Sodium-Directed Photon-Induced Assembly Strategy for Preparing Multisite Catalysts with High Atomic Utilization Efficiency

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A sodium-mediated photoreconstruction strategy to regulate metal dispersion on TiO_2 for multi-site synergistic catalysis

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Abstract: Combined atomic sites can offer new prospects to address the current difficulties in single-atom catalysis, but accurately constructing multifarious sites and rationally regulating their synergistic interactions have remained challenging. Here, we report a sodium-mediated photoreconstruction strategy to synthesize multi-site photocatalysts through interfacial redispersion of noble metal atoms over support materials for enhanced catalysis. Residual Na^+ on TiO_2 surface was employed to stabilize Au single atoms and mediate the unique Au-TiO_2 interactions. A light-induced reconstruction procedure was performed to reassemble neighboring Au atoms into nanocluster via a solid–solid route. Advanced characterizations revealed that the charge transfer between light-excited supports and Au(Na^+) ensembles enabled the redispersion of Au atoms on TiO_2 for the bottom-up construction of plasmonic fields. In the resulting photocatalyst, the cascade electron transfer from assembled Au nanoclusters to defective TiO_2 nanosheets and sodium-stabilized Au single atoms contributed to a nearly two orders of magnitude improvement in plasmon-enhanced hydrogen evolution over TiO_2 under simulated solar light, with a record TON_{Au} value

of 4600. Our reconstruction strategy proved effective in atomic-scale regulation of various noble metal-cocatalyzed protocols for synergistic catalysis. This study provides a well-defined platform to extend the boundaries of SACs for multi-site synergistic catalysis through harnessing metal-support interactions.

KEYWORDS: Bottom-up assembly, photoreconstruction, single atoms, photocatalytic water splitting, metal-support interactions

Introduction

Single-atom catalysts (SACs) have attracted considerable attention in recent years, due to the maximum utilization efficiency of metal atoms, especially for noble metals that usually act as highly reactive sites for photocatalytic reactions.[1,2] Although much progress has been made in the past few years, single atoms with high surface energy are susceptible to agglomeration, posing a significant challenge of catalyst stability for further development.[3] In addition, the performance of SACs is far from the theoretical maximum efficiency of atomic utilization, as the simplicity of single-atom sites makes it difficult to break linear scaling relationships between adsorption energies of reaction intermediates.[4] Recent studies suggest that the above issues can be addressed by creating combined atomic sites in SACs, such as dual-metal dimers, single-atom alloys, and nanoclusters.[5-7] In these protocols, coupling different sites could induce the redistribution of metal charges and optimize the adsorption/desorption of intermediates, thereby effectively improving the catalytic performance.[8,9] However, a significant challenge in developing this kind of catalyst is the difficulty of precisely controlling the formation of multifarious sites and their interactions under synthesis conditions.[10]

Supported SACs with the inherent structure complexities of the underlying substrates, such as terminal groups, defects, and surface impurities, play a decisive role in tuning the coordination environment and stability of metal active sites.[11] From a synthesis perspective, the spatial distribution of dispersed metal atoms on a support material could be regulated by the metal-support interplay. This enables the possibility of redispersing supported single atoms via solid-state reactions, which can not only give rise to a bottom-up approach to construct multifarious atomically dispersed sites but also offer an opportunity to overcome the challenge of stability in SACs.[12]

Nevertheless, how one can manipulate the metal–support interactions in SACs remains an open question, and the application of this principle in site engineering of SACs has not been intentionally attempted yet.[13]

Here, we demonstrate a sodium-mediated photoreconstruction (denoted as SPR) strategy to construct multifarious atomic sites on 001-faceted TiO_2 nanosheets for synergistic photocatalysis (Figure 1a). This SPR strategy includes two steps: i) the formation of Au single atoms on TiO_2 with the assistance of Na^+ as an adherent mediator to regulate the Au-TiO_2 interactions,[14] and ii) the formation of Au nanoclusters from self-assembling partial Au single atoms under light illumination. As demonstrated by advanced characterization techniques and theoretical simulations, sodium could stabilize the proximal Au single atoms on the TiO_2 surface by decreasing the length of the Au-O bond (Figure S1). Light radiation of presynthesized catalyst powders triggered the transfer of photogenerated electrons from Ti^{3+} to Au(Na^+) ensembles, thereby bottom-up assembled neighboring Au single atoms into Au nanoclusters with surface plasmon resonance.[15] To further promote the charge transfer, we performed vacuum heating to create oxygen vacancy (O_v) defects in TiO_2 as an electron shuttler. As such, the synthesized Au nanoclusters/TiO_2 with oxygen vacancies/Au single atoms (SC-Au/O_v-TiO_2) photocatalyst exhibited an unprecedented hydrogen evolution rate of 4.37 mmol g^{-1} h^{-1} with the TON_{Au} value of 4600, representing a new record amongst Au catalyzed TiO_2 photocatalysts. Moreover, our SPR strategy was proved to be universal for refining the active sites of various SASs, including atomically dispersed Pt, Pd, Au, and their alloys on TiO_2, BiOBr, and CeO_2 for versatile applications.

Results and Discussion

Photocatalytic properties of site-engineered TiO_2 nanosheets. 001-faceted TiO_2 nanosheets were synthesized by a typical hydrothermal method (Figure 1b, Figure S2 and S3), followed by NaOH solution washing with the formation of sodium modified TiO_2 nanosheets (detailed procedures in SI). The uniform distribution of Au single atoms on wet-impregnated TiO_2 (S-Au/TiO_2) could be identified by the numerous bright contrast spots (Figure 1c) on nanosheets in transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy

(HAADF-STEM). For photoreconstructed sample (SC-Au/TiO_2), Au nanoclusters with an average diameter of 1.4 nm (ca. 90 atoms per cluster, Figure 1d) were observed together with some isolated Au single atoms, suggesting the successful construction of synergistic atomic sites on TiO_2 supports.

Photocatalytic hydrogen evolution reactions were performed to evaluate the activities of atomic-level engineered photocatalysts. Under simulated solar light irradiation, pristine TiO_2 presented poor activity for water splitting, with a hydrogen evolution rate of 0.05 mmol g^{-1} h^{-1} (Figure 1e). The introduction of Au single atoms as cocatalysts enhanced the activity by 30 times, with a H_2 evolution rate of 1.5 mmol h^{-1} g^{-1}, which was 2 times higher than the benchmark sample synthesized by the traditional photodeposition method (P-Au/TiO_2) (Figure S4). SC-Au/TiO_2 with multifarious metal sites exhibited an additional 2-fold increase in photoactivity. With the creation of oxygen vacancies (O_v) in TiO_2 by vacuum heating (Figure S5), the final SC-Au/O_v-TiO_2 showed an unprecedented hydrogen evolution rate of 4.37 mmol g^{-1} h^{-1}, which was nearly two orders of magnitude higher than pristine 001-TiO_2.[16] When normalized by the weight of Au content, the TON_{Au} value was 4600 after three hours under simulated solar light, which represented a new record of atom utilization efficiency for Au cocatalyzed TiO_2 (Figure 1f and Table S1).[17-26] In addition, the photocatalysts exhibited good reproducibility of H_2 evolution without any obvious decrease after an 18 h test (Figure 1g). This was also verified by the retained single-atom sites and Au clusters in recycled catalysts (Figure S6). Moreover, the SPR strategy was applicable to construct a series of TiO_2-based nanoarchitectures with multifarious cocatalyst sites, such as Pt- and Pd-cocatalyzed 001-TiO_2, dual metal cocatalyzed 001-TiO_2 and Au cocatalyzed 101-TiO_2 (Figure 1h, Figure S7). All reconstructed samples exhibited more than two times higher catalytic activity than the corresponding single-atom photocatalysts (Figure S8), confirming the benefit of synergistic sites for high-performance catalysts.

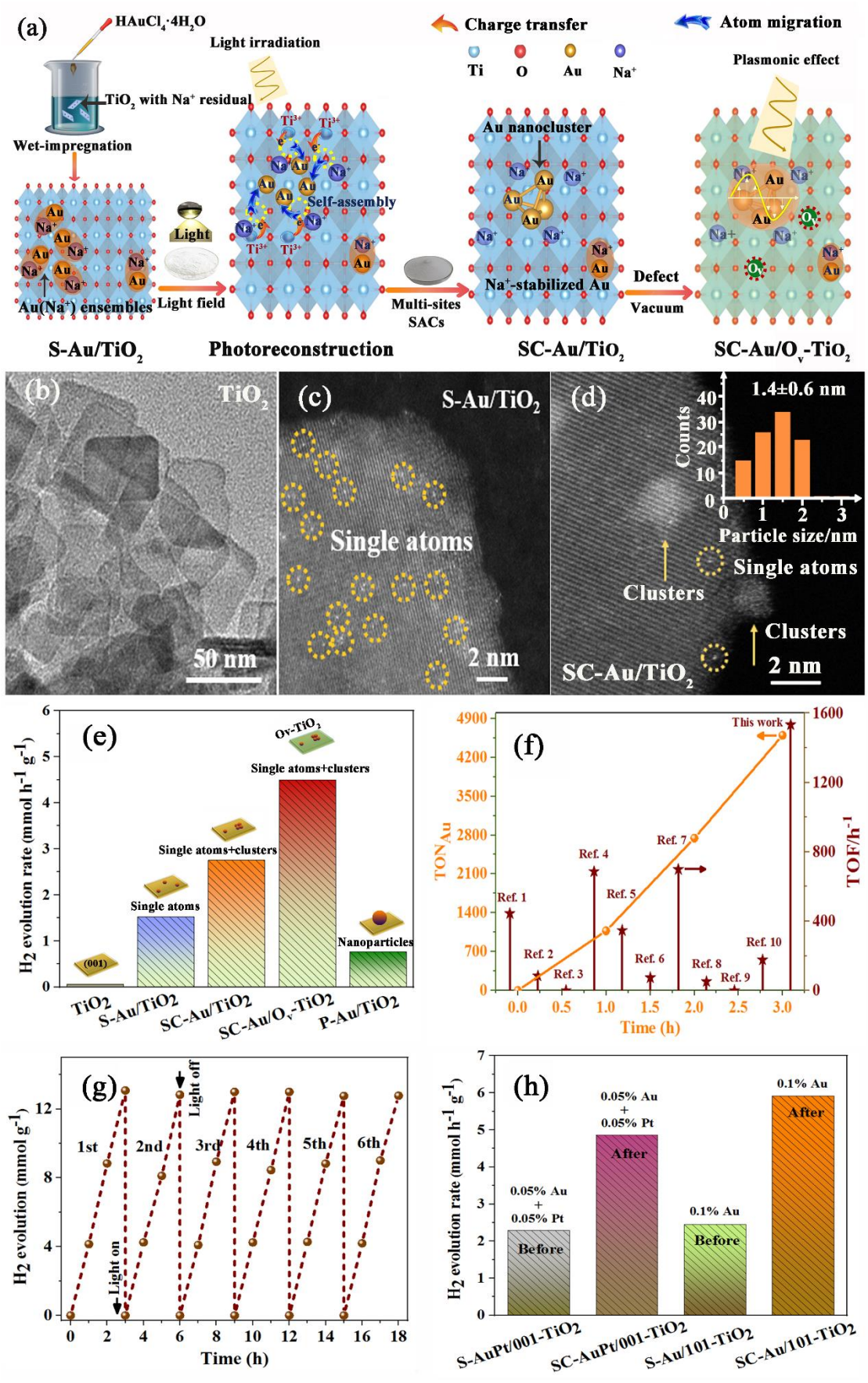

Figure 1 (a) Schematic illustration of the Na-mediated photoreconstruction strategy; (b)

TEM image of TiO_2; (c, d,) HAADF-STEM images of S-Au/TiO_2 (c) and SC-Au/TiO_2 (d). Inset of (d) is the size distribution curve of Au clusters in SC-Au/TiO_2; (e) Time-dependent H_2 evolution over TiO_2 cocatalyzed by different types of metal sites under simulated solar light irradiation (AM1.5G); (f) Calculated TON_{Au} after 3 h simulated sunlight irradiation and comparing photoactivity of photoreconstructed SC-Au/O_v-TiO_2 with reported results; (g) Cycling measurements of photocatalytic hydrogen production over SC-Au/O_v-TiO_2 for 18 hours; (h) Photoreconstruction of diverse atomically dispersed cocatalysts on TiO_2 for performance improvement.

Roles of sodium and light illumination for site reconstruction. The first critical part of our strategy was the residual sodium on TiO_2 nanosheets (originated from NaOH used for removing fluorine, Figure S9) that acted as an adherent mediator to promote the formation of Au single atoms. This could be indicated by the fact that less amount of Au atoms were anchored onto TiO_2 without the assistance of sodium (Figure S10), with a sharply decreased H_2 evolution capability of the corresponding reconstructed sample (Figure S11). To understand the detailed function of Na^+, we firstly perform inductively coupled plasma optical emission spectrometry (ICP-OES) measurements to estimate the amount of Na^+. The results indicated the weight contents of Au and Na^+ in all Au-loaded samples are almost equivalent (0.07 wt% of TiO_2) (Table S2). Considering it is difficult to visualize the Na^+, its electronic structure before and after Au atoms formation was investigated by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2a, the binding energy of Na 1s at ~1072 eV in TiO_2 samples corresponded to the ionic state of Na^+ residual. Interestingly, this peak shifted to lower bind energy after the introduction of Au single atoms, implying the strong coupling effect between Au and Na^+.[27] This can also be verified by X-ray absorption near-edge structure (XANES) and nuclear magnetic resonance (NMR) spectroscopy. As expected, we observed the decreased oxidation density of Na^+ in S-Au/TiO_2 based on the decreased intensity of the white line peak in the normalized XANES spectra (Figure 2b).[28] In the NMR spectra, the shift of the ^{23}Na signal toward a high field further confirmed the increased electron density of Na^+ (Figure 2c). Density functional theory (DFT) calculations were performed to deeply understand the mediation effect of sodium

during site reconstruction. We found that a single Au atom was prone to be linked to surface O_{2c} of 001-TiO_2 by Au-O bond. The modification of TiO_2 by Na^+ decreased the length of Au-O bond from 3.26 Å of pure TiO_2 to 2.17 Å (Figure S12). It signified that atomically dispersed Au could be firmly anchored on the surface of Na^+-modified TiO_2 via the oxygen linkages (Figure S13),[29] forming evolutionary ensembles similar to Au-$O(OH)_x$ in the reported alkali-promoted water-gas-shift catalysts.[30]

The second critical part of our strategy was the reconstruction of partial Au single atoms into nanoclusters with the assistance of light illumination. We systematically investigated the transformation details by XPS, XANES, and extended X-ray absorption fine structure (EXAFS). In contrast to the metallic Au (Au^0) in benchmark P-Au/TiO_2, Au single atoms presented +1 oxidation state (Au^+) in S-Au /TiO_2, as evidenced by the shift of Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks toward lower binding energies in the XPS spectra (Figure 2d). Light irradiation of presynthesized S-Au /TiO_2 powders led to the appearance of metallic Au species (Au^0), corresponding to the formation of Au nanoclusters. The decreased oxidation state of Au nanoclusters in SC-Au/TiO_2 could be observed in XANES and EXAFS, as the white line intensity was between the intensities of S-Au/TiO_2 and Au foil (Figure 2e).[31] We further conducted Wavelet transform (WT) and compared the Fourier transforms (FT) curves of Au L_3-edge in EXAFS to analyze the coordination environment of Au in different samples. In S-Au/TiO_2, the WT maximum correlated with Au-O bonds located at 1.6 Å (Figure 2f), which was in good agreement with the theoretically calculated value (The R-space value should be corrected by ~0.4 Å, due to the *k* dependence of total phase shift),[32] confirming the stabilization of Au single atoms on the sodium modified TiO_2. While in SC-Au/TiO_2, the appearance of an additional Au-Au bond at 2.5 Å confirmed the partial conversion of Au single atoms into metallic nanoclusters. Combined with the Au 4f deconvolution results, the percentages of Au^+ and Au^0 were calculated to be around 63% and 37%, respectively. Another interesting result is the change of the chemical environment of Na^+ after light illumination. As mentioned in the last paragraph (Figure 2a), the electron density of Na^+ on TiO_2 increased after the introduction of Au single atoms. While the formation of nanocluster restored the electron density of Na^+ close to

that of in pristine Na^+ modified TiO_2, implying the separation of partial $Au(Na^+)$ ensembles during photoreconstruction.

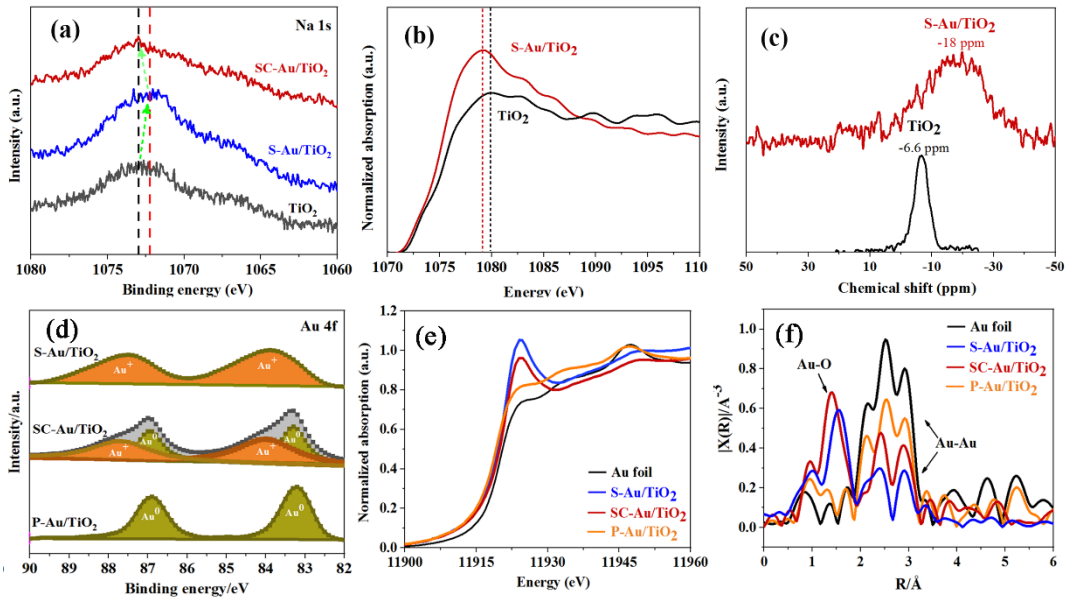

Figure 2 (a) Na 1s XPS spectra of TiO_2, S-Au/TiO_2, and SC-Au-TiO_2; (b) Na K-edge XANES spectra of TiO_2 and S-Au/TiO_2; (c) ^{23}Na NMR spectra of TiO_2 and S-Au/TiO_2; (d) Au 4f XPS spectra, (e) Au L_3-edge XANES spectra of different photocatalysts. (f) Fourier transform (FT) Au L_3-edge (k) of different photocatalysts.

To understand the underlying mechanism of Na-mediated photoreconstruction, we firstly studied the interplay between Au and TiO_2 by XPS analysis (Figure S14). As shown in Figure 3a, the binding energy of Ti 2p was decreased after the introduction of Au single atoms, indicating a strong interaction between $Au(Na^+)$ ensembles and TiO_2 supports, consistent with the formation of Au-O bond as mentioned above. We employed synchronous XPS to in-situ monitor the chemical environment of Ti in pristine TiO_2 and S-Au-TiO_2 upon light illumination. As shown in Figure 3b, the illumination shifted the Ti 2p peak to a lower value, which could be explained by the generation of delocalized electrons. Interestingly, the binding energy of Ti 2p in S-Au/TiO_2 showed an opposite shift upon illumination, implying the restructuring of cocatalyst sites via the electron transfer from excited TiO_2 to Au single atoms. This process could also be assessed by the quasi-in-situ electron spin resonance (ESR) experiments. As shown in Figure 3c, pristine TiO_2 exhibited an intense resonance signal at g=2.004 under illumination, attributed to the trapping of photogenerated electrons by

oxygen vacancies. However, this signal disappeared in S-Au/TiO_2 and a sharp spin peak from Ti^{3+} at g=1.98 emerged.[33] Under continuous illumination, the Ti^{3+} signal weakened and shifted to g=1.977, confirming the electron transfer from excited TiO_2 to sodium-stabilized Au single atoms via Ti^{3+}. With reducing capability, these transferred electrons could practically weaken the Au-O bond, thereby facilitating the agglomeration of adjacent Au single atoms into nanoclusters.[34]

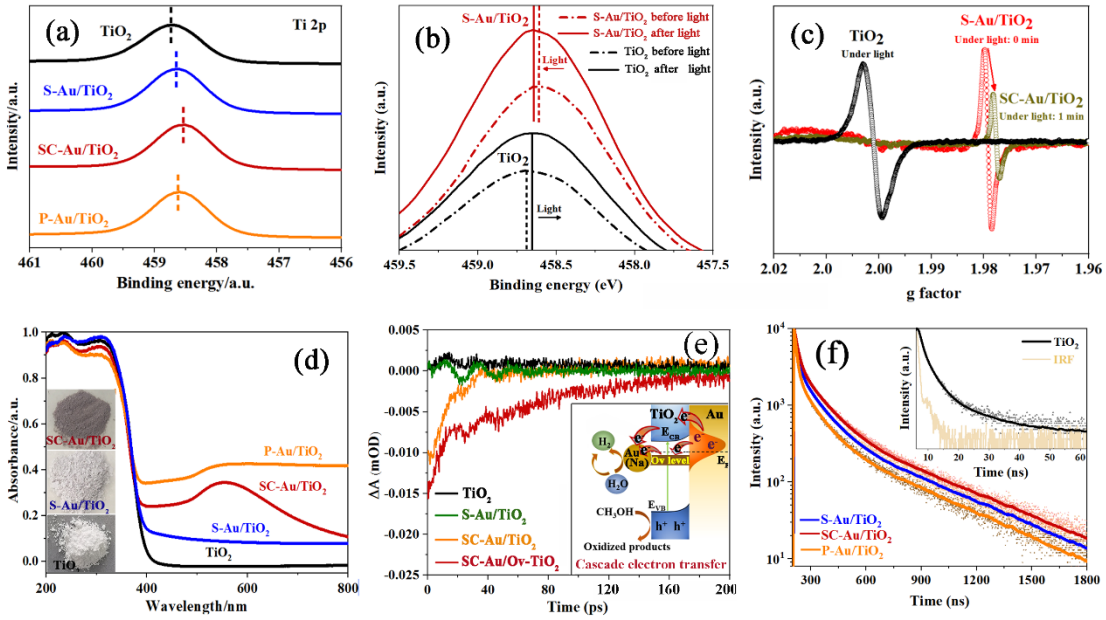

Figure 3 (a) Ti 2p XPS spectra of different photocatalysts; (b) Synchronous illumination XPS spectra of TiO_2 and S-Au/TiO_2; (c) ESR spectra of TiO_2 and S-Au/TiO_2 under light irradiation; (d) UV-vis DRS of different samples. Insets show the photographs of TiO_2, S-Au/TiO_2, and SC-Au/TiO_2; (e) Transient absorption kinetics probed at 550 nm for TiO_2, S-Au/TiO_2, SC-Au/TiO_2, and SC-Au/O_v-TiO_2. Inset shows the synergistic mechanism of SC-Au/O_v-TiO_2 for plasmonic water splitting; (f) Time-resolved photoluminescence (TRPL) decay curves of different samples. Inset displays the curve of blank TiO_2 and the instrument response function (IRF).

Mechanism of multi-site synergistic catalysis. We now turn to reveal the working mechanism of synergistic sites in SC-Au/O_v-TiO_2 for activity enhancement. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) showed that the absorption edge of pristine TiO_2 was located around 400 nm, and the introduction of Au single atoms slightly impact the absorption property of TiO_2 (Figure 3d). After the reconstruction of

Au atoms, SC-Au/TiO_2 exhibited a broad plasmonic absorption centered at 550 nm with a color of dark purple (Inset of Figure 3d), indicating the creation of an oscillating electromagnetic field by the bottom-up assembly of Au sites. The kinetics of hot carrier transfer was thereafter evaluated by TAS using a pump light pulse at 525 nm. As shown in Figure 3e, photoexcitation of SC-Au/TiO_2 caused ground state bleaching at 550 nm, while no obvious signal for pristine TiO_2 and S-Au/TiO_2,[35] confirming the role of Au nanoclusters as hot spots to concentrate incident light for generating hot charge carriers.[36] Meanwhile, retained Au single atoms with lower work function could serve as electron reservoirs to capture these hot electrons from TiO_2, as evidenced by the positively shifted Fermi level of S-Au/TiO_2 (Figure S15). The further introduction of oxygen vacancies in TiO_2 induced larger interfacial band bending, proving new channels for shuttling energetic hot electrons from Au nanoclusters to adjacent TiO_2 supports, as reflected in the prolonged recovery lifetime of SC-Au/O_v-TiO_2 in TAS analysis. Overall, the creation of multifarious sites generated a stronger built-in electric field to boost the charge separation (Figure S16), significantly increased the donor (electron) density (Table S3), and prolonged the carrier lifetimes (Figure 2f, Figure S17, and Table S4). Correspondingly, the cascade charge transfer in SC-Au/O_v-TiO_2, contributed to the 50-fold-increased visible light activity of reconstructed photocatalysts for plasmon resonance-enhanced photocatalysis (Figure S18).[37]

The hydrogen adsorption Gibbs free energies (ΔG_H) over sodium-stabilized Au single atoms were examined by theoretical calculations (Figure 4a). As shown in Figure 4b, the adsorption of one H onto isolated Au formed the structure of Au(1H) with a Gibbs free energy of -1.07 eV. The introduction of one Na^+ dramatically decreased ΔG_H, with a minimum value of 0.03 eV for 1-Au(1H)(Na^+). No further improvement was achieved with one more Na^+, confirming the significant contribution of Au(Na^+) interactions for HER activity. To investigate the downhill of ΔG_H, the electronic structure of Au(1H)(Na^+) was further explored by the density of states (DOS). From the projected density of states (PDOS) for Ti (Figure 4c), the emergence of Ti^{3+} indicated the strong electronic coupling between Au, Na, and Ti. Compared to Au(1H) and 2-Au(1H)(Na^+), the peak shape of Ti^{3+} was much sharper in 1-Au(1H)(Na^+) (Figure S19),

proving the capability of Au single atoms for electron reserving. Based on the PDOS for Au, Na, and H in Au(1H)(Na^+), H-s orbital of Au(1H)(Na^+) was occupied and located at a low energy level, which meant that it was easy to be desorbed from the Au site and thus promoted the hydrogen reduction ($H^+ + e \rightarrow H_2$) (Figure 4d). Based on these results, we conclude that sodium not only played a critical role in the stabilization of isolated Au atoms for multi-site construction but also contributed to the reduced energy barrier for water splitting reaction.

Versatility of photoreconstruction strategy. The generality of our SPR strategy for developing efficient multi-site synergistic catalysts was demonstrated by various metal oxide and noble metals for versatile reactions. The introduction of Au single atoms (S-Au/BiOBr) enhanced the photoactivity of BiOBr for nitrogen fixation, while solid-state reconstruction (SC-Au/BiOBr) further doubled the ammonia production rate (Figure S20). Redispersion of Au single atoms was conducted to improve the performance of CeO_2 for CO oxidation (Figure S21). As shown in Figure 4e, the impregnation of CeO_2 nanorods by 0.5 wt% Au single atoms (S-Au/CeO_2) decreased the complete conversion temperature from 350 ℃ to 80 ℃. Photoreconstructed SC-Au/CeO_2 with synergistic sites could efficiently oxidize CO at room temperature, signifying its great potential for gas purification. We also performed solid-state reconstruction of Ru single atoms on TiO_2 for the enhanced catalytic conversion of biomass into aromatic compounds. As expected, the reconstructed SC-Ru/001-TiO_2 exhibited two and four times higher activity than S-Ru/001-TiO_2 with single site and benchmark Ru/P25, respectively (Figure 4f). The extended applications of our SPR strategy well demonstrated the significance of site engineering for the rational design of high-performance catalysts.

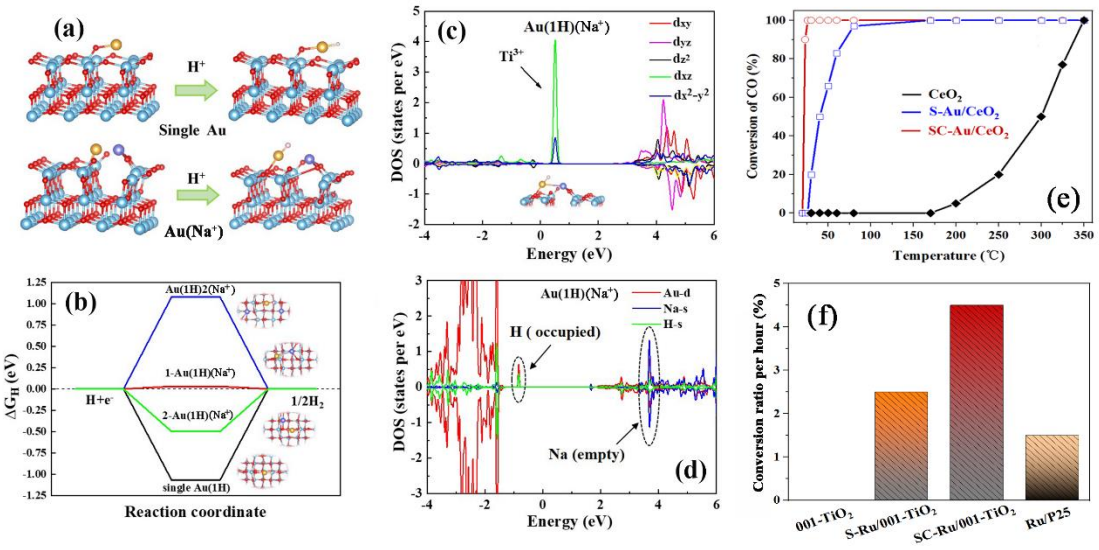

Figure 4 (a) Local atomic structures of hydrogen adsorption configurations on single Au and Au-Na dimer. Blue, red, yellow, purple, and white spheres represented Ti, O, Au, Na, and H atoms, respectively. (b) The ΔG_H for different Au sites mediated by Na^+. Different sites were considered and the represented ones were denoted as 1-Au(1H)(Na^+) and 2-Au(1H)(Na^+). (c) The Projected DOS of Ti around Au-O bond in Au(1H)(Na^+) dimer. (d) The Projected DOS of Au, Na, and H in Au(1H)(Na^+). (e) Photoreconstruction of Au single atoms on CeO_2 significantly improved the room temperature activity for CO oxidation. (f) Photoreconstrction promoted the activity of Ru-cocatalyzed 001-TiO_2 for converting biomass into aromatic compounds. Phenyl ether was selected as a model of α-O-4 and β-O-4 ether lignin intralinkages in woody biomass.

Conclusions

In summary, we have successfully developed an SPR strategy to construct advanced catalysts with multifarious active sites for versatile applications. As demonstrated by experimental and theoretical investigations, Na^+ could stabilize noble metal single toms through mediating the metal-support interactions, while light illumination of presynthesized powders induced the charge transfer from Ti^{3+} to Au single atoms, facilitating their partial agglomeration into nanoclusters via solid-state reactions. The co-construction of Au nanoclusters and sodium-stabilized Au single atoms act as plasmonic hot spots and electron reservoirs, respectively. The further creation of

oxygen vacancies in TiO_2 promotes shuttling energetic hot electrons from Au nanoclusters to Au single crystals . The final reconstructed SC-Au/Ov-TiO_2 photocatalysts with the cascade charge transfer exhibited a nearly two orders of magnitude enhancement in hydrogen evolution than that of blank TiO_2 under simulated solar light. The TON_{Au} reached a benchmark value of 4600 among all reported Au cocatalyzed TiO_2 photocatalysts. The SPR strategy could be easily extended to prepare a wide scope of noble metal cocatalyzed nanostructures with enhanced performance for kinds of catalytic reactions. This work not only provides new insights into comprehending and harnessing the metal-support interactions in SACs for activity enhancement but also opens a new avenue to construct advanced catalysts with multifarious sites for overcoming the current issues facing SACs.

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