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Efficient methanol upcycling toward divergent C–C coupling synthesis by radical homo-coupling and addition-elimination pathway

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Abstract

Direct photocatalytic conversion of methanol into high-value multi-carbon chemicals through precisely controlled C–C coupling represents an extremely appealing but challenging goal. Herein, we demonstrate the efficient photoredox-driven dehydrocoupling of methanol into divergent synthesis of ethylene glycol (EG) and glycolaldehyde (GLD) concomitantly with H_2 production by structural regulation of atomically dispersed Ni species. We showcase distinctly different reaction pathway for divergent C–C coupling of methanol over two types of atomically dispersed Ni cocatalyst-decorated CdS quantum dots, namely those with single Ni atoms (Ni_1-CdS/SiO_2) and Ni clusters (Ni_n-CdS/SiO_2). The Ni_1-CdS/SiO_2 catalyst generates EG with a selectivity of 90% by a radical homo-coupling pathway, whereas the Ni_n-CdS/SiO_2 catalyst achieves a high selectivity of 96% towards GLD by a radical addition-elimination pathway with an impressive apparent quantum yield of 17.2%. This work not only offers a fascinating nonpetroleum route for the divergent C–C coupling synthesis of EG and GLD but also underscores the broad vista of modulating non-selective radicals toward selective transformation of methanol into multi-carbon products.

Introduction

Methanol, which can be sourced from diverse carbon resources, including CO_2, natural/shale gas, coal and biomass, functions as a vastly abundant one-carbon (C_1) building block in today's chemical industry[1-6]. Catalytic methanol transformation involves the activation/conversion of methanol into many types of value-added chemicals, in which the construction of C–C bond represents the most fascinating yet challenging reaction[1]. Presently, methanol conversions associated with C–C bond formation are mainly confined to dehydrative oligomerizations, such as industrial methanol-to-gasoline (MTG) and methanol-to-olefin (MTO) processes, which suffer from restricted selectivity towards target products[7-9]. Against the backdrop of escalating interest in the methanol economy, it is of urgency and great significance to develop novel and alternative routes for the transformation of

methanol via controllable C−C coupling with high reaction efficiency and selectivity.

In principle, the transformation of methanol inevitably involves the activation of either its α-C–H or C−O/O−H bond[1,4]. Of note, the preferential activation of C−O/O−H bond in methanol usually brings along value-reduced oxidation products, especially formaldehyde (HCHO) and even CO_2[10-12]. To access two-carbon (C_2) products via C−C coupling, the selective activation of targeted α-C–H bond in methanol is crucial but challenging[13-16]. Recent years have witnessed the application of metal sulfide semiconductors as photocatalysts to selectively activate the inert α-C–H bond in methanol with the O−H bond intact, thus affording high-reactive hydroxymethyl (•CH_2OH) radicals for the synthesis of ethylene glycol (EG)[1,17-22]. Nevertheless, these previous catalytic systems not only encounter the trade-off between activity and selectivity, but also fail to produce other value-added C_2 products because of the pervasive difficulty in steering non-selective •CH_2OH radicals toward controllable C−C coupling pathway for divergent synthesis of C_2 feedstocks. In particular, glycolaldehyde (GLD), a highly attractive C_2 chemical with versatile applications[23-26], has usually been synthesized with low activity and selectivity. These unsolved problems stem from the failure to efficiently manipulate the •CH_2OH radical conversion pathway after the preferential activation and cleavage of α-C–H bond in methanol is achieved. In such a scenario, upon overcoming α-C–H bond-breaking event, the precise regulation of activity/selectivity by preferably steering non-selective •CH_2OH radical conversion route presents a brand-new challenge in advancing methanol chemistry and holds great academic significance.

Herein, we report the unique ensemble of atomically dispersed Ni-decorated CdS quantum dots (QDs) supported on spherical SiO_2 (Ni-CdS/SiO_2) for the tunable, high-performance photochemical C−C coupling of methanol into EG and GLD integrated with concomitant H_2 production at ambient conditions. The present CdS QDs can selectively activate the unreactive α-C–H bond in methanol with the O−H group intact, thus affording sufficient high-reactive •CH_2OH radicals. Loading CdS QDs onto the SiO_2 support not only regulates the dielectric environment of CdS QDs via the near-field scattering promoted optical absorption model for enhanced light-capturing property[15,27,28], but also improves their antiphotocorrosion ability and recyclability. Two types of atomically dispersed Ni species, single Ni atoms for Ni_1-CdS/SiO_2 and Ni clusters for Ni_n-CdS/SiO_2, act as active sites to govern •CH_2OH radicals conversion pathway for precisely tailoring the C−C coupling synthesis between EG and GLD formation reaction, along with significantly enhanced activity. As an outcome, EG is generated with 90% selectivity over the Ni_1-CdS/SiO_2 catalyst, and a high selectivity of 96% towards GLD is obtained over the Ni_n-CdS/SiO_2 catalyst. Mechanistic insights by joint theoretical and experimental studies unveil that the divergent synthesis of EG and GLD over Ni-CdS/SiO_2 originates from the single Ni atoms-assisted homo-coupling of •CH_2OH radicals and Ni clusters-catalyzed radical addition-elimination mechanism, respectively.

Results

Preparation and characterization of Ni-CdS/SiO_2 with atomically dispersed Ni species

The schematic diagram of the fabrication of atomically dispersed Ni-decorated CdS QDs supported on spherical SiO_2 (Ni-CdS/SiO_2) is depicted in **Fig. 1a**. Initially, CdS QDs were prepared by a one-pot synthesis using 3-mercaptopropionic acid (MPA) as capping molecule (**Supplementary Table 1**), and then loaded onto the SiO_2 support (CdS/SiO_2) through an electrostatic self-assembly strategy. Transmission electron microscopy (TEM) images afford the detailed insights into the microscopic structures and morphologies of CdS/SiO_2 composite. In contrast to the smooth surface of SiO_2 sphere (**Supplementary Fig. 1a** and **b**), the uniform distribution of CdS QDs can be distinctly identified on the

surface of SiO_2 sphere within the CdS/SiO_2 composite (**Fig. 1b**). Subsequently, photodeposition of Ni species onto CdS/SiO_2 was performed using $NiCl_2{\cdot}6H_2O$ as the precursor under 0.5 h of xenon-lamp irradiation. The CdS/SiO_2 composite contains abundant dangling –COOH groups originating from MPA, which serve to adsorb and anchor Ni^{2+} cations (**Supplementary Fig. 2**)[28,29]. The Ni-CdS/SiO_2 composites with different Ni loading contents were obtained by regulating the amount of Ni precursor (**Supplementary Table 2**, the two representative samples of $Ni_{0.1}$-CdS/SiO_2 and $Ni_{1.0}$-CdS/SiO_2 with the lowest and highest Ni loading amounts are denoted as Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2, respectively). High-resolution TEM (HR-TEM, **Supplementary Fig. 1c** and **d**) analysis exhibits the ordered lattice fringe with a *d*-spacing of 0.335 nm, ascribed to the (111) crystal plane of cubic CdS[28]. No formation of Ni-derived nanoparticles is observed in high-resolution TEM images of both the Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2, certifying that the Ni species in these two catalysts are both atomically dispersed on CdS/SiO_2. As illustrated in **Supplementary Fig. 1e**, elemental mapping results further validate the even dispersion of Cd, S and Ni elements throughout the SiO_2 support. From aberration-corrected high-angle annular dark-field scanning TEM (**Supplementary Fig. 3**), high-density bright dots assigned to the overlapped image contrast of Cd atom and Ni atom are observed in Ni_n-CdS/SiO_2, confirming the formation of Ni clusters.

To gain the local coordination structure of Ni species, X-ray absorption spectroscopy (XAS) measurements were performed. **Fig. 1c** shows the Ni K-edge X-ray absorption near-edge structure (XANES) spectra of Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2 in reference to Ni foil and NiO. The threshold energy of Ni_1-CdS/SiO_2 falls between Ni foil and NiO, suggesting an electron-deficient state of $Ni^{\delta+}$ ($0 < \delta < 2$)[30,31], and that of Ni_n-CdS/SiO_2 is close to standard NiO, manifesting that the electronic state of Ni species in Ni_n-CdS/SiO_2 is approximate to +2[29,32], consistent with the X-ray photoelectron spectroscopy (XPS) results (**Supplementary Fig. 4** and **5**). As sketched in **Fig. 1d**, the extended X-ray absorption fine structure (EXAFS) spectrum of Ni_1-CdS/SiO_2 only features a prominent peak at 1.38 Å from Ni–O coordination, suggesting the formation of isolated Ni atom in Ni_1-CdS/SiO_2[28,33]. For Ni_n-CdS/SiO_2, an additional peak at about 2.69 Å from Ni–Ni coordination emerges, corroborating the formation of Ni clusters[29]. The trend can also be clearly resolved from the wavelet transform on Ni K-edge EXAFS oscillations (**Fig. 1e**,**f** and **Supplementary Fig. 6**). From the fitting structural parameters (**Fig. 1g**,**h**, **Supplementary Fig. 7** and **Supplementary Table 3**), the Ni-O coordination number in Ni_1-CdS/SiO_2 is evaluated to be 2.6 ± 0.2, indicating the Ni single atoms with a $Ni–O_3$ moiety. In addition, the Ni-O and Ni–Ni coordination numbers of Ni clusters in Ni_n-CdS/SiO_2 are calculated to be 6.4 ± 0.2 and 3.5 ± 0.3, respectively. The above results elucidate that these two catalysts exhibit distinct difference in electronic structure as well as in coordination environment. With the further aid of density functional theory (DFT) optimization calculations, the most stable structures of Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2 are sketched in **Supplementary Fig. 8**.

Selective dehydrocoupling of methanol to produce EG or GLD

Subsequently, we evaluated the application of Ni-CdS/SiO_2 for dehydrocoupling of methanol to EG or GLD integrated with H_2 evolution, in one tunable photoredox catalytic system (**Fig. 2a**). As displayed in **Fig. 2b** and **c**, the blank CdS QDs exhibit low EG and H_2 production rates, reaching only 1.9 and 2.8 mmol $g_{Ni\text{-}CdS}^{-1}$ h^{-1}, respectively. Compared to bare CdS QDs, CdS/SiO_2 presents much higher EG formation rate of 4.1 mmol $g_{Ni\text{-}CdS}^{-1}$ h^{-1}; meanwhile, the production rate of H_2 improves from 2.8 to 6.4 mmol $g_{Ni\text{-}CdS}^{-1}$ h^{-1}, which is attributed to the distinctly enhanced optical absorption correlated to the scattering resonances of the SiO_2 supports (**Supplementary Fig. 9**)[15,28]. Upon decorating with Ni, the Ni_1-CdS/SiO_2 exhibits significantly enhanced EG formation rate (16.8 mmol $g_{Ni\text{-}CdS}^{-1}$ h^{-1}) by 3.1 times as

compared to CdS/SiO_2, along with a high EG selectivity of 90% (**Supplementary Fig. 10-14**). Remarkably, as the Ni loading increases, the selective product in the dehydrocoupling of methanol transitions from EG to GLD (**Supplementary Fig. 10-14**). Consequently, over Ni_n-CdS/SiO_2, a GLD evolution rate of 24.1 mmol $g_{Ni\text{-}CdS}^{-1}$ h^{-1} is achieved with an excellent selectivity of 96% (**Fig. 2b**). In addition, the production of H_2 increases along with Ni loading amount, and the ratios of electrons (consumed for the reduction product H_2) to holes (consumed for the oxidation products EG/GLD/HCHO) over different catalysts are calculated to be approximately 1:1 (**Supplementary Table 4**), indicating a stoichiometric dehydrocoupling reaction. It is noteworthy that HCHO (a major by-product of methanol oxidation) consistently maintains an exceedingly low evolution rate (< 1.2 mmol $g_{Ni\text{-}CdS}^{-1}$ h^{-1}) in the current catalysis system. In addition, the optimized apparent quantum yields (AQYs) of 12.3% for EG and 17.2% for GLD are attained over Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2 respectively, at λ = 370 nm (**Fig. 2d**). Compared with previously reported catalytic systems (**Supplementary Table 5**)[1,17-22], this work represents the first report on photocatalytic methanol coupling for the divergent synthesis of EG and GLD concomitantly with H_2 production.

The stability of Ni-CdS/SiO_2 was then investigated by cycle experiments, as shown in **Fig. 2e** and **f**. After five repeated tests of totaling 50 h, the catalytic performance for EG (or GLD) and H_2 coproduction over Ni_1-CdS/SiO_2 (or Ni_n-CdS/SiO_2) remains relatively stable; nevertheless, that of unsupported CdS QDs decreases by 42.8% for EG and 43.6% for H_2 (**Supplementary Fig. 15**). The high-resolution XPS analysis in **Supplementary Fig. 16** illustrates the good maintenance of element composition in used Ni_1-CdS/SiO_2 compared with fresh Ni_1-CdS/SiO_2. In addition, element leakage after 10 h of continuous light irradiation was evaluated. As shown in **Supplementary Table 6**, only slight Cd^{2+} leakages of 1.34 μg and 1.12 μg are observed in Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2 respectively, which are much lower than those of bare CdS QDs (7.35 μg for Cd^{2+}). These results collectively illustrate that this self-assembly strategy suppresses the photocorrosion of CdS QDs and facilitates the recovery of CdS QDs from the reaction solvent. Furthermore, taking into account that single atoms may aggregate under light irradiation[34,35], we performed additional XAS characterizations on Ni_1-CdS/SiO_2 after five consecutive reaction cycles. Notably, in the EXAFS spectrum of the used Ni_1-CdS/SiO_2 after 50 h of light exposure, an additional weak peak emerges at approximately 2.64 Å from Ni–Ni coordination (**Supplementary Fig. 17**), indicating the partial agglomeration of single Ni atoms during the prolonged light irradiation (**Supplementary Table 7**), which accounts for the slight decrease in EG selectivity (**Fig. 2e**).

Mechanism insight for dehydrocoupling of methanol

Given that the charge separation dynamics usually restricts the catalytic performance, photo-electrochemical characterizations were first carried out. As depicted in **Supplementary Fig. 18a**, the transient photocurrent densities of these samples increase in the following sequence: CdS/SiO_2 < Ni_1-CdS/SiO_2 < Ni_n-CdS/SiO_2, implying that decorating CdS/SiO_2 with Ni species remarkably enhances the charge separation efficiency, which was further verified by the electrochemical impedance spectroscopy (EIS) analysis (**Supplementary Fig. 18b**). These results distinctly indicate that the incorporation of atomically dispersed Ni species into CdS/SiO_2 facilitates the conversion of methanol to EG or GLD for a significantly boosted activity by expediting the separation and transfer of photogenerated electrons and holes.

To probe the reaction mechanism of methanol coupling to EG/GLD integrated with H_2 evolution in the present catalytic system, the band structure of CdS QDs was measured. As displayed in **Fig. 3a**, Tauc plot indicates the bandgap energy (E_g) of CdS QDs to be around 2.48 eV. The conduction-band (CB)

edge of CdS QDs is measured with the value of −0.72 V vs NHE based on the Mott–Schottky curve, and the valence-band (VB) edge of CdS QDs is thus calculated to be 1.76 V vs NHE. Taking into account both the limited interfacial contact between Ni species and CdS QDs enabled by the capping molecule of MPA and the low Ni loading amount (0.1 to 1%)[36-38], anchoring Ni species is insufficient to induce significant alterations to the band structure of CdS QDs. In addition, the redox potential of methanol is evaluated at about 0.61 V vs NHE by virtue of the cyclic voltammograms (**Supplementary Fig. 19**)[39-41]. Obviously, the CB edge of CdS QDs is higher than $E(H^+/H_2)$ (−0.41 V vs. NHE), and the VB edge is lower than E(methanol/methanol$^{\bullet+}$), which fulfills the thermodynamic constraints for the synchronous occurrence of these two half-reactions (**Fig. 3b**)[11].

To further decipher the function-oriented effects of Ni decoration with regard to the selectivity regulation in methanol coupling to EG and GLD, we performed a set of control experiments. As shown in **Supplementary Fig. 20**, the catalytic performance (including EG, GLD and H_2 production rates as well as EG/GLD selectivity) of both $Ni_{1\text{-IM}}$-CdS/SiO_2 and $Ni_{n\text{-IM}}$-CdS/SiO_2 synthesized through impregnation method is significantly lower than that of the corresponding Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2, suggesting the unique structural advantages of atomically dispersed Ni species afforded by the photodeposition strategy. In the absence of catalyst or light, the photocatalytic reaction cannot proceed at all (**Fig. 3c** and **d**). The introduction of CCl_4 as an electron scavenger almost terminates the H_2 production, and moreover, the generation of EG or GLD is decelerated considerably once adding triethanolamine (TEOA) as a hole scavenger, indicating the joint participation of photogenerated electrons and holes in the evolution of H_2 and EG/GLD. In addition, comparative reaction with EG employed as the reactant was performed to investigate the possible consecutive oxidation of EG. Notably, no product is detected over both Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2 during the experimental process, which suggests that EG can exist stably and GLD is not originated from the overoxidation of EG. Furthermore, the time-dependent product distributions for the dehydrocoupling of methanol illustrate that the production of EG over Ni_1-CdS/SiO_2 increases as the reaction time extends (**Fig. 3e**). An induction period is clearly observed, since stabilizing both the adsorption-desorption equilibrium of reactants (i.e., methanol molecules) on the catalyst surface and the accumulation of initial reaction intermediates demands a short duration. Meanwhile, the yields of GLD and HCHO exhibit an upward trend, albeit with extremely low values during the reaction process. In contrast, although HCHO also maintains a relatively low output over Ni_n-CdS/SiO_2, its generation presents a trend of first increasing and then decreasing with the reaction proceeding (**Fig. 3f**), which indicates that in this catalytic system, HCHO is not a by-product but an intermediate for the production of target product GLD.

To gain further insights, in-situ electron paramagnetic resonance (EPR) spectroscopic studies were adopted to monitor the radical intermediates involved in the dehydrocoupling of methanol using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin-trapping reagent (**Fig. 3g**). Under light irradiation, the generated $\bullet CH_2OH$ radical is trapped by DMPO, as manifested by the characteristic peaks belonging to the DMPO-CH_2OH adduct[1]. Upon Ni decoration, an obvious increase in the evolution rate of $\bullet CH_2OH$ radical is observed over Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2, indicating that Ni species significantly promotes the cleavage of α-C−H bond in methanol. It is noted that the methoxyl ($CH_3O\bullet$) radical, commonly generated in the conversion of methanol[1,17], is absent in the EPR spectra, which is maybe due to the small amount of $CH_3O\bullet$ radical generated in this catalytic system as well as its short-lived nature[1]. In addition, through the in-situ capture of $\bullet CH_2OH$ radical by 1,1-diphenylethylene (DPE)[18], the product of 3,3-diphenylpropan-1-ol (DPE-CH_2OH) is obtained over Ni_1-CdS/SiO_2, with a selectivity of 95% according to the gas chromatography results (**Fig. 3h**, **Supplementary Fig. 21** and **22**). Another trace product of 3-methoxy-3,3-diphenylpropan-1-ol (CH_3O-DPE-CH_2OH) is attributed to the addition

of methoxy radical (CH_3O•) to DPE-CH_2OH. These findings illustrate that the preferential cleavage of α-C−H bond to generate •CH_2OH radical in methanol than the O−H bond occurs readily on Ni_1-CdS/SiO_2, thereby generating EG via •CH_2OH radical coupling[1,18]. By contrast, for the case over Ni_n-CdS/SiO_2, capturing radicals by DPE affords the products of DPE-CH_2OH and CH_3O-DPE-CH_2OH with selectivities of 79% and 21%, respectively—corresponding to the radical selectivities of 83% for •CH_2OH radical and 17% for CH_3O• radical, indicating that the cleavage of both α-C−H and O−H bond in methanol occurs concurrently on Ni_n-CdS/SiO_2. This distinctly enhanced generation of CH_3O• radical originating from O−H cleavage of methanol is answerable for the formation of HCHO intermediate[42]. As corroborated by the dynamic trend of HCHO yield (first increasing and then decreasing) observed in **Fig. 3f**, the as-generated HCHO intermediate subsequently reacts with the •CH_2OH radical to afford GLD via the Ni clusters-assisted addition-elimination mechanism, as further confirmed by our theoretical calculations below.

Upon gathering the above results, DFT calculations were further carried out to shed light on the selectivity regulation between EG and GLD synthesis and the overall reaction pathways for the dehydrocoupling of methanol over Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2. Based on the EXAFS analysis, single Ni atoms and Ni clusters coordinated with the capping molecule of MPA on the surface of CdS QDs are selected to represent the catalytic sites on Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2, respectively (**Supplementary Fig. 23**-**26**). As sketched in **Fig. 4a**, both methanol adsorption steps over Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2 composite are thermodynamically downhill with the values of −0.056 and −0.453 eV, respectively. For the Ni single atom-assisted catalytic mechanism, the first deprotonation step of methanol over Ni_1-CdS/SiO_2 is endergonic to afford •CH_2OH radical via overcoming the relative energy of 0.494 eV. Subsequently, a homo-coupling pathway for EG production is thermodynamically favorable (0.015 eV) compared with the addition-elimination mechanism for GLD production (0.702 eV) or the second deprotonation route for HCHO production (1.135 eV). Under the catalytic mechanism supported by the Ni cluster, the homo-coupling of •CH_2OH radical is exothermic with the values of −0.368 eV; nevertheless, the desorption step of EG is considerably more difficult owing to the high relative energy of 1.095 eV. On the contrary, a thermodynamically more feasible reaction pathway is that, the •CH_2OH radical undergoes an addition-elimination pathway with a negligible condensation energy of 0.090 eV, followed by an exergonic deprotonation to produce GLD (−0.539 eV). The desorption process of GLD is regarded as the rate-limiting step by overcoming a moderate relative energy of 0.633 eV. Taking the above theoretical and experimental results into account together, the overall catalytic reaction mechanism for highly selective and divergent synthesis of EG and GLD over Ni_1-CdS/SiO_2 with single Ni atoms and Ni_n-CdS/SiO_2 with Ni clusters is put forward correspondingly, as displayed in **Fig. 4b**.

Discussion

In summary, we report the efficient photoredox-catalyzed dehydrocoupling of methanol into tunable EG by a radical homo-coupling pathway and GLD by a radical addition-elimination pathway over the different atomically dispersed Ni-decorated CdS/SiO_2 composite under ambient conditions. EG (90% selectivity) and GLD (96% selectivity) are preferentially generated over Ni_1-CdS/SiO_2 with single Ni atoms and Ni_n-CdS/SiO_2 with Ni clusters, respectively, along with excellent reactivity compared with other catalytic systems. Mechanistic insights into the divergent synthesis of EG and GLD are proposed based on joint experimental results and DFT calculations. The structure-performance relationship established over atomically dispersed Ni cocatalysts advances our understanding of catalyst design for methanol conversion, paving the way for future progress in devising catalysts for efficient and divergent

synthesis of sustainable chemicals.

Methods

Catalyst preparation. Synthesis of Ni-CdS/SiO_2 composite: Ni-CdS/SiO_2 was prepared based on a facile photodeposition strategy. Typically, 50 mg of CdS/SiO_2 was dissolved in a 50 mL of mixed solution of deionized (DI) water (40 mL) and ethanol (10 mL) that contained a certain amount of $NiCl_2 \cdot 6H_2O$ (17.04 μmol/mL (that is 1 mg_{Ni}/mL), 50 μL, 100 μL, 250 μL and 500 μL). Subsequently, the suspension was irradiated with a 300 W xenon lamp (PLS-SXE 300D, Beijing Perfectlight Co., Ltd.) under nitrogen (N_2) atmosphere for 0.5 h. The obtained products were collected via centrifugation and washed by DI water. Followed by blow-drying with N_2, the Ni-CdS/SiO_2 composites with different Ni weight loading (0.1%, 0.2%, 0.5% and 1.0%) were obtained.

Photoactivity testing. Selective dehydrocoupling of methanol to EG or GLD integrated with H_2 generation was carried out in a double-walled quartz reactor, which was maintained at 25 °C by a flow of circulating water. Typically, 20 mg of sample was added into 10 mL methanol. The reaction solution was purged with Ar gas for 15 min. Then, a 300 W xenon lamp (PLS-SXE 300D, Beijing Perfectlight Co., Ltd.) was used as light source, and the light power density is measured to be approximately 0.18 W cm^{-2}. The generated H_2 was quantified by a gas chromatography (Shimadzu GC-8A 2014C), and EG or GLD was analyzed by the gas chromatography-mass spectrometry. In addition, the by-product of HCHO was quantified by the acetylacetone colorimetric determination method, which can be found in Supporting Information.

Computational details. The present first principle DFT calculations were performed by Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method[43]. The exchange-functional was treated using the generalized gradient approximation (GGA) of Perdew-Burke-Emzerhof (PBE) functional[44]. The Spin-polarizations were carried out for all calculations. The energy cutoff for the plane wave basis expansion was set to 450 eV and the force on each atom less than 0.05 eV/Å was set for convergence criterion of geometry relaxation. The Brillouin zones (BZ) were sampled by using the surfaces structures of 2 × 2 × 1 Monkhorst-Pack K point. The self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. The DFT-D3 method was employed to consider the van der Waals interaction. A 15 Å vacuum was added along the z direction in order to avoid the interaction between periodic structures. In addition, the lattice parameters of the two models are consistent, with a = b = 16.803 Å, c = 33.182 Å, α = β = 90°, and γ = 120°. Structural relaxation calculations were performed for all structures, and the convergence criteria for energy and force mentioned earlier were satisfied. During the optimization process, the bottom two atomic layers were fixed to simulate the properties of the bulk phase, while all remaining atoms were allowed to relax freely. The free energies of the reaction steps were calculated by the equation:

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S$$

where ΔE_{DFT} is the DFT electronic energy difference of each step, ΔE_{ZPE} and ΔS are the correction of zero-point energy and the variation of entropy, respectively, which are obtained by vibration analysis, T is the temperature (T = 300 K). The details of Zero-Point Energy (ZPE) correction and entropy values are supplemented in **Supplementary Table 8**.

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

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Competing interests

The authors declare no competing financial interests.

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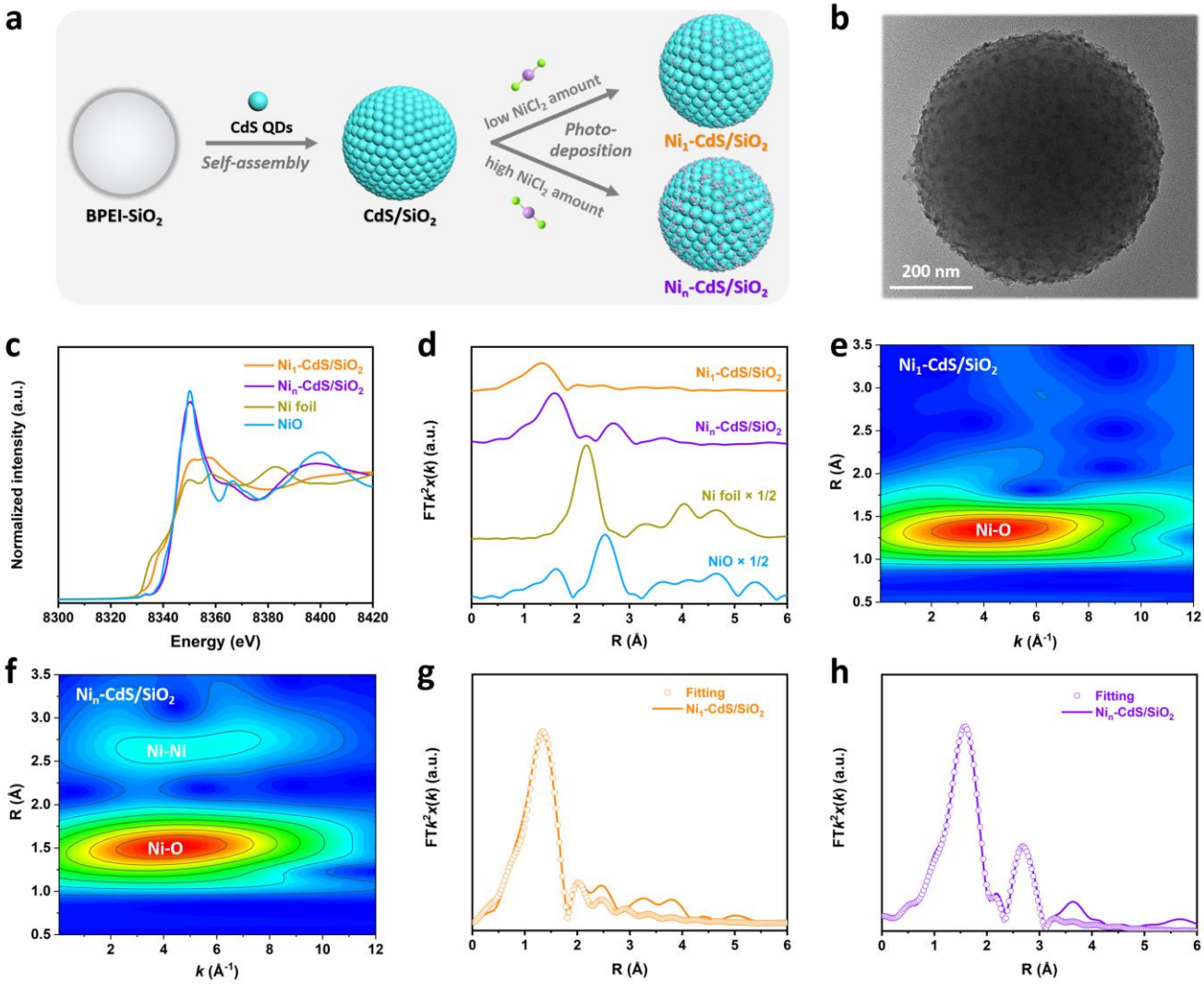

Fig. 1 | Preparation and characterization of Ni-CdS/SiO_2 with atomically dispersed Ni species. a, Synthesis procedure for the Ni-CdS/SiO_2 composite. **b**, TEM image of CdS/SiO_2 composite, **c**,**d** Normalized Ni K-edge XANES spectra (**c**) and FT-EXAFS spectra (**d**) of Ni-CdS/SiO_2 along with Ni foil and NiO as references. Wavelet transform for Ni K-edge EXAFS spectra of (**e**) Ni_1-CdS/SiO_2 and (**f**) Ni_n-CdS/SiO_2. **g**,**h**, EXAFS fitting curves for (**g**) Ni_1-CdS/SiO_2 with single Ni atoms and (**h**) Ni_n-CdS/SiO_2 with Ni clusters.

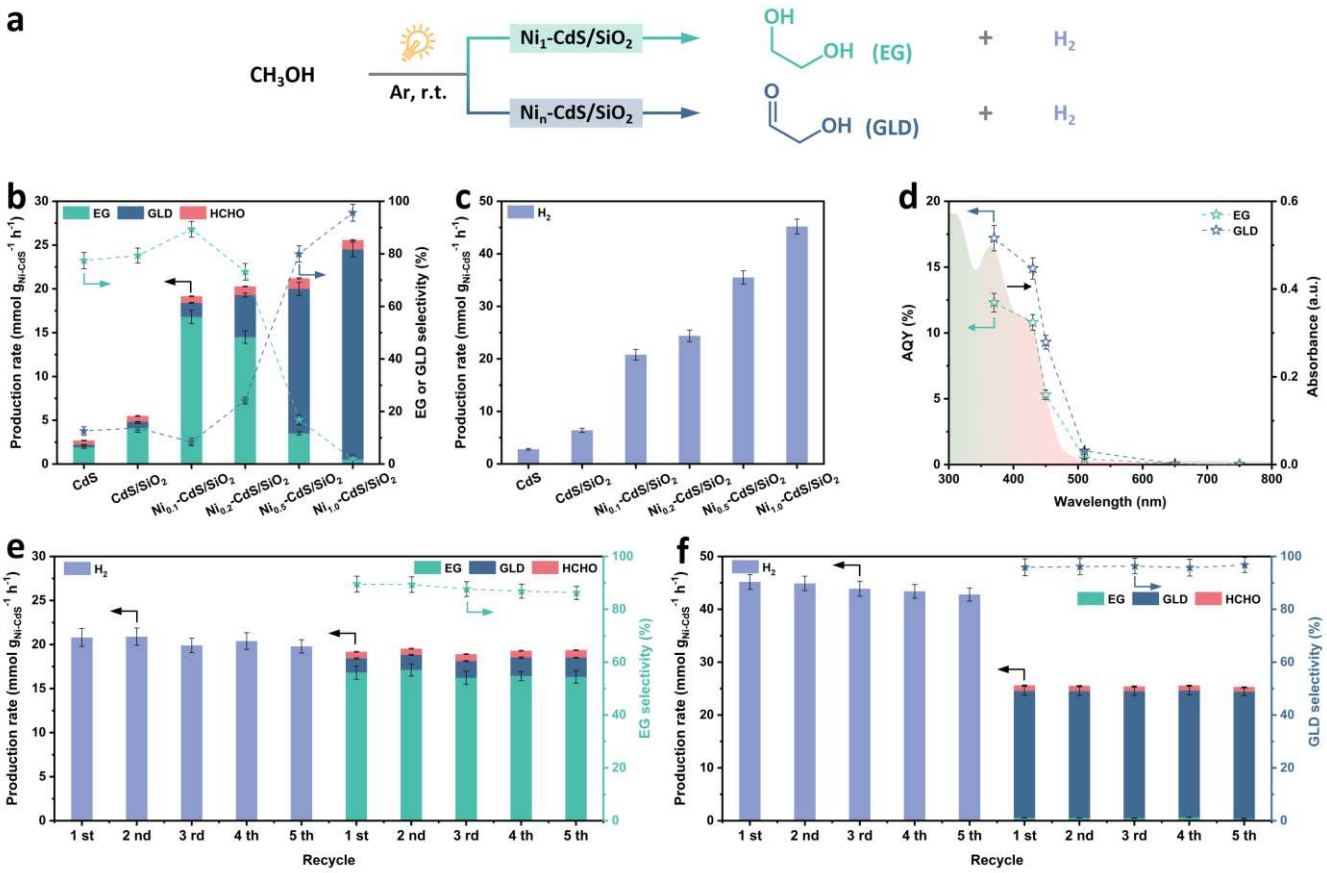

Fig. 2 | Selective switchable dehydrocoupling of methanol to produce EG or GLD. a, Schematic representation of the chemical reactions for conversion of methanol into EG or GLD as well as H_2. **b**, Production rate of various products and EG or GLD selectivity over CdS, CdS/SiO_2 and Ni-CdS/SiO_2 composites with different Ni loading amounts. **c**, H_2 production rate over CdS, CdS/SiO_2 and Ni-CdS/SiO_2 composites with different Ni loading amounts. Standard conditions: 20 mg catalyst in 10 mL of methanol solution, Ar atmosphere, 300 W xenon lamp, 10 h, room temperature. **d**, Diffuse reflectance spectroscopy (DRS) spectrum of CdS/SiO_2 composite and AQYs for EG or GLD production over Ni-CdS/SiO_2 composite under different monochromatic lights. **e**,**f**, Recycling performance of (**e**) Ni_1-CdS/SiO_2 composite with single Ni atoms and (**f**) Ni_n-CdS/SiO_2 composite with Ni clusters.

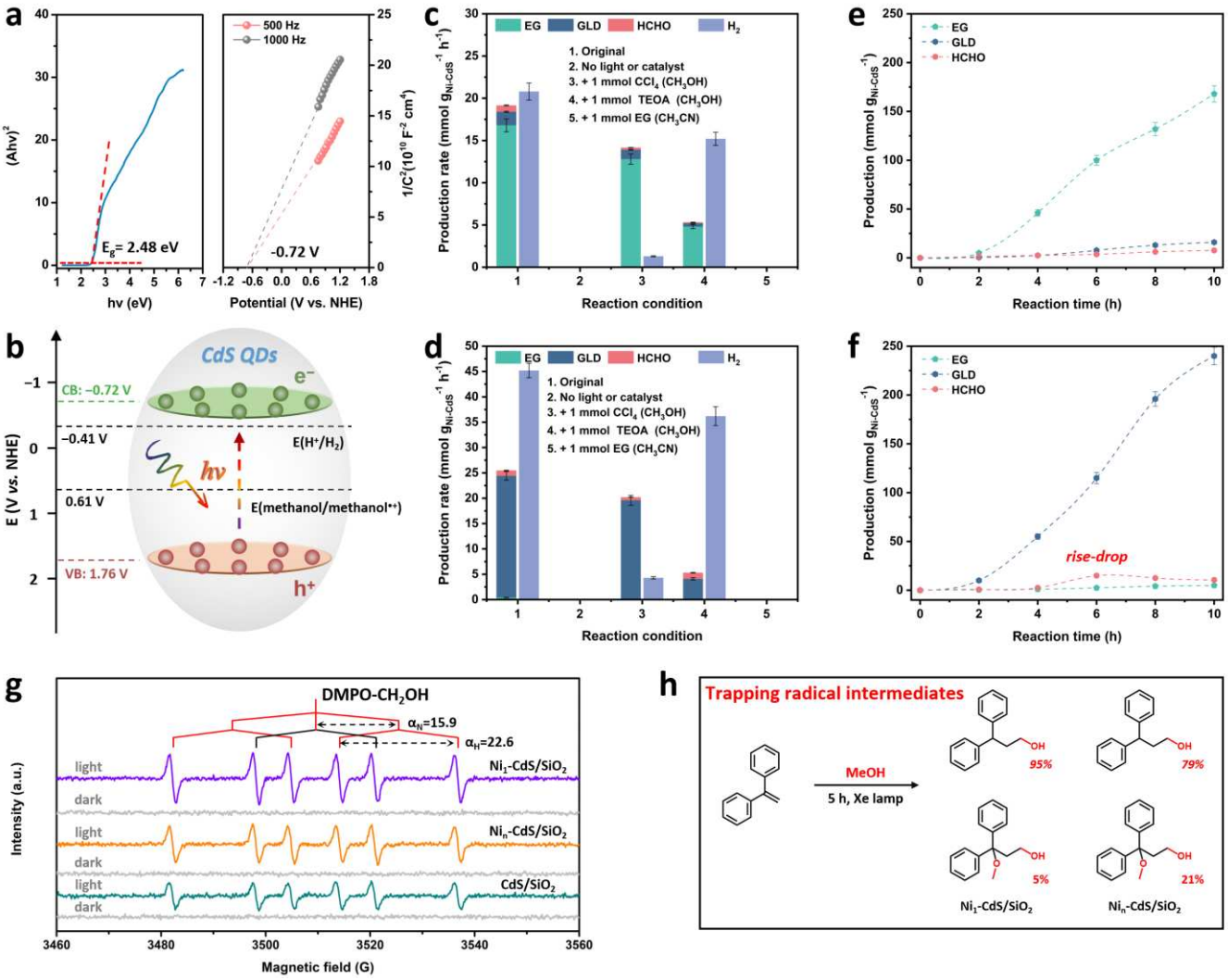

Fig. 3 | Mechanism insight for dehydrocoupling of methanol. a, Tauc plot (left) and Mott-Schottky plots (right) for CdS QDs. **b**, Redox potentials of methanol oxidation and H_2 evolution against the VB and CB edges of CdS QDs. **c**,**d**, Control experiments with different additives catalyzed by (**c**) Ni_1-CdS/SiO_2 and (**d**) Ni_n-CdS/SiO_2 composite. Standard conditions: 20 mg catalyst in 10 mL of CH_3OH (entries 1-4) or CH_3CN solution (entry 5), Ar atmosphere, 300 W xenon lamp, 10 h, room temperature. **e**,**f**, Time profiles of products evolution over (**e**) Ni_1-CdS/SiO_2 and (**f**) Ni_n-CdS/SiO_2 composite. **g**, In-situ EPR spectra of CdS/SiO_2, Ni_1-CdS/SiO_2 and Ni_n-CdS/SiO_2 composite in Ar saturated methanol solution in the presence of DMPO. **h**, Capturing radical intermediates by DPE in dehydrocoupling of methanol. Standard conditions: 20 mg catalyst in 10 mL of CH_3OH solution with 1 mmol of 1,1-diphenylethylene, Ar atmosphere, 300 W xenon lamp, 5 h, room temperature.

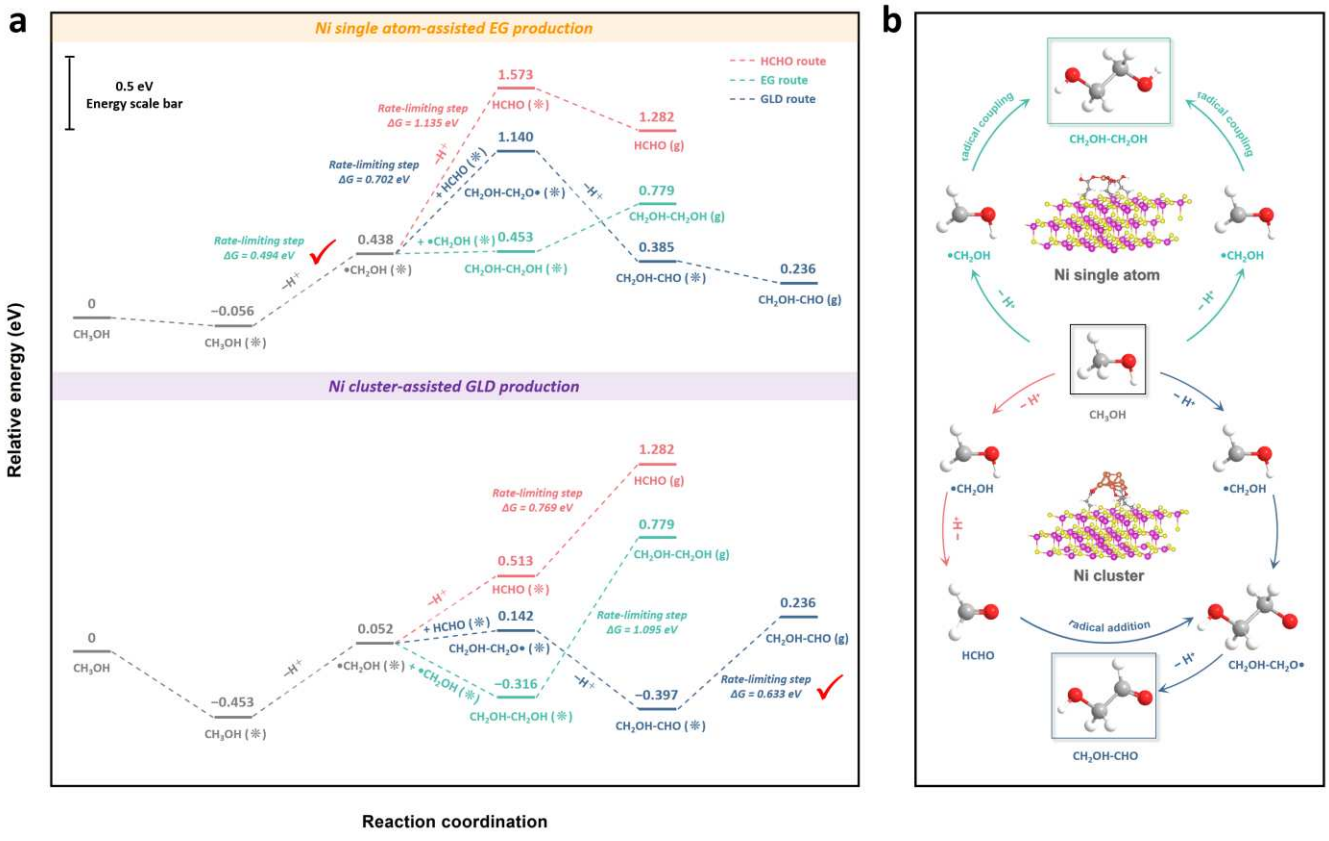

Fig. 4 | DFT calculations and proposed mechanism. a, Calculated potential energy diagrams for dehydrocoupling of methanol catalyzed by Ni_1-CdS/SiO_2 with Ni single atoms and Ni_n-CdS/SiO_2 with Ni clusters, respectively. **b**, Proposed mechanism for switchable methanol C−C coupling to EG or GLD.