



Recent developments in dark photocatalytic hydrogen production over smart catalysts

Xiaoyu Dong¹, Yifan Zhou¹, Xiao Fang¹, Yong Ding^{1,2,*}

¹State Key Laboratory of Natural Product Chemistry, Key Laboratory of Advanced Catalysis of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, Gansu, China.

²State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China.

***Correspondence to:** Yong Ding, State Key Laboratory of Natural Product Chemistry, Key Laboratory of Advanced Catalysis of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, Gansu, China. E-mail: dingyong1@lzu.edu.cn

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Abstract

Widespread application of solar-driven hydrogen production is hampered by two major challenges: the safety risks associated with high-pressure H₂ storage and transport, and the intermittent nature of solar energy. Inspired by the natural spatial and temporal separation of light and dark reactions in photosynthesis, the emerging strategy of dark photocatalysis aims to separate the collection and conversion of solar energy. In the past few years, encouraging progress has been made in the dark photocatalytic production of hydrogen. Therefore, we summarize the advances in this field over the past few years. This review first discusses various charge storage mechanisms in depth. Then, a comprehensive review of key material systems is conducted, covering carbon-nitrogen-based materials, metal-organic frameworks, polyoxometalate-based materials, two-dimensional layered materials, as well as heterojunction/interface engineering and the combination of semiconductors with polyoxometalates. Furthermore, the performance of photo-charging and dark hydrogen evolution is analyzed in detail. Finally, we look forward to the future development direction of this field. This review aims to offer valuable insights and guidance for the design of efficient and stable dark photocatalytic materials.

Keywords: Dark photocatalytic hydrogen production, photoinduced charge separation, electron storage, persistent catalysis, semiconductor

1. Introduction

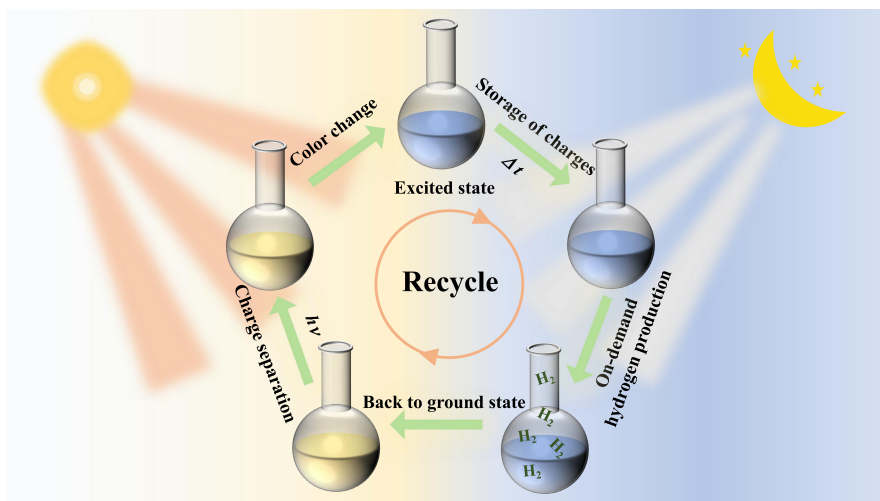
Under the global drive toward carbon neutrality and the growing urgency to address fossil energy depletion, hydrogen energy has emerged as a pivotal clean energy carrier, thanks to its high energy density and zero-emission characteristics^[1-7]. Photocatalytic hydrogen evolution has long been regarded as a green pathway to link solar utilization and hydrogen production^[8-15]. However, it still faces a critical bottleneck: the intermittency of solar energy. When light ceases, photogenerated electron-hole pair separation halts, and hydrogen production stops entirely. This light dependence not only affects hydrogen production output but also raises costs for subsequent storage and transportation, creating an urgent need for strategies that enable solar storage by day and hydrogen production at any time.

Against this backdrop, dark photocatalytic hydrogen evolution has emerged as a transformative solution, integrating solar capture, energy storage, and dark-state hydrogen production into a single system^[16-29]. Unlike traditional photocatalytic hydrogen evolution, dark photocatalytic hydrogen evolution achieves temporal and spatial decoupling of solar energy and hydrogen production. Under light irradiation, semiconductors absorb photons to generate electrons, which are separated and stored via structural design (e.g., trap sites, ion intercalation), while holes are consumed by sacrificial agents and then stored electrons are released to catalytic sites to reduce protons into hydrogen under the dark conditions, in which working principle is similar to the separation process of light and dark reaction in natural photosynthesis (Scheme 1)^[29].

In recent years, dark photocatalytic hydrogen evolution research has seen steady progress, with diverse material systems developed to support electron storage and dark hydrogen evolution (Figure 1), including carbon nitrides^[16], polyoxometalates (POMs)^[22], metal-organic frameworks (MOFs)^[17], heterojunction and interface engineering^[26], metallic oxide^[23], the combination of semiconductors and POMs^[29]. Each system brings unique advantages: carbon nitrides excel in stable electron trapping^[30-34], MOFs



offer precise structural tunability^[35-39], POMs enable molecular-level electron transfer^[40-50], oxides support efficient charge conduction^[25] and the combination of semiconductors and POMs can achieve extremely high dark hydrogen evolution activity^[29]. However, the field still faces critical challenges. Firstly, most materials only respond to ultraviolet-visible light, leaving near-infrared solar energy largely underutilized. Secondly, electron storage capacity and lifetime remain insufficient to sustain long-term dark operation. Thirdly, many materials suffer from poor stability in aqueous environments, while noble metal catalysts significantly drive-up costs for most dark photocatalytic reaction. Additionally, the dynamic process of electron storage and release is not fully understood for most materials, and device integration for large-scale production is still lacking.



Scheme 1. The schematic diagram for dark photocatalytic hydrogen evolution mechanism.

To synthesize these advances and guide future research, this review focuses on the core of dark photocatalytic hydrogen evolution, electron storage, by systematically summarizing progress in dark photocatalytic hydrogen evolution. It avoids a narrow focus on single materials or overly technical details, instead centering on the “structure–performance–mechanism” relationship across key material systems. The review first elaborates on dark photocatalytic hydrogen evolution’s basic principles and performance metrics, then classifies and discusses core material systems, analyzes factors influencing performance and corresponding regulation strategies, and finally outlines current challenges and future directions. By organizing these insights around electron storage, the review aims to provide a clear, holistic view of dark photocatalytic hydrogen evolution and inspire innovations to overcome its existing limitations.

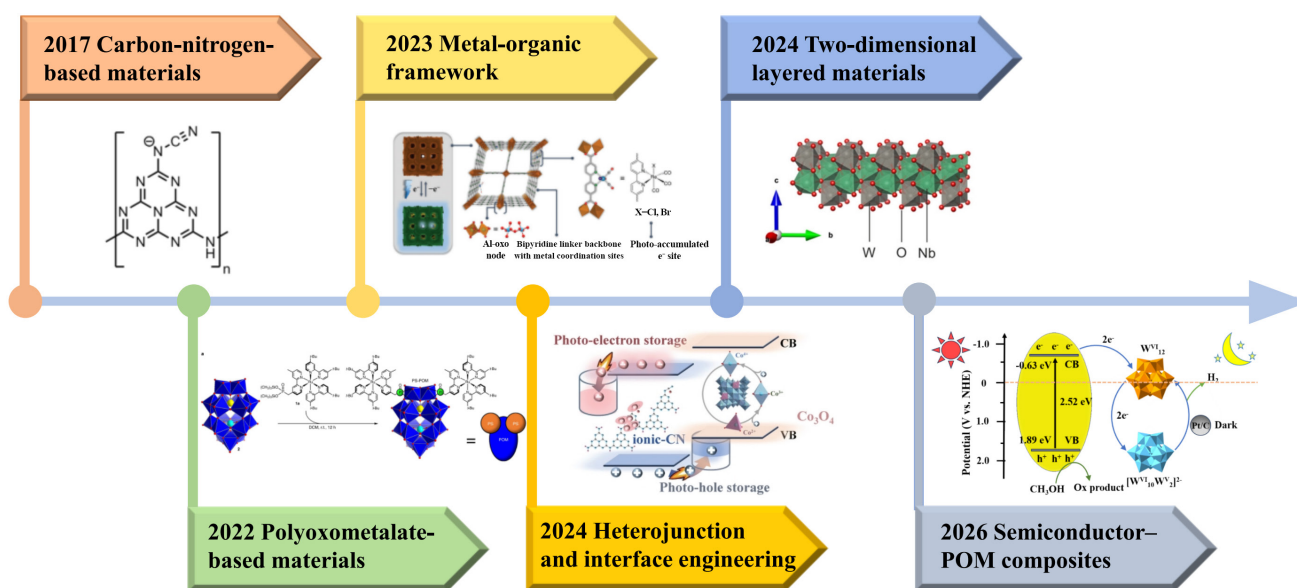


Figure 1. A brief timeline of NCN-CN_n, PS-POM, ReCl-253, ionic-CN/Co₃O₄, NbWO₆, g-C₃N₄/W₁₂. Reproduced from^[16,17,23]. CC BY 4.0; Reproduced with permission from reference^[22]. Copyright © 2022 Springer Nature; reference^[26]. Copyright © 2024 John Wiley & Sons; reference^[29]. Copyright © 2025 John Wiley & Sons. PS: polystyrene; POM: polyoxometalate.

2. The Basic Mechanism of Dark Light Catalysis

2.1 Separation and storage of photogenerated charges

The storage of photogenerated electrons is achieved primarily through intrinsic “electron traps” or integrated “electron reservoirs” within the material design. In carbon nitride-based materials, functionalization with cyanamide groups (e.g., in NCN-CN_x or K⁺-poly (heptazine imide))^[16] creates effective sites for electron localization. Upon irradiation in the presence of a sacrificial electron donor, long-lived radical species are formed, with lifetimes exceeding 12 hours (Figure 2a). Electron paramagnetic resonance (EPR) spectroscopy and computational studies indicate that the unpaired electron is localized on a single heptazine unit, stabilized by the cyanamide group and charge-balancing cations, endowing the system with a highly reductive character (Figure 2b). Furthermore, optimizing the crystallinity and cyanamide concentration through molten-salt synthesis can enhance this electron-storage capability. An optimal concentration balances efficient electron trapping against the detrimental formation of recombination centers.

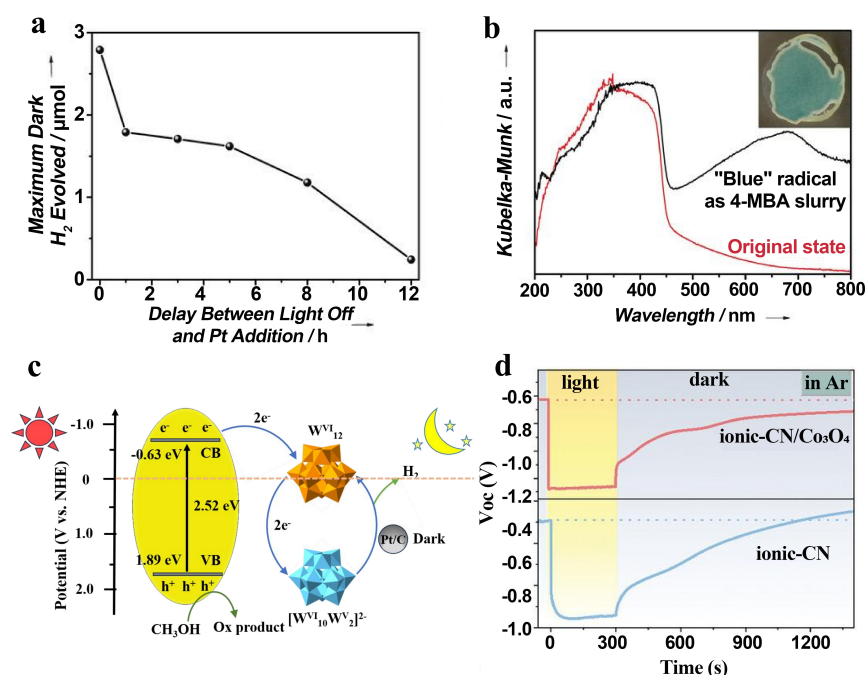


Figure 2. (a) Maximum dark hydrogen yield as a function of the delay time between light cessation and Pt colloid injection. Reproduced from^[16]. CC BY 4.0; (b) UV-vis diffuse reflectance spectra of NCN-CN before and after irradiation. Reproduced from^[16]. CC BY 4.0; (c) Semiconductor/POM composites. Reproduced with permission from reference^[29]. Copyright © 2025 John Wiley & Sons; (d) Open circuit voltage decay curves of ionic-CN and ionic-CN/Co₃O₄ with 300 s. Reproduced with permission from reference^[26]. Copyright © 2024 John Wiley & Sons. UV-vis: ultraviolet-visible; POM: polyoxometalate; NCN: nitrogen-carbon-nitrogen; CN: carbon nitride; 4-MBA: 4-mercaptobenzoic acid.

POMs represent another major class of electron storage media due to their well-defined structures and remarkable capacity for reversible multi-electron redox reactions^[29]. In composite systems, POMs such as ammonium metatungstate can accept electrons from an excited semiconductor like graphitic carbon nitride. Efficient electron transfer and storage, evidenced by the formation of heteropoly blue species (e.g., W⁵⁺), are facilitated by favorable band alignment and robust electrostatic self-assembly between oppositely charged components (Figure 2c). Beyond these, heterojunction engineering and interface design also promote charge separation and intermediate storage. For instance, bipolar charge storage junctions formed between ionic carbon nitride and metal oxides can drive directional electron transfer and temporary trapping at the interface (Figure 2d)^[26].

Two-dimensional layered materials may stabilize electrons through polaron formation aided by ion intercalation (Figure 3a)^[23]. The performance of electron storage is governed by multiple factors, including the intrinsic material properties such as crystallinity and defect concentration, the interfacial structure governing charge transfer, and external conditions like solution pH and light intensity. The regulatory effect of external experimental conditions on charge storage performance cannot be ignored. The pH value of the solution changes the accessibility of storage sites by affecting the surface charge state of materials. For the g-C₃N₄/(NH₄)₆H₂W₁₂O₄₀ system, the protonation degree of the g-C₃N₄ surface is the highest at pH = 1.5, and the electrostatic interaction with W₁₂ is the strongest (Figure 3b)^[29]. The type of sacrificial agent determines the efficiency of hole quenching, thereby affecting the overall quantum efficiency of photoreduction. In the study by Amthor *et al.*, when ascorbic acid (Asc) is used as the sacrificial agent, the quantum efficiency of photoreduction of PS-POM (Φ = 0.25%) is significantly higher than that when triethanolamine (TEOA) is used (Φ = 0.05%) (Figure 3c)^[22]. This indicates that Asc can more effectively quench holes, reduce electron-hole recombination and thereby

improve the efficiency of light energy utilization. The intensity and wavelength of light directly affect the efficiency of electron generation and storage. Due to the strong absorption of NbWO_6 in the near-ultraviolet region, when exposed to 365 nm UV for 30 minutes, its charge storage capacity can reach 3.2 mA h g^{-1} , which is approximately 18 times that of the capacity (0.18 mA h g^{-1}) under 1 sun simulated sunlight (100 mW cm^{-2}) (Figure 3d)^[23]. This significant difference is mainly attributed to the efficient matching of the light wavelength and the absorption characteristics of the material, rather than just the increase in light.

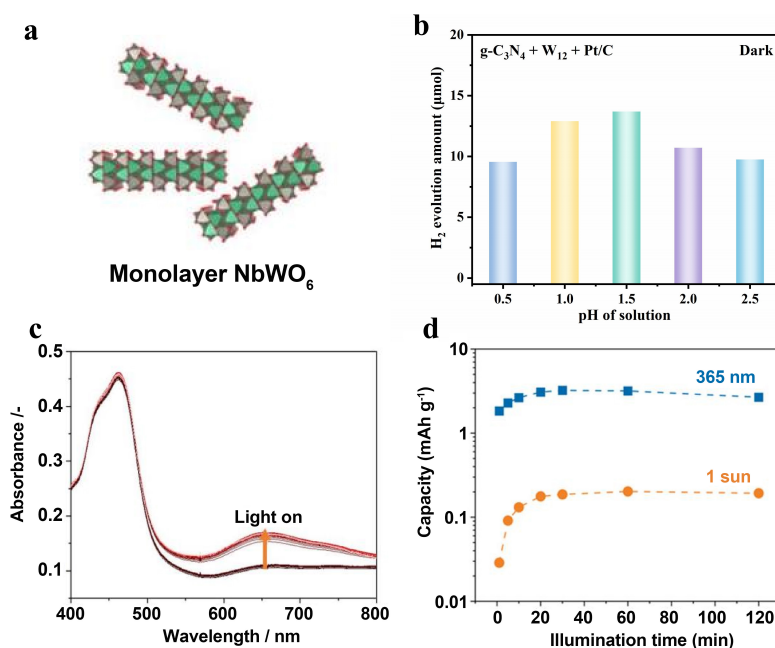


Figure 3. (a) Schematic illustration of 2D NbWO_6 nanosheets. Reproduced from^[23]. CC BY 4.0; (b) Dark H_2 evolution activity under various pH conditions. Reproduced with permission from reference^[29]. Copyright © 2025 John Wiley & Sons; (c) Time-resolved spectral evolution during the photochemical reduction of PS-POM with Asc as the sacrificial electron donor. Reproduced with permission from reference^[22]. Copyright © 2022 Springer Nature; (d) Various illumination durations at discharge current densities of 0.48 mA g^{-1} for 1 sun illumination and 4.8 mA g^{-1} for 365 nm UV irradiation, respectively. Reproduced from^[23]. CC BY 4.0. PS: polystyrene; POM: polyoxometalate; UV: ultraviolet.

2.2 Charge release and catalytic reactions in the dark state

The ultimate goal of dark photocatalysis is the controlled and efficient release of stored electrons to drive proton reduction, achieving hydrogen production independent of illumination. This dark reaction is typically triggered by introducing a catalytic site for proton reduction, most commonly a hydrogen evolution co-catalyst^[51–55].

In a charged system, these co-catalysts provide a pathway for the stored electrons to reduce protons. As demonstrated in the $\text{g-C}_3\text{N}_4/\text{W}_{12}$ system^[29], adding Pt/C to the electron-rich blue suspension triggers immediate H_2 evolution, accompanied by the bleaching of the color as the stored electrons are consumed. Without the co-catalyst, negligible H_2 production occurs despite significant electron storage. In molecular dyad systems, the release can be initiated simply by adding a proton source. For example, introducing sulfuric acid to a solution of the reduced Ru-POM dyad results in instantaneous H_2 generation and re-oxidation of the POM unit within seconds. Thermodynamically, the driving force for this release stems from the potential difference between the reduction potential of the electron storage site and the H^+/H_2 couple. Therefore, tuning the energy band structure of the storage material is crucial for optimizing the release kinetics.

The hydrogen evolution reactions (HER) pathway in the dark follows the fundamental steps of proton reduction, albeit with electrons supplied from the storage reservoirs rather than directly from a photoexcited state. Electrons migrate from storage sites (e.g., cyanamide groups, reduced W^{5+} centers) to catalytic active sites, where they combine with protons. The kinetics of dark HER are typically rapid, with the majority of gas evolved within the initial minutes to an hour, directly correlating with the depletion of the stored electron reservoir. Record dark photocatalytic H_2 evolution rates, such as $4,800 \mu\text{mol g}^{-1} \text{ h}^{-1}$ achieved in the TiOx/CN/Pt system^[24], highlight the potential of this approach. The release kinetics are influenced by catalyst loading, proton concentration, temperature, and the efficiency of electron transfer from the storage medium to the catalyst.

Different charge release mechanisms exhibit significant differences in applicable scenarios and efficiency. The noble metal co-catalyst-triggered mechanism (e.g., Pt/C in the $\text{g-C}_3\text{N}_4/\text{W}_{12}$ system) has the advantage of a fast release rate, with the initial dark hydrogen evolution rate reaching $3,220 \mu\text{mol g}^{-1} \text{ h}^{-1}$. However, the reliance on scarce noble metals limits large-scale application. In

the PS-POM system, the proton source (e.g., H_2SO_4) triggers the reaction directly without requiring a co-catalyst. Electron release originates from the interaction between protons and the storage sites, resulting in extremely fast hydrogen evolution kinetics. However, this mechanism is currently only applicable to molecular storage systems.

For practical application, the cyclic stability of the entire system is important. This involves the stability of both the electron storage material and the catalyst over repeated charging-discharging cycles. Promisingly, some systems, like the g- $\text{C}_3\text{N}_4/\text{W}_{12}$ composite, show nearly constant dark activity over multiple cycles, indicating good stability of the POM storage unit. However, challenges remain, including the potential degradation of functional groups in carbon nitrides and the reliance on scarce noble metal co-catalysts for high performance. Developing efficient, stable, and earth-abundant alternatives to platinum and engineering robust interfaces between storage materials and co-catalysts are critical directions for future research aimed at enabling scalable implementation of dark photocatalytic hydrogen production.

3. Key Material System and Design Strategy

3.1 Mechanisms and structural design of typical dark photocatalytic systems

Figure 4 systematically compares the charge storage-release mechanisms of six representative material systems, highlighting both their common operating principles and structural specificities^[16,17,22,23,26,29]. All systems operate via a core “light excitation-charge separation-storage-dark release-hydrogen evolution” process. Under illumination, semiconductors or light-absorbing units generate electron-hole pairs. Holes are rapidly quenched by sacrificial agents to prevent recombination, while electrons are stored at specific sites within the material. In the subsequent dark phase, these stored electrons are released in a controlled manner to drive proton reduction, thereby achieving the spatiotemporal decoupling of light absorption and HER.

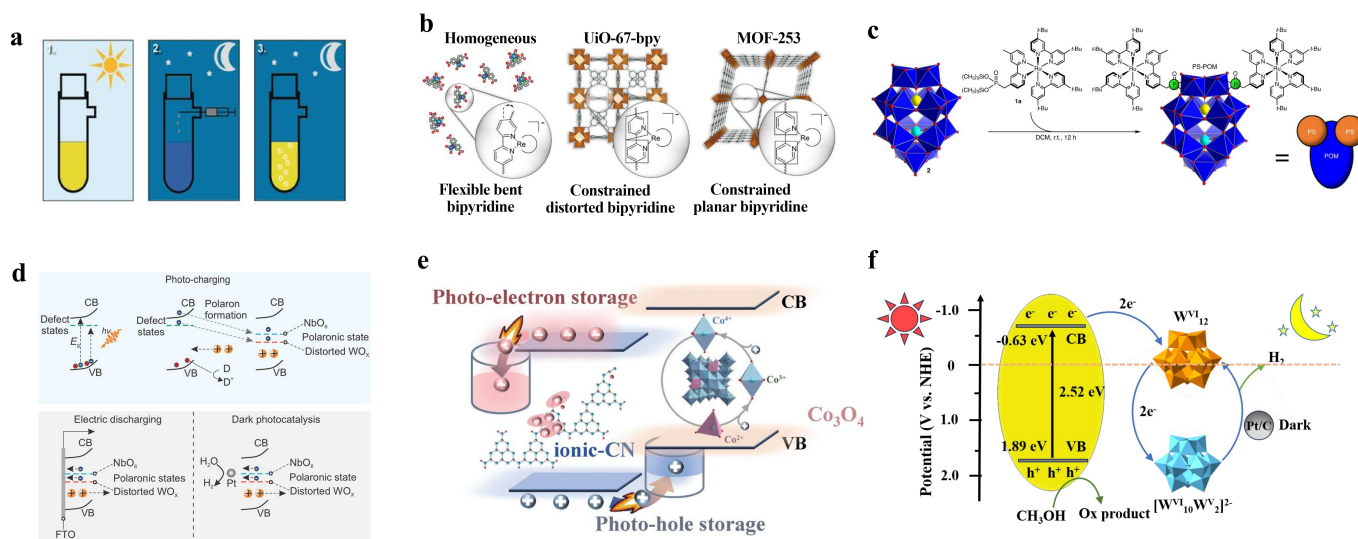


Figure 4. Schematic diagrams of six systems for dark photocatalytic hydrogen evolution. (a) Carbon-nitride-based materials. Reproduced from^[16]. CC BY 4.0; (b) MOF-based materials. Reproduced from^[17]. CC BY 4.0; (c) POM-based materials. Reproduced with permission from reference^[22]. Copyright © 2022 Springer Nature; (d) 2D layered materials. Reproduced from^[23]. CC BY 4.0; (e) Heterojunctions. Reproduced with permission from reference^[26]. Copyright © 2024 John Wiley & Sons; (f) Semiconductor/POM composites. Reproduced with permission from reference^[29]. Copyright © 2025 John Wiley & Sons. MOF: metal-organic framework; POM: polyoxometalate.

Despite these shared principles, distinct mechanistic differences arise from the unique structural design of each material system. Carbon-nitrogen-based materials (NCN-CN_x) create electron localization sites within the heptazine unit network through the synergistic effect of cyanamide groups ($-\text{NCN}$) and K^+ ions (**Figure 4a**)^[16]. Photogenerated electrons are stored as long-lived radicals with a lifetime exceeding 12 hours. In the presence of a sacrificial electron donor, long-lived radicals with lifetimes exceeding the diurnal cycle are generated upon illumination. EPR spectroscopy^[56–59] and density functional theory^[60–65] calculations confirm that unpaired electrons are localized on single heptazine units, stabilized by the synergistic effect of cyanamide groups and charge-balancing cations (e.g., K^+), endowing the material with strong reducibility (reduction potential $< -0.445\text{V}$ vs. normal hydrogen electrode). Their release is triggered by a Pt co-catalyst. In contrast, MOF-based materials (ReCl-253) leverage the confinement effect of the MOF pores to force the bipyridine units of the Re complex into a planar structure, thereby stabilizing photogenerated radical anions ($[\text{ReCl}(\text{CO})_3(5,5'\text{-dcbpy})]^-$)^[17]. This results in an exceptional electron storage lifetime exceeding 4 weeks and a capacity retention of approximately 90% after 10 cycles. Electron release in this system is dependent on a $\text{Co}(\text{dmgH})_2(4\text{-COOH-py})$ co-catalyst (**Figure 4b**).

POM-based materials (PS-POM) integrate Ru-based photosensitizers with Dawson-type POMs ($\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$)^[66–75] via phosphonate-mediated covalent bonding (**Figure 4c**)^[22]. Each molecule stores two electrons under illumination, forming heteropoly

blue species through the reduction of W^{6+} to W^{5+} . Notably, electron release does not require a noble metal co-catalyst and can be triggered solely by adding a proton source (H_2SO_4). The HER completes within 10 seconds, achieving 40% of the theoretical yield. Two-dimensional layered materials ($NbWO_6$) operate through a different mechanism, forming small polarons via WO_x sublattice distortion (Figure 4d)^[23]. This process is accompanied by Li^+/H^+ photointercalation to balance charge, with intrinsic oxygen vacancies providing initial electron traps at a W^{6+}/W^{5+} ratio of approximately 7:1. This system achieves an electron storage capacity of 3.2 mA h g^{-1} and offers dual functionality as a “solar battery” and for dark hydrogen evolution, retaining 76% of its initial capacity after 30 cycles.

Heterojunction systems (ionic-CN/ Co_3O_4) are constructed via electrostatic self-assembly to form a bipolar charge storage junction. With matched energy levels, ionic-CN functions as the electron storage component while Co_3O_4 serves as the hole storage layer, enabling efficient charge separation (Figure 4e)^[26]. This design yields a high photo-charging rate of 0.86 A g^{-1} , which is 6.61 times that of pristine ionic-CN. At an optimal Co_3O_4 loading of 10 wt.%, the system achieves a dark hydrogen evolution yield of 1.57 mmol g^{-1} . Finally, semiconductor-POM composites ($g\text{-}C_3N_4/W_{12}$) form a tight interface via electrostatic interactions between protonated $-NH_3^+$ groups on the $g\text{-}C_3N_4$ surface and anionic W_{12} clusters (Figure 4f)^[29]. The favorable energy-level alignment ensures spontaneous electron transfer from $g\text{-}C_3N_4$ to W_{12} , resulting in the formation of heteropoly blue species. This system exhibits a remarkable dark hydrogen evolution rate of $3,220 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$, and maintains a rate of $954 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ under natural sunlight.

In essence, these mechanistic variations originate from the rational design of electron storage sites whether radicals, polarons, or heteropoly blues, and the nature of interfacial interactions, including covalent bonding, electrostatic forces, and confinement effects. These design choices fundamentally dictate the performance trade-offs of each system regarding storage lifetime, capacity, and release kinetics.

3.2 Dark hydrogen evolution activity of dark photocatalytic systems

Table 1 compares the dark hydrogen evolution activity of six typical dark photocatalytic material systems, intuitively presenting the differences in catalytic activity of each system^[16,17,22,23,26,29]. In terms of activity data, the semiconductor-POM composite ($g\text{-}C_3N_4/W_{12}$) exhibits the optimal dark hydrogen evolution rate of $3,220 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$, with an outdoor hydrogen evolution rate of $954 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ under natural sunlight^[29]. Its high activity originates from the efficient energy level matching and tight electrostatic interface between $g\text{-}C_3N_4$ and W_{12} . The heterojunction system (ionic-CN/ Co_3O_4) ranks second, with a dark hydrogen evolution rate of $1,350 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ when the Co_3O_4 loading is 10 wt.%, benefiting from the enhanced charge separation and rapid photo-charging characteristics (0.86 A g^{-1}) of the bipolar junction structure^[26]. The POM-based material (PS-POM) has the fastest hydrogen evolution kinetics, with the reaction triggered within 10 s and a yield of 40% of the theoretical value, but its dark photocatalytic activity ($284.04 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$) is slightly lower than the previous two systems^[22]. For the carbon nitride-based material (NCN-CN_x), the rate of dark hydrogen evolution reaches $37.5 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ with a catalyst loading of 10 mg ^[16]. Although its absolute activity is much lower than composite systems, this material has an ultra-long electron storage lifetime ($> 12 \text{ h}$) and is a pioneering work in dark photocatalysis for simulating circadian rhythms. The two-dimensional layered material ($NbWO_6$) has a dark hydrogen evolution rate of $2.86 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$, and its advantage lies in dual functionality with an electron storage capacity of 3.2 mA h g^{-1} , which can also be used in solar batteries^[23]. The dark hydrogen evolution rate of the MOF-based material (ReCl-253) is $110 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$, but its electron storage lifetime exceeds 4 weeks, with a capacity retention rate of about 90% after 10 cycles, showing outstanding stability^[17].

Table 1. Summary of the catalysts for the dark photocatalytic hydrogen production.

Catalyst	Sacrificial reagent	Catalyst amount (mg)	Dark reaction time (hour)	Dark H_2 rate ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)	Stability
NCN-CN _x	4-MBA	20	2.0	37.5	over 15 cycles with gradual decay.
PS-POM	Sodium ascorbate	0.96	0.22	284.04	-
ReCl-253	TEOA	3	0.67	110	90% capacity retention over 10 cycles
ionic-CN/ Co_3O_4	MeOH	10	0.2	1,350	-
$NbWO_6$	MeOH	95	2.5	2.86	76% capacity retention over 30 cycles
$g\text{-}C_3N_4/W_{12}$	MeOH	34.5	0.08	3,220	Stable in 5 cycles

NCN: nitrogen-carbon-nitrogen; CN: carbon nitride; 4-MBA: 4-mercaptobenzoic acid; PS: polystyrene; POM: polyoxometalate; TEOA: triethanolamine.

Overall, the activity differences among various systems are closely related to the structure of electron storage sites, the mode of interfacial interaction, and the type of co-catalyst. High-activity systems mostly rely on efficient charge transfer and rapid electron release, which reflects the inherent trade-off relationships between “activity-lifetime-capacity” in the field of dark photocatalysis.

3.3 Photo-charging characterization of dark photocatalytic catalysts

The color change of the dark photocatalytic catalyst before and after the reaction is very obvious, which can be observed through the significant changes in the UV-vis diffuse reflectance spectrum^[76–85] before and after the reaction. **Figure 5a** shows the photo-charging characterization features of carbon-nitrogen-based material NCN-CN_x^[16]. Irradiating NCN-CN_x under oxygen-free conditions leads to the formation of characteristic blue radicals in the system, and its UV-vis diffuse reflectance spectrum changes significantly. The electron-localized blue radical state extends the material's light absorption to 500–750 nm, thus enhancing solar energy utilization. Meanwhile, the EPR signal shows an obvious growth trend of radical signals with irradiation time, confirming the generation and accumulation of long-lived radicals. **Figure 5b** provides a comparative visual analysis of the ReCl-253 material in two distinct end states^[17]. It shows the ReCl-253 after undergoing a full discharge and subsequent drying process, where the color reverts to its original orange appearance. This comparison provides clear and immediate visual proof of the reversibility of the photo-charging and discharging cycles, which confirms the reversible switching characteristics between the charging state and the discharge state endpoints. While **Figure 5c** exhibits the photochromic and absorption spectral evolution characteristics of two-dimensional layered material NbWO₆ under 365 nm UV light irradiation^[23]. With the irradiation time extending from 0 min to 60 min, the UV-vis absorption spectrum of NbWO₆ suspension shows a broadened absorption enhancement in the range of 400–800 nm, among which the absorption intensity at 575 nm increases continuously with irradiation time and gradually stabilizes. This characteristic absorption is directly related to polarons formed by trapped photogenerated electrons, which intuitively reflects the photo-charging process of the material and the change of charge storage capacity, and is also the spectral embodiment of the photochromism of NbWO₆ (changing from milky white to blue).

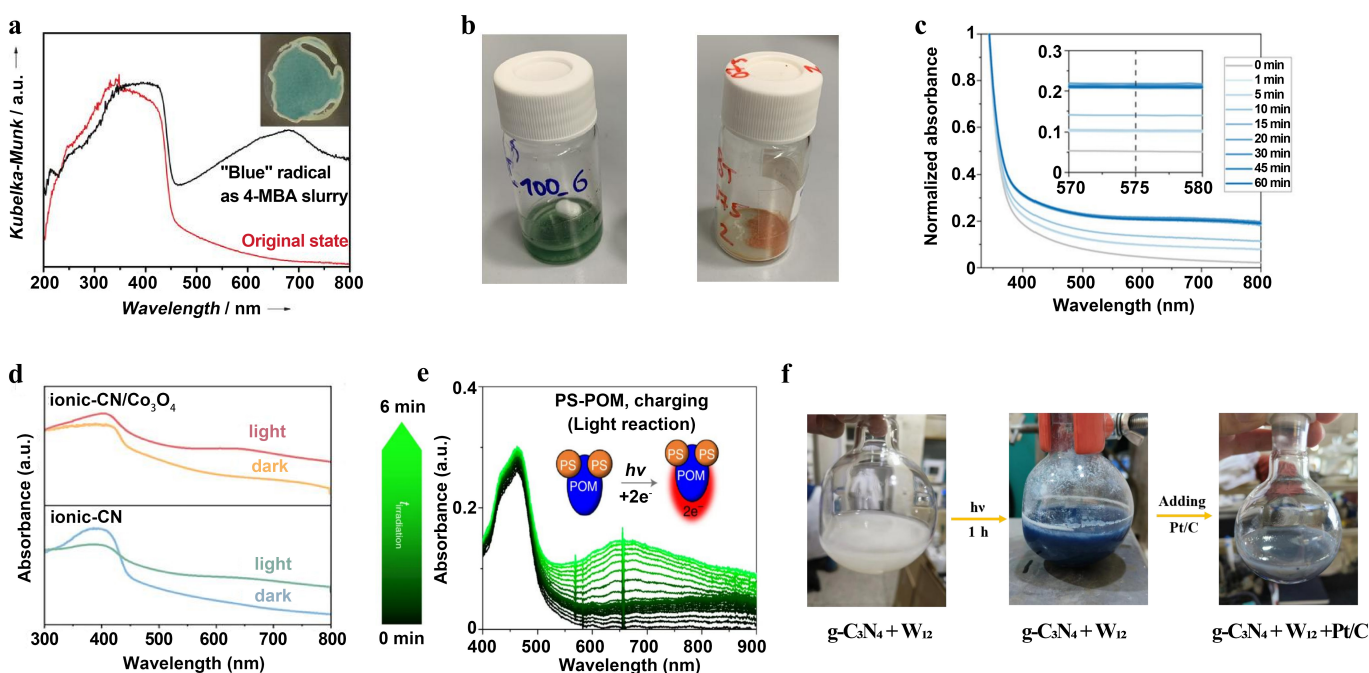


Figure 5. (a) UV-vis diffuse reflectance spectra of NCN-CN before and after irradiation. Reproduced from^[16]. CC BY 4.0; (b) Visual comparison of the photo-charged and discharged states. Reproduced from^[17]. CC BY 4.0; (c) Normalized operando UV-vis absorbance spectra of NbWO₆ suspension under 365 nm UV illumination for different times. The inset shows the magnified region between 570 and 580 nm. Reproduced from^[23]. CC BY 4.0; (d) UV-vis absorption spectra of ionic-CN and ionic-CN/Co₃O₄ before and after 60 s illumination. Reproduced with permission from reference^[26]. Copyright © 2024 John Wiley & Sons; (e) UV-vis spectral changes of PS-POM upon irradiation using a monochromatic LED in the presence of a sacrificial electron donor. Reproduced with permission from reference^[22]. Copyright © 2022 Springer Nature; (f) Color before irradiation and color after irradiation and color after adding Pt/C. Reproduced with permission from reference^[29]. Copyright © 2025 John Wiley & Sons. UV-vis: ultraviolet-visible; NCN: nitrogen-carbon-nitrogen; CN: carbon nitride; PS: polystyrene; POM: polyoxometalate; LED: light-emitting diode.

In addition, **Figure 5d** presents the UV-vis absorption spectrum comparison of the ionic-CN/Co₃O₄ bipolar charge storage junction before and after photo-charging^[26]. After light irradiation, an obvious characteristic absorption band appears in the material in the range of 550–750 nm, and the color of the sample changes from initial yellow to blue. This phenomenon is directly related to the formation of long-lived photoinduced radical species by heptazine units in ionic-CN capturing photogenerated electrons, confirming the efficient photogenerated electron storage capacity of the system. Meanwhile, the rapid capture of photogenerated holes by Co₃O₄

further promotes charge separation and storage. In contrast, Figure 5e shows the photo-charging spectral characterization of the POM-based material PS-POM^[22]. Under visible light irradiation and in the presence of a sacrificial electron donor, a broadened characteristic absorption band gradually appears and intensifies at 650 nm for PS-POM, which is a typical spectral signal of its photo-charging process, corresponding to the generation of reduced species after stable electron storage on the POM framework. This process is a light-driven electron storage process, without such spectral changes in the dark state, and the generated reduced solution can achieve long-term stable storage.

Finally, Figure 5f depicts the light absorption change of semiconductor-POMs composite g-C₃N₄/W₁₂ during the photo-charging process and the dark-state triggering process^[29]. Under light irradiation, the UV-vis absorption spectrum of g-C₃N₄/W₁₂ system changes significantly. Due to the rapid transfer of photogenerated electrons from g-C₃N₄ to W₁₂ and the reduction of W⁶⁺ to W⁵⁺, heteropoly blue species are formed, and the system suspension changes from pale yellow to deep blue. When Pt/C co-catalyst is added to the photo-charged system and placed in the dark state, the characteristic absorption of the system gradually disappears with the release of stored electrons and proton reduction for hydrogen evolution, which intuitively reflects the complete process of electron storage during photo-charging and electron release in the dark for this composite material.

3.4 Key photo-charging performance of various dark photocatalytic systems

Photo-charging performance is a core index for evaluating dark photocatalytic materials, which directly determines the electron storage capacity and subsequent dark hydrogen evolution efficiency of materials. Different material systems exhibit distinctive photo-charging and charge storage characteristics due to the differences in structural design and regulation strategies. Figure 6a shows the comparison of dark hydrogen evolution kinetics between carbon-nitrogen-based material NCN-CN_x and pristine Melon^[16]. The light irradiation stage is the process of electron trapping and radical generation in the system, with no significant hydrogen evolution. After the irradiation, Pt colloid is added to the system, and NCN-CN_x can rapidly trigger HER in the dark state. The hydrogen production increases gradually with the duration of dark reaction and reaches a peak at about 2 h, and the dark hydrogen evolution rate is highly consistent with the decay law of blue radicals. In contrast, Melon without potassium thiocyanate ionothermal modification has no obvious dark hydrogen evolution effect under the same experimental conditions due to the lack of cyanamide functional groups. This result directly confirms the core role of cyanamide groups in the formation of long-lived radicals and dark photocatalytic hydrogen evolution. Meanwhile, the dark hydrogen production of the system is positively correlated with the material loading and the concentration of sacrificial agent 4-MBA, further verifying that radicals are the core carriers for electron storage.

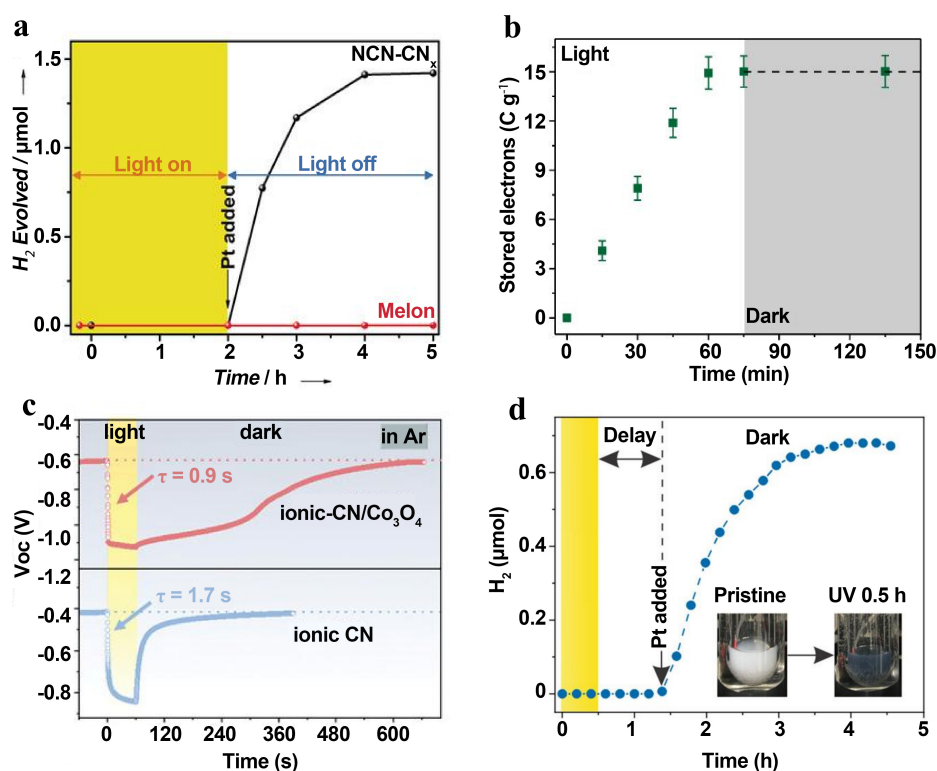


Figure 6. (a) Dark hydrogen evolution kinetic curves of NCN-CN_x and Melon. Reproduced from^[16]. CC BY 4.0; (b) Change in charge storage capacity of ReCl-253 during photo-charging. Reproduced from^[17]. CC BY 4.0; (c) Open circuit voltage decay curves of ionic-CN and ionic-CN/Co₃O₄. Reproduced with permission from reference^[26]. Copyright © 2024 John Wiley & Sons; (d) Dark hydrogen evolution kinetic curve of NbWO₆ after photo-charging. Reproduced from^[23]. CC BY 4.0. NCN: nitrogen-carbon-nitrogen; CN: carbon nitride.

In comparison, MOF-based materials exhibit excellent charge storage stability by virtue of the unique spatial confinement effect^[17]. **Figure 6b** shows the change of charge storage performance of ReCl-253 under 450 nm light irradiation. With TEOA as the sacrificial agent, its charge storage capacity increases nearly linearly with the extension of irradiation time and reaches saturation at about 90 min, with a saturated storage capacity of $15.1 \pm 1.0 \text{ C gMOF}^{-1}$, which is much higher than that of halogen variant ReBr-253 ($11.5 \pm 0.9 \text{ C gMOF}^{-1}$), clearly reflecting the significant regulatory effect of halogen ligands on the charge storage capacity of the material. In the dark storage stage after complete photo-charging, the material shows no obvious charge decay within more than 150 min of observation time. At the same time, the cyclic charge-discharge test under Ar atmosphere shows that ReCl-253 still retains about 90% of its initial charge capacity after 10 consecutive cycles, which not only proves its outstanding charge storage stability but also confirms the good reversibility of the photo-charging process of this MOF-based system.

Heterojunction engineering, on the other hand, achieves the dual improvement of photo-charging rate and charge storage stability by constructing a bipolar charge storage junction^[26]. **Figure 6c** shows the comparison of open circuit voltage decay curves between ionic-CN and ionic-CN/ Co_3O_4 bipolar charge storage junction. After 60 s of light irradiation, the ionic-CN/ Co_3O_4 heterojunction has an open circuit voltage drop of about 0.50 V, and it takes 600 s to complete the potential recovery, while pure ionic-CN only has a voltage drop of 0.44 V and can quickly recover to the initial potential within 180 s. The performance difference between the two directly proves that the heterojunction can more stably confine photogenerated electrons in trapping sites through the directional separation and separate storage of electrons and holes, effectively suppressing non-radiative recombination pathways. Precisely based on this core optimization effect, ionic-CN/ Co_3O_4 achieves a high photo-charging rate of 0.86 A g^{-1} , which is 6.61 times higher than that of pure ionic-CN (0.13 A g^{-1}), making it a highly advantageous efficient dark photocatalytic system under short-time photo-charging conditions.

Two-dimensional layered materials realize the effective storage and dark-state controllable release of photogenerated charges relying on the synergistic effect of ion intercalation and lattice distortion^[23]. **Figure 6d** shows the dark hydrogen evolution kinetic characteristics of two-dimensional layered material NbWO_6 after 0.5 h of 365 nm UV light irradiation. After adding platinum nanoparticle co-catalyst to the system in the dark state, the photogenerated electrons stored in the material are gradually released to drive the reduction of protons to generate hydrogen, with a final hydrogen production of about $0.68 \mu\text{mol}$ and a maximum turnover frequency of 0.13 h^{-1} . At the same time, the system has good cyclic usability, which can complete multiple “light-charge-dark discharge” hydrogen evolution cycles with only a single addition of catalyst. In addition, its charge storage capacity shows significant light source dependence, with a storage capacity of 3.2 mA h g^{-1} under 365 nm UV light irradiation, about 18 times that under 1 sun simulated sunlight. This difference does not stem from a simple increase in light intensity, but from the efficient matching of light wavelength and the intrinsic absorption characteristics of the material, which also provides a key basis for the light source selection and performance optimization of such materials.

Overall, the above four types of core material systems have realized the optimized regulation of photo-charging performance from different perspectives: carbon-nitrogen-based materials construct efficient electron trapping sites by virtue of functional group modification^[16], MOF-based materials achieve long-term stable charge storage through spatial confinement^[17], heterojunction materials break through the charge recombination bottleneck to realize fast charging via bipolar storage^[23], and two-dimensional layered materials realize controllable charge storage and release relying on ion intercalation^[23]. These differentiated regulation strategies and performance characteristics provide valuable insights and new avenues for the subsequent design and development of high-efficiency dark photocatalytic catalysts.

3.5 Structural and interfacial characterization of dark photocatalytic catalysts

Accurate structural and interfacial characterization is a key tool to analyze the structure-performance relationship and reveal the charge transport mechanism. **Figure 7** systematically demonstrates the structural design and interfacial regulation rules of different dark photocatalytic catalysts, and it intuitively reflects the regulatory effects of interface engineering and electrostatic self-assembly on material structure construction and charge transport performance. Among them, **Figure 7a** shows the crystal structure of NbWO_6 ^[23]. Its lattice consists of alternating NbO_6 and WO_6 octahedra linked by shared oxygen vertices, forming a regular 2D periodic layered structure. Tetrabutylammonium ions between layers can be separated by proton exchange and liquid exfoliation. This unique 2D layered structure provides sufficient space for ion intercalation and lays a structural foundation for photogenerated charge capture and polaron formation. It is the core structural support for storage and dark hydrogen evolution of NbWO_6 . While **Figure 7b** presents transmission electron microscopy and selected area electron diffraction (SAED) characterization of the ionic-CN/ Co_3O_4 bipolar charge storage junction, which is constructed by a facile electrostatic self-assembly strategy^[26]. Co_3O_4 nanoparticles are uniformly anchored on the surface of ionic-CN nanosheets, with uniform particle size and excellent dispersion, forming a heterostructure with intimate contact and no obvious defects. Clear diffraction rings corresponding to (111), (022), (222) and (004) crystal planes of Co_3O_4 are observed in the SAED pattern. This result directly confirms the good interfacial compatibility between heterojunction components, effectively reduces the resistance of interfacial charge transfer, and provides a structural guarantee for directional migration and separate storage of photogenerated electron-hole pairs at the interface.

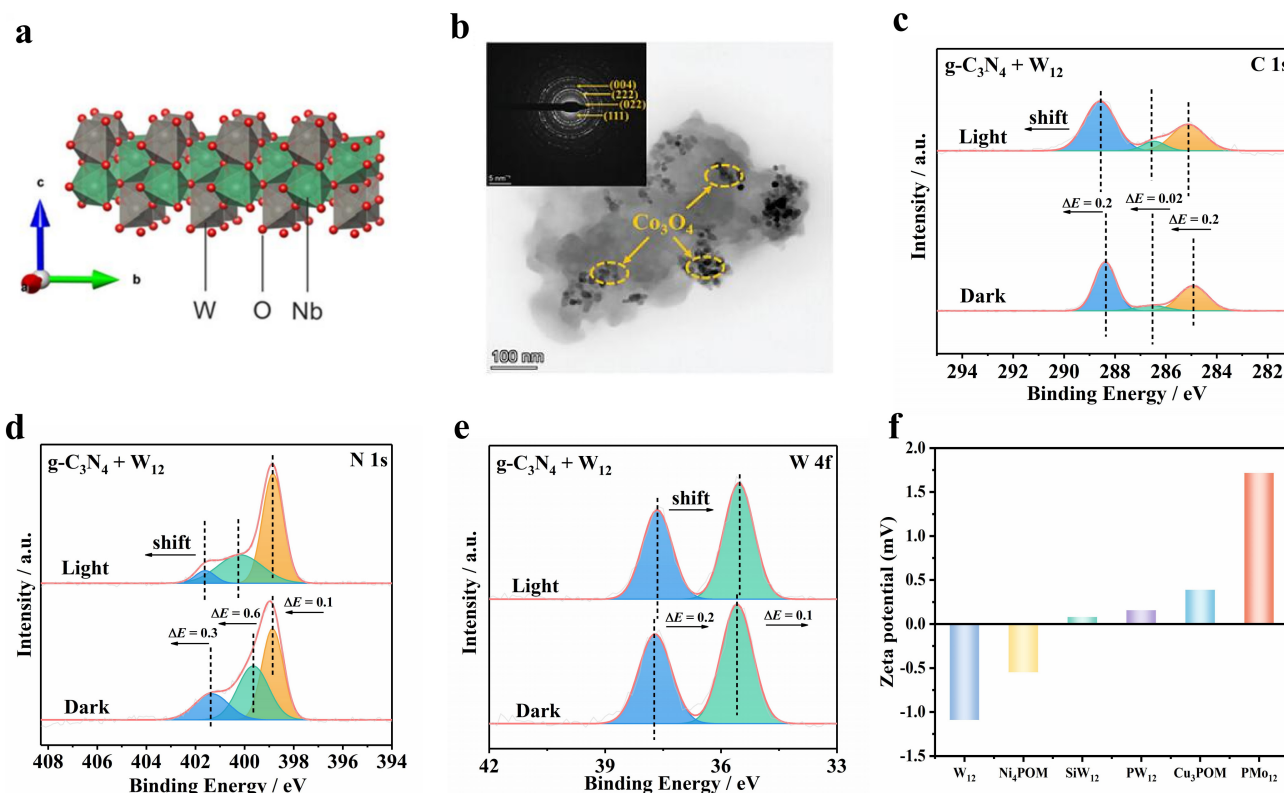


Figure 7. (a) Schematic illustration of the layered crystal structure of 2D NbWO₆. Reproduced from^[23]. CC BY 4.0; (b) TEM image of the ionic-CN/Co₃O₄ heterojunction. Inset: SAED pattern of the spinel Co₃O₄. Reproduced with permission from reference^[26]. Copyright © 2024 John Wiley & Sons; (c-e) *In situ* X-ray photoelectron spectroscopy of mixture of g-C₃N₄/W₁₂; (f) Zeta potential distributions of various polyoxometalates. Reproduced with permission from reference^[29]. Copyright © 2025 John Wiley & Sons. TEM: transmission electron microscopy; CN: carbon nitride; SAED: selected area electron diffraction.

Furthermore, Figure 7c,d,e display the *in-situ* XPS spectra of g-C₃N₄/W₁₂ composite under simulated reaction conditions, which are direct spectral evidence for light-induced interfacial charge transfer^[29]. Under light irradiation, the binding energies of C 1s and N 1s orbitals of g-C₃N₄ shift to higher energy, indicating the decrease of electron cloud density due to the migration of photogenerated electrons. The binding energy of the W 4f orbital of W₁₂ clusters shifts to lower energy, corresponding to the reduction of W⁶⁺ to W⁵⁺ by accepting photogenerated electrons from g-C₃N₄, thus forming stable heteropoly blue species. The reverse shift of binding energies of C, N and W directly confirms the directional and efficient trans-interfacial transfer of photogenerated electrons from g-C₃N₄ to W₁₂, and verifies the high efficiency of interfacial charge transport in this composite. This efficient interfacial charge transfer is closely related to the electrostatic interaction shown in Figure 7f^[29]. POMs such as W₁₂ have high-density negative charges. Under acidic experimental conditions, cyano groups on the surface of g-C₃N₄ are protonated and positively charged, forming a strong electrostatic attraction between g-C₃N₄ and W₁₂. This electrostatic interaction drives the molecular-scale close self-assembly of g-C₃N₄ and W₁₂, constructing an intimate interface for charge transport and greatly reducing the energy barrier of interfacial charge transfer. Combined with the thermodynamic driving force from the matched energy level difference between the conduction band of g-C₃N₄ and the reduction potential of W₁₂, the ultrafast trans-interfacial transfer of photogenerated electrons from g-C₃N₄ to W₁₂ is finally realized.

Generally speaking, Figure 7 clarifies the internal correlation of structural design-interfacial regulation-charge transport in dark photocatalytic catalysts through four core characterization methods. The 2D layered structure of NbWO₆ provides intrinsic sites for charge storage^[23]. The tight heterojunction interface of ionic-CN/Co₃O₄ lays a structural foundation for directional charge migration^[26]. The *in-situ* XPS of g-C₃N₄/W₁₂ directly confirms the actual process of interfacial charge transfer. The Zeta potential distribution of various POMs reveals the core mechanism of electrostatic assembly regulating interfacial charge transport, and these characterization results mutually corroborate^[29]. They not only provide direct evidence for analyzing the charge transport rules of different catalysts, but also point out the key direction for the subsequent structural design and interface engineering optimization of dark photocatalytic materials.

3.6 Cycling stability of dark photocatalytic catalysts

Cycling stability and environmental tolerance are core indices for evaluating the practical potential of dark photocatalytic catalysts, which directly determine their long-term working capacity and practical application adaptability. Figure 8 systematically

characterizes the cycling performance and environmental adaptability of typical dark photocatalytic catalysts from four aspects: charge-discharge cycle, light-dark hydrogen evolution cycle, composite system cycle and oxygen tolerance, fully reflecting the performance retention capacity of different material systems in cyclic use and actual working conditions. Among them, **Figure 8a** shows the charge-discharge cycle capacity retention curve of ReCl-253 in an acetonitrile system under an argon atmosphere^[17]. After 10 consecutive photo-charging and dark-discharging cycles, the material retains about 90% of its initial charging capacity with an average capacity loss of only 1% per cycle. The slight attenuation is only caused by the gradual blocking of MOF pores by sacrificial agents and solvent molecules during the cycle, which directly confirms the good reversibility of ReCl-253 in the photo-charging and discharging process. While **Figure 8b** presents the cyclic hydrogen evolution stability curve of NbWO₆^[23]. After photo-charging with 365 nm UV light, the catalyst can complete multiple “light-charge-dark discharge” hydrogen evolution cycles with a single addition of co-catalyst, and the hydrogen evolution performance remains stable during the cycle. Meanwhile, as a solar battery anode, it still retains 76% of its initial capacity after 30 photo-charging and electro-discharging cycles, fully demonstrating the excellent structural stability and cyclic service performance of NbWO₆. In addition, **Figure 8c** displays the cycling stability curve of the g-C₃N₄/W₁₂ composite^[29]. After multiple photo-charging and dark discharging cycles, the dark hydrogen evolution activity of the composite remains nearly constant without obvious attenuation, which confirms the high stability of the W₁₂ electron storage unit in the composite system. The robust interface between g-C₃N₄ and W₁₂ ensures efficient charge transport in the cyclic reaction, laying a foundation for the long-term operation of the composite system.

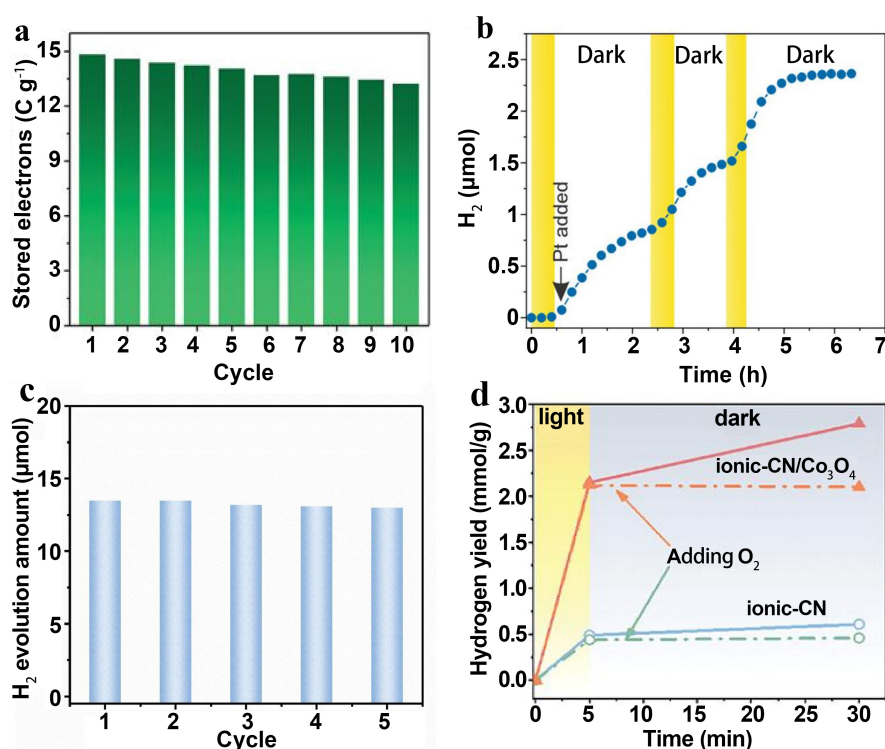


Figure 8. (a) Cyclic stability test of ReCl-253 under inert atmosphere. Reproduced from^[17]. CC BY 4.0; (b) Hydrogen evolution stability of NbWO₆ over multiple light-dark cycles. Reproduced from^[23]. CC BY 4.0; (c) Cyclic stability tests of g-C₃N₄/W₁₂. Reproduced with permission from reference^[29]. Copyright © 2025 John Wiley & Sons; (d) Effect of oxygen on dark H₂ evolution over ionic-CN and the ionic-CN/Co₃O₄ junction. Reproduced with permission from reference^[26]. Copyright © 2024 John Wiley & Sons. CN: carbon nitride.

Finally, **Figure 8d** compares the oxygen's effect on the dark hydrogen evolution performance of ionic-CN and ionic-CN/Co₃O₄^[26]. Oxygen quenching experiments show that after introducing oxygen as an electron scavenger, the dark hydrogen evolution rates of both catalysts drop sharply to near zero, in sharp contrast to the high efficiency hydrogen evolution under oxygen free conditions. This result directly proves that the dark hydrogen evolution completely depends on the photogenerated electrons stored during the photo-charging stage. Oxygen will rapidly consume the stored electrons and terminate the HER, clarifying that an oxygen-free environment is a key working condition requirement for dark photocatalytic hydrogen evolution.

In summary, the above three core material systems all exhibit good cycling stability. Materials with different structural designs achieve long term charge storage and cyclic hydrogen evolution through their own structural advantages. The significant inhibitory effect of oxygen on dark hydrogen evolution also provides a clear reference for the environmental conditions of the practical application of dark photocatalytic materials. These characterization results not only verify the long-term working capacity of typical dark photocatalytic catalysts, but also provide an important basis for the subsequent structural optimization and application scenario

design of such catalysts.

4. Conclusion and Outlook

The inherent contradiction between charge storage capacity, storage lifetime, and release kinetics is a core scientific issue in dark photocatalytic hydrogen evolution. High-capacity charge storage often requires deep energy level traps, which reduce the electron release rate and result in slow dark hydrogen evolution kinetics; conversely, shallow traps can accelerate electron release but significantly decrease storage capacity and lifetime^[16]. This contradiction stems from the correlation between electron trap depth and electron transfer barrier: the deeper the trap, the stronger the electron binding, the more stable the storage, but the higher the energy required for electrons to escape the trap and transfer to catalytic sites, resulting in slower kinetics. How to break this trade-off through material design to achieve the synergy of “high capacity-long lifetime-fast release” is a key challenge in this field^[16–29].

In addition to the above fundamental bottleneck, the practical application of dark photocatalytic hydrogen evolution faces dual challenges of system integration and energy efficiency. In terms of system integration, most studies focus on dispersed systems of powder catalysts, lacking device design for practical applications, such as structural optimization and stability improvement of integrated devices for solar energy capture-charge storage-hydrogen evolution. In terms of energy efficiency, the overall solar-to-hydrogen conversion efficiency of current dark photocatalytic systems remains low. This limitation stems from a series of consecutive energy losses. Firstly, the system has insufficient absorption of near-infrared light, resulting in incomplete utilization of the spectrum. Secondly, a high recombination rate of photogenerated electron-hole pairs weakens the charge separation effect. Furthermore, non-radiative recombination and oxidative side reactions during electron storage further reduce storage efficiency; and during the hydrogen evolution stage, the energy barrier for electron transfer to catalytic sites contributes to significant energy loss. At the same time, the continuous consumption and challenging regeneration of sacrificial agents, coupled with the scarcity and high cost of co-catalysts such as Pt, severely constrain the system’s sustainability and prospects for large-scale application.

Against these challenges, dark photocatalytic hydrogen evolution, as an emerging solar-energy utilization strategy, successfully realizes the capture-storage-on-demand conversion of solar energy by simulating the spatiotemporal decoupling mechanism of natural photosynthesis, providing an effective way to overcome the intermittency of solar energy and the challenges of hydrogen storage and transportation. In this review, we systematically summarize the basic principles, charge storage mechanisms, key material systems, and design strategies of dark photocatalytic hydrogen evolution, clarifying the core progress and challenges in this field. Existing studies have developed various high-performance systems such as carbon-nitrogen-based materials, MOF-based materials, POM-based materials, two-dimensional layered materials, and heterojunction composites. Through design strategies such as functional modification, confinement effect, and interface engineering, significant improvements in charge storage capacity, lifetime, and hydrogen evolution efficiency have been achieved. Among them, the TiO₂/CN/Pt composite has become the most efficient system currently, with a dark hydrogen evolution rate of 4,800 $\mu\text{mol g}^{-1} \text{h}^{-1}$, MOF-253-Re shows long-term energy storage potential with an electron storage lifetime exceeding 4 weeks, and NbWO₆ realizes the integration of solar battery and dark hydrogen evolution dual functions.

Future research should be advanced in a coordinated manner from the following dimensions: Firstly, in material design, innovative strategies such as multi-element doping and defect engineering must be employed to overcome the inherent trade-off between charge storage and release, thereby developing new material systems with broad-spectrum response, high storage capacity, and long cycle life. Secondly, in mechanistic investigation, advanced *in-situ* characterization techniques including *in-situ* EPR, *in-situ* XPS, and femtosecond transient absorption spectroscopy should be extensively applied to dynamically elucidate the microscopic mechanisms and evolution pathways during charge storage and release. In addition, in system integration, focused efforts are needed to construct integrated devices that combine solar energy capture, charge storage, and hydrogen evolution functions, with optimization of electrode structures and interfacial contacts to enhance operational stability and scalability. Finally, in sustainability, priority should be given to develop sacrificial-agent-free systems and non-noble-metal co-catalysts to effectively reduce overall costs and environmental impacts, thereby steering the technology toward practical and eco-friendly applications. With the deepening of material design and mechanism research, dark photocatalytic hydrogen evolution is expected to realize practical applications in distributed energy supply, hydrogen production and storage, providing important support for building a carbon-neutral energy system.

Declarations

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Doubao and DeepSeek were employed during manuscript preparation, solely for language polishing to improve the fluency of the text. The authors take full responsibility for the integrity, originality, and accuracy of the work.

Authors contribution

Ding Y: Conceptualization, supervision, writing-review & editing.

Dong X: Writing-original draft.

Zhou Y, Fang X: Writing-review & editing.

Conflicts of interest

The authors declare no conflicts of interest.

Ethical approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

Not applicable.

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