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Highly Efficient Photoelectrocatalytic Reduction of CO₂ to Methanol by a p–n Heterojunction CeO₂/CuO/Cu Catalyst

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Zhengbin Pan and Ershuan Han have contributed equally to this work.

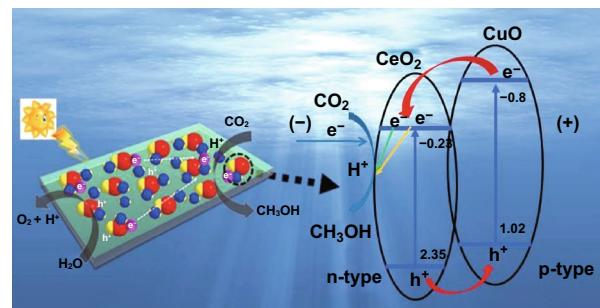
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HIGHLIGHTS

- Flower-like CeO₂ nanoparticles enhance the performance of CuO nanoparticle/Cu.
- The system benefits from the heterojunction between p-type CuO and n-type CeO₂.
- The selective reduction of CO₂ to methanol on the target catalyst is studied.

ABSTRACT Photoelectrocatalytic reduction of CO₂ to fuels has great potential for reducing anthropogenic CO₂ emissions and also lessening our dependence on fossil fuel energy. Herein, we report the successful development of a novel photoelectrocatalytic catalyst for the selective reduction of CO₂ to methanol, comprising a copper catalyst modified with flower-like cerium oxide nanoparticles (CeO₂ NPs) (a n-type semiconductor) and copper oxide nanoparticles (CuO NPs) (a p-type semiconductor). At an applied potential of -1.0 V (vs SCE) under visible light irradiation, the CeO₂ NPs/CuO NPs/Cu catalyst yielded methanol at a rate of $3.44 \mu\text{mol cm}^{-2} \text{h}^{-1}$, which was approximately five times higher than that of a CuO NPs/Cu catalyst ($0.67 \mu\text{mol cm}^{-2} \text{h}^{-1}$). The carrier concentration increased by $\sim 10^8$ times when the flower-like CeO₂ NPs were deposited on the CuO NPs/Cu catalyst, due to synergistic transfer of photoexcited electrons from the conduction band of CuO to that of CeO₂, which enhanced both photocatalytic and photoelectrocatalytic CO₂ reduction on the CeO₂ NPs. The facile migration of photoexcited electrons and holes across the p–n heterojunction that formed between the CeO₂ and CuO components was thus critical to excellent light-induced CO₂ reduction properties of the CeO₂ NPs/CuO NPs/Cu catalyst. Results encourage the wider application of composite semiconductor electrodes in carbon dioxide reduction.

**KEYWORDS** CO₂ reduction; Photoelectrocatalysis; p–n heterojunction; Cerium oxide; Copper oxide

1 Introduction

Since the beginning of the industrial revolution in the late 1700s, humans have heavily relied on cheap and abundant fossil fuels as an energy source. Indeed, modern societies are still very heavily reliant on fossil fuels for energy and as a feedstock for the manufacture of commodity chemicals. However, fossil fuels are a non-renewable energy source, meaning that they will likely be exhausted over the next few hundred years, motivating the development alternative renewable energy technologies (especially solar and wind) as a means of achieving energy supply security. A further downside of using fossil fuels for energy is the associated CO₂ emissions, which directly promote global warming via the greenhouse effect [1–4]. However, if viewed from another perspective, the CO₂ produced via combustion of fossil fuels or biomass sources represents a cheap C₁ building block (i.e., a resource to be exploited rather than an annoying waste product) [5, 6]. Accordingly, over the past decade, and enormous amount of research effort has been directed toward the development of efficient technologies for converting CO₂ into valuable chemical and fuels via processes such as catalytic hydrogenation [7, 8], photocatalytic (PC) reduction [9, 10], electrocatalytic (EC) reduction [11, 12], photoelectrocatalytic (PEC) reduction [13, 14], and biotransformation to solve environmental and energy issues [15, 16]. Among these, EC, PC, and PEC are perhaps the three most promising approaches for future large scale CO₂ reduction. In EC, CO₂ is reduced via the transfer of electrons and also protons to CO₂, though most metal electrodes suffer from high overpotentials for CO₂ reduction, and thus produce large amounts of H₂ along with any products of CO₂ reduction (i.e., the electrodes generally have poor selectivity for CO₂ reduction) [17, 18]. In CO₂ reduction by semiconductor photocatalysis, light irradiation causes electrons to be promoted from the semiconductor valence band into the conduction band (CB), thus giving rise to charge carriers capable of reducing CO₂ to CO and other products when the semiconductors valence band (VB) and CB are suitably positioned relative to the redox processes needed for CO₂ reduction and typically water oxidation, respectively [19]. However, the efficiency and performance of most photocatalysts for CO₂ reduction are limited by bulk recombination of photoexcited electrons and holes. In this context, PEC is a particularly promising method for CO₂ reduction, wherein

an applied potential is used to prevent the bulk recombination of bulk photoelectrons and holes, thereby increasing the availability of photoexcited electrons for reaction with CO₂. Various semiconductors have been studied in relation to PC and PEC CO₂ reduction. In order to maximize solar spectrum utilization, it is desirable to use a semiconductor with a narrow band gap that absorbs in the visible regime [20]. However, the narrower the band gap, the more rapid the electron–hole pair recombination, and hence many narrow band gap semiconductors show poor PC efficiencies for CO₂ reduction. Thus, PEC systems are generally preferred, with various approaches being adopted to enhance the conversion efficiency of PEC catalysts for CO₂ reduction including the introduction of co-catalysts [21, 22], bulk doping of the semiconductor with metal cations to increase the light absorption range and/or to introduce electron traps [23, 24], p–n junction construction [25], among others. Furthermore, by nanostructuring semiconductor PC or by creating hierarchical semiconductor arrays, materials with large specific surface areas and abundant active sites for adsorbing CO₂ can be created, thereby facilitating CO₂ reduction under direct sunlight or simulated sunlight [26].

Copper oxide-based semiconductors have received much attention in relation to the catalytic reduction CO₂. CuO has excellent EC activity for CO₂ reduction, exhibiting very high selectivity to CH₃OH [27, 28]. Further, Gusain et al. [29] demonstrated that reduced graphene oxide–copper oxide nanocomposites were able to convert CO₂ to CH₃OH photocatalytically under visible light irradiation. Kim et al. [30] developed a highly efficient p–n–p Cu₂O/S–TiO₂/CuO heterojunction for the photocatalytic conversion of CO₂ to CH₄. Although CuO can readily be photoexcited using visible light, rapid recombination of photogenerated electrons and holes limits its photocatalytic activity [31]. Combining CuO with other semiconductors through heterojunction is effective in suppressing electron–hole pair recombination, offering a pathway to greatly improve the PC performance of CuO. Other strategies for suppressing electron–hole pair recombination include the addition of suitable co-catalysts or photosensitizers that can supply electrons or remove holes effectively from CuO, or alternatively enhance the absorption incoming visible light [32]. CeO₂ is an inexpensive rare earth semiconductor that finds widespread use in solar cells, optical devices, sensors, and sunscreen materials [33, 34]. It is also widely used in catalysis as a support due to its outstanding oxygen storage behavior, which arises from valence change switching

between Ce^{3+} and Ce^{4+} [35, 36]. Considering the relative positions of the conduction and valence bands of n-type CeO_2 and p-type CuO , we hypothesized that the construction of a CeO_2/CuO heterojunction should be highly beneficial for improving the PC and PEC performance for CO_2 reduction. Under light irradiation, electrons photoexcited into the CB of CuO would be transferred into the CB of CeO_2 , whereas holes (h^+) created in the VB of CeO_2 under light irradiation would migrate into the VB of CuO . Via such exchange of electrons holes between CuO and CeO_2 , more charge carriers should be available to drive CO_2 reduction to methanol (the dominant product for CO_2 reduction over CuO -based catalysts). To date, very little work has been done relating to the application of CeO_2/CuO heterojunctions in solar-driven CO_2 reduction to fuels, motivating a detailed investigation.

Herein, we systematically explored the performance of a $\text{CeO}_2/\text{CuO}/\text{Cu}$ catalyst system for PEC CO_2 reduction under visible light. Flower-like n-type CeO_2 nanoparticles were grown on a p-type CuO NPs/ Cu foil catalyst by electrodeposition, with the resulting heterojunction catalyst (denoted herein as CeO_2 NPs/ CuO NPs) then being subjected to detailed physicochemical and electrochemical characterization, along with PEC CO_2 reduction tests in a CO_2 -saturated aqueous KHCO_3 solution. The overarching aim of the research was to establish whether CeO_2 addition could significantly enhance the PEC performance of CuO -based catalyst for reduction CO_2 to CH_3OH .

2 Experimental Section

2.1 Preparation of the CuO NPs Catalyst

All reagents were supplied by Aladdin Reagent Co., Ltd. A pure copper foil (99.99% Cu, $50 \times 20 \times 1 \text{ mm}^3$) was polished with coarse sandpaper, then metallographic sandpaper, to achieve a mirror finish. The polished Cu foil was washed repeatedly with anhydrous ethanol and then air-dried. The Cu foil was then anodized in an ethylene glycol–water solution (volume ratio 97:3) containing 0.25wt% NH_4F . A polished Ti foil (99.99% Ti, $50 \times 20 \times 1 \text{ mm}^3$) was used as the cathode. The separation between the anode and cathode was 1 cm, and the temperature of electrolyte maintained at 20°C . Under magnetic stirring, CuO NPs were formed by holding the Cu foil electrode at a potential of 30 V for 1.5 h. The prepared electrode was then washed with distilled water before

being heated from room temperature to 300°C in a tube furnace under O_2 . The catalyst was held at 300°C for 3 h and then cooled to 20°C at a rate of 1°C min^{-1} [13]. The obtained catalyst is denoted herein as CuO NPs.

2.2 Preparation of the Flower-like CeO_2 NPs/ CuO NPs Composite Catalyst

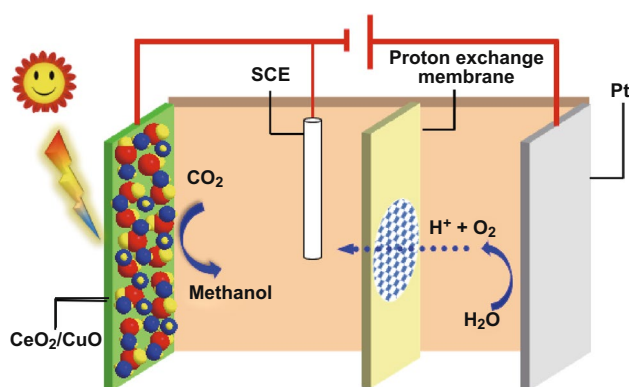
Flower-like CeO_2 NPs were subsequently deposited on the CuO NPs catalyst via an electrochemical method that used a three-electrode system, comprising the CuO NPs catalyst as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The flower-like CeO_2 NPs were introduced by electrodeposition at a constant current density of 2 mA cm^{-2} for 2 h. An aqueous electrolyte containing 10 mM $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 50 mM KCl, and 50 mM NH_4Cl , with the electrolyte temperature maintained at 70°C [37]. The obtained catalyst, denoted herein as the flower-like CeO_2 NPs/ CuO NPs, was washed with distilled water and air-dried at room temperature.

2.3 Catalysts Characterization

The surface morphologies of the catalysts were examined using scanning electron microscopy (SEM, Hitachi SU8010). The particle size was calculated by the Nano Measurer 1.2 software. The microscope was operated at an acceleration voltage of 5.0 kV for the imaging. High-resolution transmission electron microscopy (HRTEM) analyses were performed on a JEM-2100 microscope operating at 200 kV. The crystal structure of the samples was probed by X-ray diffraction (XRD) on a Rigaku D/MAX-rA diffractometer (Japan) equipped with a $\text{Cu-K}\alpha$ source ($\lambda = 0.154178 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) measurements were performed on a ESCALAB 250 equipped with a monochromatic Al $\text{K}\alpha$ source ($h\nu = 1486.7 \text{ eV}$). UV–visible diffuse reflectance spectra (UV–Vis DRS) were collected on a UV–Vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd.), and the wavelength ranged from 400 to 700 nm. Dielectric constants were measured at room temperature using a TH2826 LCR digital bridge (Shanghai Double Asa Electronics Co., Ltd.) operating at 2 MHz. The electrochemical properties of the catalysts were evaluated using a CHI660D potentiostat (Shanghai Chenhua Instrument Co., Ltd.).

2.4 Photoelectrocatalytic CO₂ Reduction Experiments

PEC CO₂ reduction experiments were conducted in a quartz reaction cell containing a three-electrode array comprising the CeO₂ NPs/CuO NPs composite catalyst as the working electrode, a Pt plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The cell was interfaced with a CHI660D potentiostat and a circulating water device to maintain a constant temperature of 25 °C. Scheme 1 shows a schematic of the PEC cell used for reduction CO₂ reduction. The cathode electrolyte was aqueous 0.1 mol L⁻¹ KHCO₃ (40 mL), with CO₂ gas bubbled through the cathode electrolyte at a rate of 40 mL min⁻¹ during the reaction. In fresh form of 0.1 mol L⁻¹ KHCO₃, it has pH (8.34), but the reaction is carried out under CO₂, so pH change to 6.8. The LSV is affected by different pH, experiments have been done under pH = 7.0 and pH = 9.0, and the impact was also calculated, which is 0.12%. So the proton reduction has almost no impact on the experimental conclusion [38]. A 500-W xenon lamp (420 ≤ λ ≤ 800 nm, 100 mW cm⁻²) was used for the PEC CO₂ reduction tests, which were performed over a testing period of 6 h. The qualitative and quantitative analysis of products was performed by gas chromatography. The gas chromatograph (GC-9A, Shimadzu) was equipped with an air pump and hydrogen generator, FID and TCD detectors, and a Porapak Q (80–100) glass packed column. The column temperature was maintained at 180 °C and the detector temperature at 200 °C. The carrier gas used was high purity N₂ (flow rate 30 mL min⁻¹).



Scheme 1 The PEC cell for CO₂ reduction

3 Results and Discussion

3.1 Characteristics of the CuO NPs and CeO₂ NPs/CuO NPs Catalysts

The surface morphologies and structural properties of the CuO NPs and CeO₂ NPs/CuO NPs catalysts were examined by SEM, TEM, and XRD, with data for these electrodes being summarized in Fig. 1. As shown in Fig. 1a, anodizing the surface of the Cu foil was effective in covering the surface of the foil with CuO NPs. The CuO NPs were pseudo-spherical and relatively uniform in size, with the average size around 180 nm (Fig. 1a₂). XRD results confirmed the formation of CuO NPs (Fig. 1c). Flower-like CeO₂ NPs were grown on the CuO NPs catalyst by electrodeposition (Fig. 1b). The flower-like CeO₂ NPs morphology with thin petals was expected to be near ideal for promoting PEC CO₂ reduction on the hybrid heterojunction catalyst, offering a very large specific surface area for CO₂ adsorption and reduction (Fig. S1). XRD results further confirmed the successful growth of nanocrystalline CeO₂ on the CuO NPs catalyst (Fig. 1c). Diffraction peaks appearing at 2θ = 28.58, 33.13, 47.56, and 56.43 could readily be assigned to the (111), (200), (220), and (311) reflections of CeO₂ (JCPDS No. 65-5923). In addition, a small amount of Ce₂O₃ was detected, implying that the modified electrode contained an abundance of Ce³⁺/Ce⁴⁺ species and thus likely strong oxygen storage capacity [39]. The structure of the flower-like CeO₂ NPs was examined further using HRTEM. Figure 1d shows that the sample was composed of CeO₂ nanocrystals. The inset in Fig. 1d shows lattice fringes with spacings of 0.31, 0.19, and 0.27 nm, corresponding to the interlayer distance between the (111), (220), and (200) lattice planes, respectively, of cubic CeO₂ [40]. These results are consistent with the XRD findings (Fig. S2). Previous studies have shown the CeO₂ (111) plane to be very important for PC applications, as it is thermodynamically stable and very sensitive to light [35, 36].

The visible light absorption characteristics of the as-prepared CuO NPs and flower-like CeO₂ NPs/CuO NPs catalysts were examined by UV–Vis DRS (Fig. 2a). The flower-like CeO₂ NPs/CuO NPs catalyst exhibited absorption across the visible region than CuO NPs catalyst, as expected since nanocrystalline CeO₂ is optically active at visible wavelengths (a pale yellow color). Band gaps (E_g)

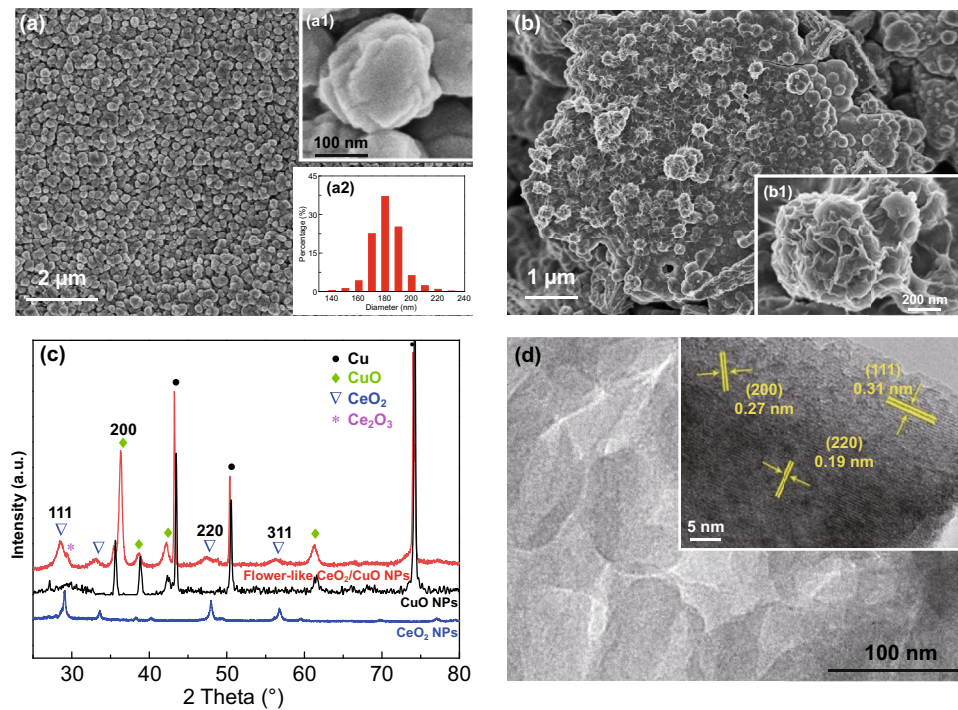


Fig. 1 SEM images of CuO NPs at **a** low magnification and **a₁** high magnification. **a₂** Particle size distribution for CuO NPs. SEM images for flower-like CeO₂ NPs at **b** low magnification and **b₁** high magnification. **c** XRD patterns for CuO NPs and flower-like CeO₂ NPs/CuO NPs. **d** HRTEM image of CeO₂ NPs. The inset shows a high magnification image, revealing lattice fringes characteristic for CeO₂

for the different electrodes were estimated using the Tauc equation (Eq. 1) [41]:

$$ahv = A(hv - E_g)^n \tag{1}$$

here α is the reciprocal of the absorption length, $h\nu$ is the photon energy, and A is a constant. For direct band gap transitions, the index $n=0.5$ and for indirect band gap transition $n=2$. The band gap of the CuO NPs catalyst was calculated by applying a linear fit to a plot of $(ahv)^{0.5}$ and $h\nu$ experimental curves, with the analysis yielding an E_g of 1.82 eV (Fig. 2b). This value is in good accord with prior literature reports for CuO [32]. For the flower-like CeO₂ NPs/CuO NPs catalyst, the estimated E_g value was 2.10 eV (Fig. 2c), representing the weighted sum of the band gap values of CuO and CeO₂. The data in Fig. 2 confirm that both electrodes showed a good optical response at visible wavelengths, as required for visible light-driven PC and PEC processes.

When a semiconductor is in contact with an electrolyte, a space charge layer will be formed in the semiconductor surface due to the difference in Fermi level between the bulk and the surface (resulting in band bending), while a Helmholtz layer will be formed on the electrolyte side of

the semiconductor/electrolyte interface. For such a system where a semiconductor is in contact with an electrolyte, a capacitance (C) results through coupling of the space charge layer capacitance (C_{sc}) in series with the solution Helmholtz layer capacitance (C_H) (note: C_H is usually negligible relative to C_{sc}). Changing the polarization potential (E) of a semiconductor can change the space charge layer capacitance of the semiconductor, which can be described by the Mott–Schottky equation (Eq. 2) [42]:

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon_0 \epsilon_r N_A A^2} \left(E - E_{fb} - \frac{kT}{e} \right) \tag{2}$$

here C_{sc} , N_A , ϵ_0 , A , ϵ_r , E , k , T , E_{fb} and e are the space charge layer capacitance, doping concentration, vacuum dielectric constant, the contact area between the electrode and the solution, dielectric constant of the semiconductor, polarization potential, the Boltzmann constant, absolute temperature, the flat band potential, and the electric charge, respectively. By plotting C_{sc} versus the polarization voltage E , a straight-line section is obtained. Extending the tangent to that straight-line section to the polarization voltage axis yields obtain the flat band potential E_{fb} of a material. Figures 2d and S3 show Mott–Schottky plots for the flower-like CeO₂ NPs/CuO

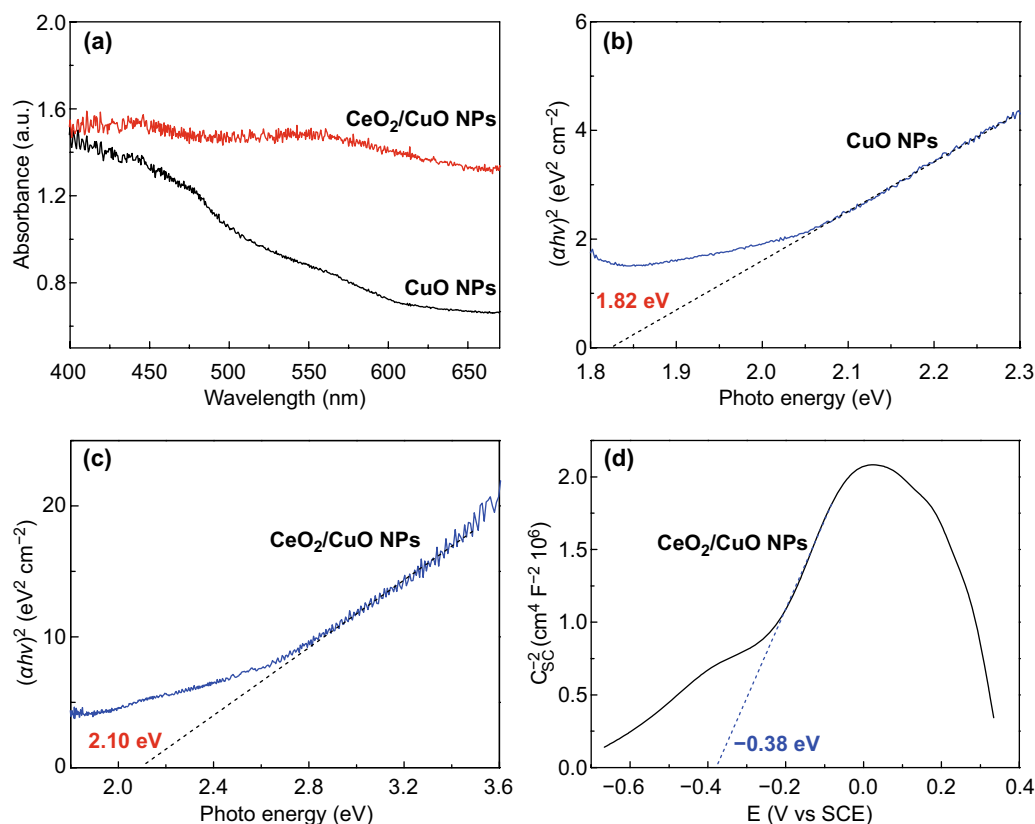
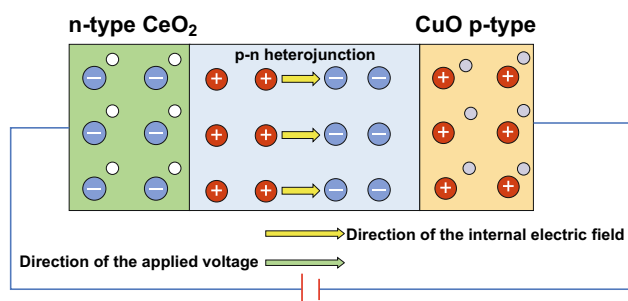


Fig. 2 **a** UV–Vis absorbance spectra for CuO NPs and flower-like CeO₂ NPs/CuO NPs. Tauc plots for **b** CuO NPs and **c** flower-like CeO₂ NPs/CuO NPs. **d** Mott–Schottky plots for flower-like CeO₂ NPs/CuO NPs

NPs catalyst and CuO NPs catalyst, respectively. The slope of the first half is positive, while the slope of the second half is negative, it shows p–n semiconductor characteristics after the CeO₂ NPs deposited on the CuO NPs (Fig. 2d). E_{fb} of CuO NPs and CeO₂ NPs/CuO NPs estimated from the plots were 0.82 eV (Fig. S3) and -0.38 eV (Fig. 2d), respectively. The valence band maximum (VBM) of p-type semiconductor is approximately located at 0.2 eV below the flat band potential, so the VB of the CuO NPs is located at 1.02 eV [43]. Taking the fermi level for each electrode and using the Mott–Schottky equation, the acceptor concentrations (N_A) for the CuO NPs catalyst and flower-like CeO₂ NPs/CuO NPs catalyst were calculated to be 3.47×10^{-5} and $2.93 \times 10^4 \text{ m}^{-3}$, respectively. The carrier concentration for the flower-like CeO₂ NPs/CuO NPs catalysts was thus a remarkable 10^8 times higher than that of the CuO NPs electrode. These data provide convincing evidence that the decoration of the CuO NPs catalyst with flower-like CeO₂ NPs was effective in enhancing the separation of photogenerated electrons and holes. To explain this, the intrinsic properties of CuO (p-type conductor) and CeO₂ (n-type conductor) need to be considered. On electrodepositing CeO₂ onto

the CuO NPs catalyst, p–n heterojunctions are formed at the interface between the two components (Fig. 2d). The experimental data suggest that when an external voltage is applied, the internal charge within the heterojunction actually opposed the applied external voltage, thus increasing the conductivity in the interfacial region [44–46]. Thus, creation of p–n heterojunctions is highly advantageous for promoting interfacial charge transfer and enhancing charge carrier mobilities [47]. Under the conditions used in the PEC CO₂ reduction tests below, a negative voltage (-1.0 V) was used, in which case the net flow of electrons will be from CuO to CeO₂ (as depicted in Scheme 2), with CeO₂ acting as the adsorption and reduction site for CO₂.

In order to further probe the excellent properties of the flower-like CeO₂ NPs/CuO NPs system, XPS was applied to examine the chemical speciation of Cu, O, and Ce in the electrode. Figure 3a shows the Cu 2p XPS spectrum of the catalyst. The spectrum shows a set of peaks in a 2:1 area ratio (readily assigned to Cu p_{3/2} and Cu 2p_{1/2} signals, respectively), along with a corresponding shake-up satellites at higher binding energies, indicating the presence of Cu²⁺ (3 d⁹). The binding energy of the Cu



Scheme 2 Charge separation under an applied the voltage in the p–n junction flower-like CeO₂ NPs/CuO NPs system

$2p_{3/2}$ peak at 933.8 eV is also consistent with Cu²⁺ in CuO. The O 1s peak at 529.8 eV (Fig. 3b) contains unresolved contributions from CuO (529.6 eV) and CeO₂ (529.2 eV). The Ce 3d spectrum (Fig. 3c) showed a multitude of peaks, which could be assigned to Ce⁴⁺ and Ce³⁺ species following the description by Burroughs et al. [48] wherein v and u represent different $3d_{5/2}$ and $3d_{3/2}$ states, respectively. The characteristic peaks of Ce⁴⁺ are labeled v , v'' , v''' , u , u'' and u''' . The peaks labeled v' and u' are associated with Ce³⁺ ($3d_{5/2}$ and $3d_{3/2}$, respectively), indicating the presence of oxygen vacancies on the surface of the CeO₂ [49]. The percentage of Ce³⁺ in the flower-like CeO₂ NPs/CuO NPs system was estimated to be around 34.82%, with the balance being Ce⁴⁺. The valence of Ce is analyzed in Table 1, and the result is consistent with the CeO₂ existing in the form of CeO_{2-x}.

Based on the aforementioned experimental studies of the flower-like CeO₂ NPs/CuO NPs catalyst, mechanisms can be proposed for charge separation and thus CO₂ reduction under EC, PC, and PEC regimes. On forming a CeO₂/CuO heterojunction, an internal electric field will form at the interface between n-type CeO₂ and p-type CuO, which inhibit the transfer of carriers between the two semiconductors.

If an external voltage is applied (under EC conditions as shown in Scheme 2) in the same direction as the internal electric field, the internal electric field should have become larger, and the conductivity poorer. However, we found that the internal electrical field of the CeO₂ NP/CuO NPs was actually opposed to the external voltage (Scheme 2), increasing the interfacial conductivity, resulting in electron transfer to the CeO₂ component. Accordingly, in the presence of CO₂, rapid reduction to methanol on CeO₂ will occur aided by protons coming from the anode (see CO₂ tests below).

Under light irradiation (no voltage applied, i.e., the PC regime, Scheme 3a), electrons will be photoexcited from the VB to the CB of both CuO and CeO₂. Electrons photoexcited in CuO will be transferred to CeO₂ since the CB of CeO₂ (−0.23 eV) is more positive than that of the CuO (−0.80 eV) [50]. Conversely, holes created in the VB of CeO₂ will migrate into the VB of CuO. It results in the suppression of electron–hole pair recombination and an increase in the availability of electrons for reducing CO₂ on the CeO₂ nanoparticles.

When light and electricity are applied simultaneously (Scheme 3b), the concentration of electrons reaching CeO₂ will be further enhanced through the coupling of processes described in Scheme 2 and 3a. Accordingly, PEC CO₂ reduction, which synergistically combines the advantages of EC and PC systems, was expected to offer the best performance for CO₂ reduction to CH₃OH, which was confirmed by the experiment below.

The instantaneous photocurrent density excited by visible light provides a useful indication of the efficiency of the separation of photogenerated electrons and holes on the surface of a semiconductor photocatalyst. The higher the instantaneous photocurrent density, the more sensitive the

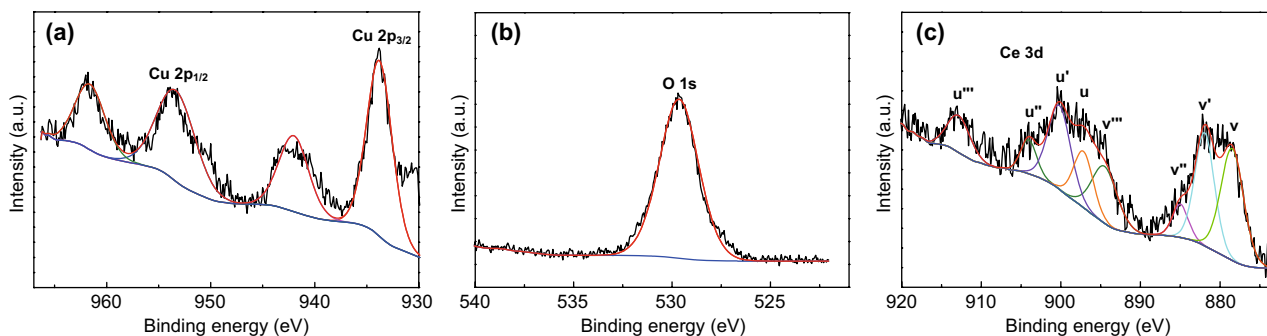
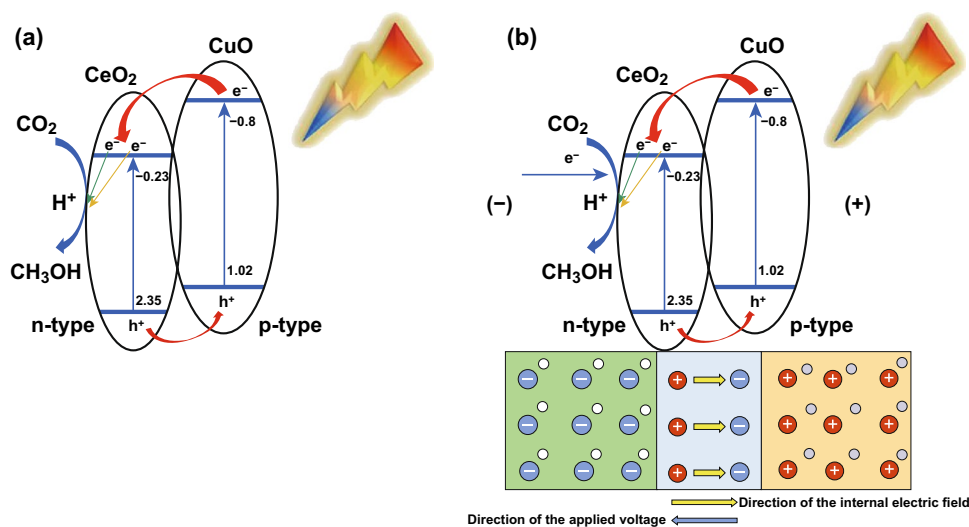


Fig. 3 XPS characterization of the flower-like CeO₂ NPs/CuO NPs composite catalyst. **a** Cu 2p region, **b** O 1s region, and **c** Ce 3d region



Scheme 3 Proposed mechanisms for **a** PC CO_2 reduction, and **b** PEC CO_2 reduction on the flower-like CeO_2 NPs/ CuO NPs composite catalyst. The mechanism of EC CO_2 reduction is shown in Scheme 2

photocatalyst is to visible light and the greater the separation of photogenerated electrons and holes. Figure 4a shows instantaneous photocurrent density changes for the CuO NPs and CeO_2 NPs/ CuO NPs catalysts over several light-on and light-off cycles of visible light irradiation. For both electrodes, the photocurrent density increased rapidly when irradiated with visible light and then dropped sharply when the light was turned off. Importantly, the photocurrent density of the flower-like CeO_2 NPs/ CuO NPs catalyst ($40.75 \mu\text{A cm}^{-2}$) was about 10 times higher than that of the CuO NPs catalyst ($4.28 \mu\text{A cm}^{-2}$) under visible light irradiation, indicating that charge separation much more effective on the CeO_2 NPs/ CuO NPs. This data provides further evidence

that CeO_2 / CuO heterojunction construction was effective in enhancing the light absorbing and availability of electrons and holes for photoreactions (by effectively facilitating charge separation). Further, the photocurrent density of CeO_2 NPs/ CuO NPs electrode appeared to be quite stable over the three on-off cycles, suggesting that the electrode had stable performance.

The XPS valence band spectrum for the flower-like CeO_2 NPs/ CuO NPs catalyst is shown in Fig. 4b. The spectrum could be fitted using two peaks at 3.97 and 5.39 eV, corresponding to valence oxygen states CeO_2 and CuO . The position of the VBM was obtained directly from the spectrum using a linear extrapolation, yielding a VBM of 1.47 eV.

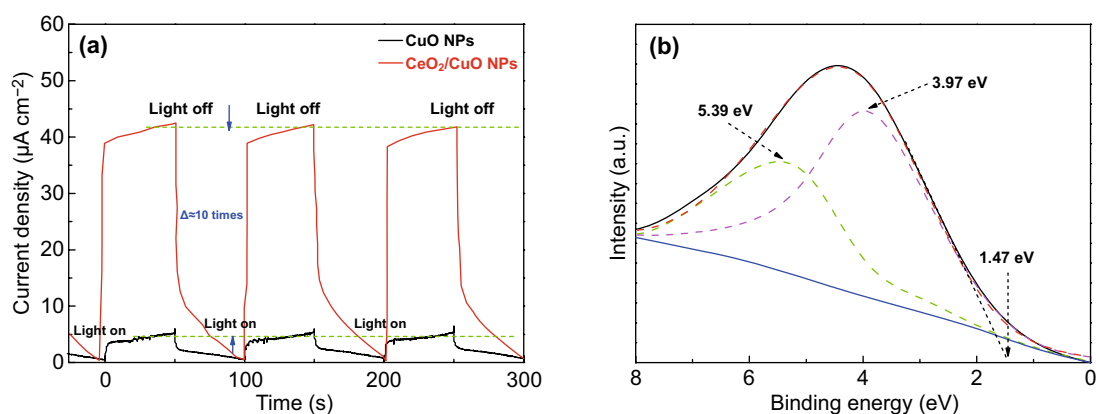


Fig. 4 **a** Instantaneous photocurrent density of catalyst, **b** VB photoemission spectrum (solid line) and Gaussian fit (dashed line) of catalyst

Since the band gap of the flower-like CeO_2 NPs/CuO NPs catalyst was estimated to be around 2.10 eV (Fig. 2c), the CB position of CeO_2 NPs/CuO NPs catalyst was thus around -0.63 eV.

3.2 Photoelectrocatalytic Reduction of CO_2

Having characterized the CuO/NPs and flower-like CeO_2 NPs/CuO NPs catalyst in detail, we then examined the performance of these two electrodes for PEC reduction CO_2 . Figure 5a shows linear sweep voltammetry (LSV) curves for each electrode in a $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ solution, under N_2 or CO_2 purging. In each case, the increase in the current observed as the potential is made more negative is due to the reduction of water and/or the catalytic reduction of CO_2 . The current response of the CeO_2 NPs/CuO NPs catalyst increased under light irradiation, under both a N_2 purge (cf. curves in Fig. 5a₂, a₃) and a CO_2 purge (cf. curves in Fig. 5a₄, a₅). Results indicate that the CeO_2 NPs/CuO NPs catalyst had good performance for PEC CO_2 reduction. Further, the PEC CO_2 reduction performance of the CeO_2 NPs/

CuO NPs catalyst was much better than that of the CuO NPs catalyst under light irradiation and with a CO_2 purge (cf. curves in Fig. 5a₅, a₁). And then the net current density ($i_{\text{CO}_2} - i_{\text{N}_2}$) of the CeO_2 NPs/CuO NPs with light and without light was compared (Fig. S4), the current density of light is much higher than dark one. It is more validated that the CeO_2 NPs/CuO NPs have more excellent ability for PEC reduction CO_2 . The photoelectric conversion efficiencies of the flower-like CeO_2 NPs/CuO NPs and CuO NPs catalysts are shown in Fig. 5b. The CO_2 to CH_3OH conversion efficiency on the CuO NPs/electrode at the applied potential of -1.0 V (vs SCE) was only 5.98%, whereas the efficiency for the same conversion on the CeO_2 NPs/CuO NPs catalyst was 55.64% (i.e., around nine times higher).

The products of PEC CO_2 reduction on the CeO_2 NPs/CuO NPs catalyst were analyzed by gas chromatography. At externally applied bias voltages ranging from -0.8 to -1.2 V, the only carbon-containing reduction product detected was methanol. Figure 5c shows the methanol yield over the CeO_2 NPs/CuO NPs catalyst at different applied potentials. As the applied voltage was increased up to

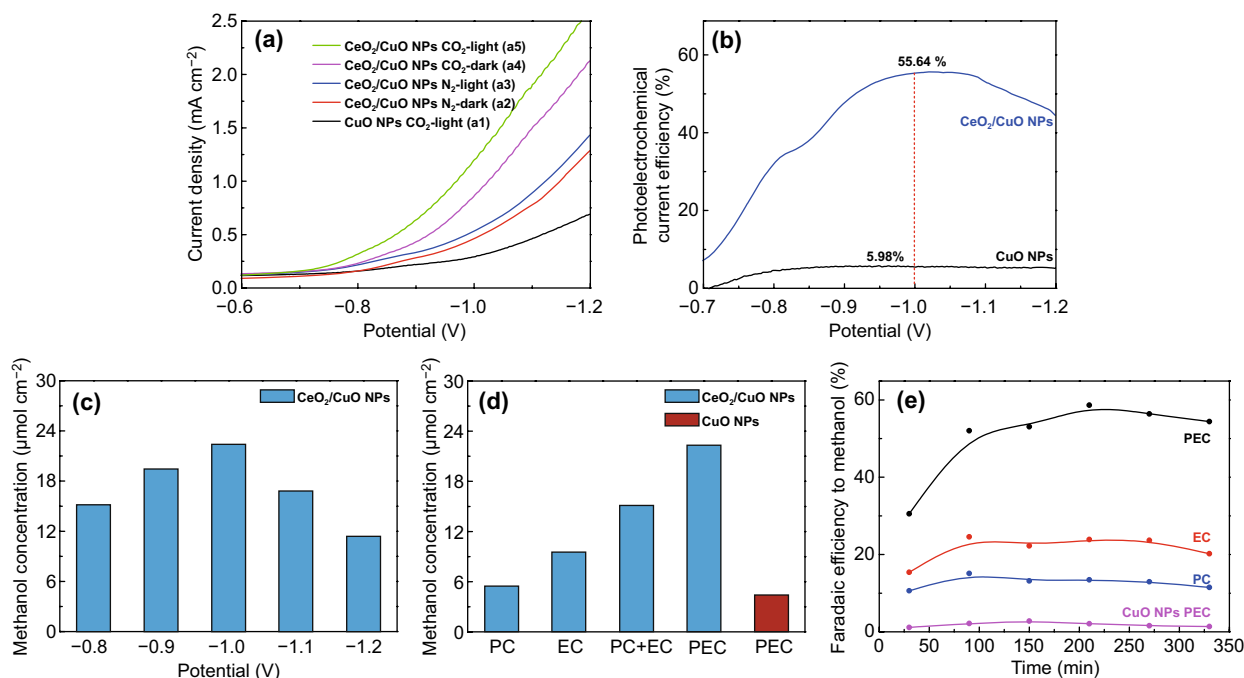


Fig. 5 **a** Linear sweep voltammetry curves for different electrodes under light illumination and in the dark. The data were collected in a $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ solution, under N_2 or CO_2 purging. **b** Photoelectric conversion efficiencies for different electrodes. **c** The methanol concentration at different potentials following 6.5 h of light illumination for the CeO_2 NPs/CuO NPs catalyst. **d** The methanol concentration after 6.5 h for PEC, EC, and PC reduction of CO_2 at -1.0 V. **e** Faradaic efficiency for CO_2 reduction to methanol under PEC, EC, and PC conditions at -1.0 V

– 1.0 V, the yield of methanol increased, reaching $22.32 \mu\text{mol cm}^{-2}$ at – 1.0 V over 6.5 h (corresponding to a methanol production rate of $3.43 \mu\text{mol cm}^{-2} \text{h}^{-1}$). As the potentials continued to increase, at higher potentials, the yield of methanol decreased. Results suggest that in the potential range from – 0.8 to – 1.0 V, the catalytic reduction of CO_2 is the dominant reaction occurring on the electrode. At more negative potentials, the hydrogen evolution reaction starts to compete with electrocatalytic CO_2 reduction.

Figure 5d shows comparison of the methanol yields for CO_2 reduction to methanol on the flower-like CeO_2 NPs/CuO NPs catalyst under PEC, EC, and PC regimes after 6.5 h of testing. Methanol yields decreased in the order PEC ($22.32 \mu\text{mol cm}^{-2}$) > EC ($9.51 \mu\text{mol cm}^{-2}$) > PC ($5.53 \mu\text{mol cm}^{-2}$). Thus, the methanol yield by PEC reduction of CO_2 was 2.35 and 4.04 times higher than the yields obtained by EC and PC. Further, the methanol yield by PEC on the CeO_2 NPs/CuO NPs catalyst ($22.32 \mu\text{mol cm}^{-2}$) was around 5 times higher than the methanol yield by PEC on the CuO NPs electrode ($4.37 \mu\text{mol cm}^{-2}$) for a reaction time of 6.5 h at a potential of – 1.0 V, indicated that CeO_2 addition greatly improved the PEC performance of the CeO_2 NPs/CuO NPs catalyst. The Faradaic efficiency for CO_2 reduction to methanol on the flower-like CeO_2 NPs/CuO NPs catalyst under different conditions (i.e., PEC, EC, and PC) in 0.1 mol L^{-1} KHCO_3 solution under a CO_2 purge is shown in Fig. 5e. The Faradaic efficiency for PEC was 58.67%, significantly higher than that realized by EC (24.57%) and PC (15.08%). Again, this reflects the action of both EC and PC processes under the PEC regime, which act cooperatively to increase the availability of electrons for CO_2 reduction. As expected, the PEC Faradaic efficiency of the CeO_2 NPs/CuO NPs catalyst for CO_2 reduction to CH_3OH at – 1.0 V was superior to that of the CuO NPs catalyst. Furthermore, the Faradaic efficiency of the CeO_2 NPs/CuO NPs catalyst remained ~55% at – 1.0 V over 6.5 h, implying that the heterojunction electrode had exceptional stability.

Considering all of the above, it can be concluded that the CeO_2 NPs/CuO NPs catalyst developed in this work demonstrated remarkable performance and stability for PEC CO_2 reduction to methanol. The electrode benefitted from the following synergies: (1) The direct electrodeposition of flower-like CeO_2 nanoparticles on the CuO NPs/Cu foil catalyst ensured intimate contact between the CeO_2 and CuO components, thus forming intimate p–n heterojunctions for electron transfer; (2) The flower-like CeO_2 offered an abundance of

active sites for CO_2 adsorption and reduction, while also minimizing electron–hole pair recombination in CeO_2 under light irradiation due to the short electron transfer distance to the CeO_2 surface distance; (3) The combination of p-type CuO and n-type CeO_2 increased the carrier concentration in the CeO_2 NPs/CuO NPs catalyst by 10^8 times relative to the CuO NPs catalyst, which greatly enhanced CO_2 reduction performance; and (4) The CeO_2 NPs/CuO NPs catalyst possessed good optical absorption characteristics under visible light, with the photoexcitation of both CeO_2 and CuO, as well as electron transfer from CuO to CeO_2 (matched by hole migration from CeO_2 to CuO), generating an abundance of electrons at the CeO_2 surface for CO_2 reduction. Thus, when light and external voltage (– 1.0 V) were simultaneously applied to the CeO_2 NPs/CuO NPs catalyst in a 0.1 M KHCO_3 solution purged with CO_2 , the reduction of CO_2 to CH_3OH occurred very efficiently evidenced by a Faradaic efficiency of almost 60% at – 1.0 V (using protons generated by water oxidation at the anode). Results encourage the development of p–n junction PEC systems for CO_2 reduction to oxygenate and fuels.

4 Conclusions

Electrodeposition of flower-like CeO_2 NPs significantly enhanced the performance of a CuO NPs/Cu catalyst for PEC CO_2 reduction to methanol under visible light irradiation. The system benefitted from the creation of intimate p–n heterojunctions between p-type CuO and n-type CeO_2 . Under both an applied electric potential of – 1.0 V, or visible light irradiation, electrons migrated from CuO nanoparticles to the flower-like CeO_2 nanoparticles, resulting in an abundance of electrons on the surface of the CeO_2 nanoparticles for CO_2 reduction to methanol. Under visible light illumination, the yield of methanol for the CeO_2 NPs/CuO NPs/Cu catalyst at – 1.0 V in a CO_2 -saturated 0.1 M KHCO_3 solution was $3.44 \mu\text{mol cm}^{-2} \text{h}^{-1}$ (cf. the CuO NPs/Cu catalyst, for which the methanol production rate was only $0.67 \mu\text{mol cm}^{-2} \text{h}^{-1}$). Further, under these conditions the CeO_2 NPs/CuO NPs/Cu catalyst displayed a high Faradaic efficiency for CO_2 reduction to CH_3OH (~60%) and excellent stability. These findings are significant for the future development of catalytic systems for CO_2 reduction, demonstrating that a simple catalyst modification (i.e., CeO_2 electrodeposition) can dramatically enhance carrier concentrations and the

availability of electrons for PEC reduction of CO₂ to valuable commodity chemicals such as methanol.

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