reaction in plasma-catalytic NH₃ decomposition.³¹ Therefore, the desorption of O_{ad} through E-R reaction is also expected. Note that, too strong of a CO₂-V_O bond makes it easy to split the CO₂ molecule, but the corresponding desorption of adsorbed O is difficult. By contrast, too weak of a CO₂-V_O bond means it could be hard to split CO₂, although the adsorbed O can easily desorb from the catalyst surface. Therefore, a catalyst with a proper binding strength between V_O sites and CO₂ benefits the conversion of CO₂ and favors the catalytic cycle.

In conclusion, plasma-catalytic CO₂ splitting over M-doped CeO₂ catalysts (M = Fe, Co, Ni, Cu, Cr, V, Mn or Mo) has been investigated. Mo-doped CeO₂ exhibited the best activity; this is attributed to the increased oxygen vacancies created by strong interaction between Mo and CeO₂, as well as the calcining atmosphere being oxygen-deficient and rich in Ar metastable species. Furthermore, oxygen vacancies were stable during the reaction, which is ascribed to the interaction between active O produced in the gas phase and the adsorbed O on the oxygen vacancy site, resulting in desorbing as O₂ molecules and recovering oxygen vacancy sites. These findings suggest that introducing proper doping on CeO₂ offers a potential route to tune properties of oxygen vacancy in CeO₂. Additionally, adding N₂ and Ar into the plasma process enhanced the CO₂ conversion, especially when adding N₂. This promotional effect is mainly attributed to the new reaction routes induced by the presence of metastable species. We found that N₂ can be used as an O scavenger to forward the chemical equilibrium and inhibit the reverse reaction to form CO₂.

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Conflicts of interest

There are no conflicts to declare.

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