# Catalysis Science & Technology

# PAPER

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Cite this: Catal. Sci. Technol., 2018, 8, 5535

Received 14th August 2018, Accepted 13th September 2018

DOI: 10.1039/c8cy01689e

rsc.li/catalysis

## Introduction

During recent years, considerable attention has been paid to the utilization of sunlight energy, which is regarded as an abundant and clean energy source for different applications (*e.g.*, driving chemical reactions).<sup>1–3</sup> In the field of catalytic reactions, exploiting low-cost and efficient catalytic systems with high stability is a major goal. Among these, photocatalytic technology is a promising strategy because it can combine catalysis with the potential utilization of solar energy.<sup>4–6</sup> Among the organic reactions, the synthesis of imines derived from amines is a kind of critical organic reaction.<sup>7–12</sup> The resultant imines are widely used intermediates, pharmaceuticals, and fine chemicals.<sup>13,14</sup>

In earlier studies, the transformation of amines to imines were performed mainly on noble metals (Pd, Au, Pt).<sup>15,16</sup> When compared with noble metals, low-cost and abundant inorganic semiconductors photocatalysts have attracted increasing attention because of their intrinsic catalytic properties.<sup>17–20</sup> Some significant studies have been

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# Hydrogenated $Cu_2OAu@CeO_2$ Z-scheme catalyst for photocatalytic oxidation of amines to imines<sup>†</sup>

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The design and fabrication of highly active visible light photocatalysts for organic synthesis reactions are particularly challenging for solar energy utilization and conversion. Herein, hydrogenated Z-scheme yolk-shell  $Cu_2O|Au@CeO_2$  (H- $Cu_2O|Au@CeO_2$ ) photocatalysts were synthesized using cubic  $Cu_2O$  as the starting core material *via* surface Au deposition and oxidation etching process, followed by hydrogenation treatment. When compared with  $CeO_2$ ,  $Cu_2O@CeO_2$ , and  $Cu_2O@CeO_2|Au$  nanocomposites, optimized H- $Cu_2O|Au@CeO_2$  showed remarkably higher visible light oxidation activity for the synthesis of imines from amines at ambient pressure and room temperature. The remarkably enhanced photoactivity of the H- $Cu_2O|Au@CeO_2$  composite mainly derives from the enhanced photoinduced charge separation efficiency, porous yolk-shell structure, proper surface defects, and well-maintained strong oxidation/reduction capabilities. The Z-scheme charge transfer process and photocatalytic reaction mechanism of the H- $Cu_2O|Au@CeO_2$  composites were also provided through spectral and photoelectrochemical analyses together with the investigation of structure and photocatalytic oxidation reactions. This study provides a probable approach for designing unique Z-scheme catalysts.

conducted involving the reactions of amines to imines. For example, oxide semiconductors (e.g., TiO2, CeO2, Nb2O5), metal sulfides (e.g., CdS, ZnIn<sub>2</sub>S<sub>4</sub>), and mesoporous graphite C<sub>3</sub>N<sub>4</sub> have showed photocatalytic oxidation ability of amines to imines.<sup>21-25</sup> Unfortunately, fast photoinduced charge recombination rate of a single-component catalyst is difficult to meet the stringent requirements of practical applications, including selectivity and productivity. As compared to singlecomponent catalysts, heterostructured catalysts constructed by coupling two semiconductors have been confirmed to show considerably enhanced photoactivity; therefore, the construction of a heterostructure material was considered to be an effective approach to resolve the disadvantages mentioned above.<sup>26,27</sup> For instance, for type-II band alignment, heterostructured Cu2O/CeO2 photocatalysts have exhibited higher visible light photocatalytic degradation performance than single Cu<sub>2</sub>O and CeO<sub>2</sub> because of their accelerated separation rate of photogenerated carriers.<sup>28-30</sup> However, the decreased oxidation/reduction ability of the Cu<sub>2</sub>O/CeO<sub>2</sub> heterostructure is detrimental to any improvements in the photocatalytic activity.<sup>31</sup> Therefore, simultaneously improving photogenerated charge carriers separation and maintaining individual oxidation/reduction ability is considerably desirable. The construction of a Z-scheme system photocatalyst can effectively realize this objective. Recently, the Z-scheme system photocatalysts have garnered increased attention because the strong oxidation and reduction capabilities of the

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<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/ c8cy01689e

components in the composite can be maintained.<sup>32-37</sup> In addition, the morphology and structure considerably influence the photocatalytic activity. Some special structures, such as hollow and core-shell structures, have demonstrated increased photocatalytic activity.<sup>38</sup> In particular, yolk-shell nanostructures possess the advantages of both core-shell and hollow structures, which can significantly enhance light utilization and photocatalytic activity. For example, Pt@CeO<sub>2</sub> composites with tunable yolk-shell and core-shell structures have been prepared, which have exhibited remarkable visible light photocatalytic activity.<sup>39</sup> However, no Z-scheme system involving Cu<sub>2</sub>O/CeO<sub>2</sub> yolk-shell nanostructure composites has been designed and applied in photocatalytic organic reactions up to now.

In this work, in order to implement the synthesis of imines from amines under visible light irradiation, hydrogenated Z-scheme yolk-shell Cu<sub>2</sub>O\Au@CeO<sub>2</sub> photocatalyst was prepared, and its fabrication route is illustrated in Scheme S1.† Cubic Cu<sub>2</sub>O was first prepared. Then, the surfaces of cubic Cu<sub>2</sub>O were loaded with Au nanoparticles via chemical reduction. The following oxidation etching process produced the Z-scheme yolk-shell Cu<sub>2</sub>O\Au@CeO<sub>2</sub> composite. The photocatalytic activity of the optimal Z-scheme yolk-shell Cu<sub>2</sub>O\Au@CeO<sub>2</sub> composite was remarkably higher than that of the control samples, such as individual CeO<sub>2</sub> and common yolk-shell Cu<sub>2</sub>O@CeO<sub>2</sub> composite. Moreover, the subsequent hydrogenation treatment can further improve the photocatalytic performance by reforming the surface/interface defects of Cu<sub>2</sub>O\Au@CeO<sub>2</sub>. The origin of significantly enhanced photocatalytic performance and reaction mechanism for the optimal Z-scheme yolk-shell composite catalyst were explored.

### Experimental section

#### Synthesis of cubic Cu<sub>2</sub>O nanocrystals

Firstly, 0.0372 g EDTA–2Na and 0.0250 g  $CuSO_4 \cdot 5H_2O$  were separately added into 100 mL distilled water to form an aqueous solution (0.01 M). An appropriate amount of D-glucose and NaOH were also dissolved in 10 mL distilled water to form 0.1 M and 1 M aqueous solutions, respectively. Then, 100 mL EDTA–2Na solution and 10 mL D-glucose solution were put in a 250 mL breaker containing 100 mL CuSO<sub>4</sub> aqueous solution. After NaOH solution (10 mL, 1 M) was mixed with the above solution, the beaker containing the mixed solution was put into a water bath (80 °C) and kept for 30 min. After filtration, the obtained precipitate (cubic Cu<sub>2</sub>O) was washed, followed by drying at 60 °C.

#### Synthesis of Cu<sub>2</sub>O\Au

In a typical synthesis process, 0.05 g Cu<sub>2</sub>O was added in distilled water (28 mL); then, 10 mL 1% PVP (polyvinyl pyrrolidone; mol. wt: 10 000) solution was added in the above solution under stirring (30 min). Finally, the optimal 0.7 mL HAuCl<sub>4</sub> solution ( $2.5 \times 10^{-3}$  g mL<sup>-1</sup>) was mixed with the above solution. After stirring for 3 h, the obtained precipitate was filtrated and washed, followed by drying at 60 °C. For comparison, the experiments of Cu<sub>2</sub>O loaded with different Au contents were also done. Here, 0.35 mL, 1.05 mL, and 1.40 mL HAuCl<sub>4</sub> solutions were used to prepare the Cu<sub>2</sub>O\Au samples.

#### Synthesis of hydrogenated Cu<sub>2</sub>O\Au@CeO<sub>2</sub> (H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub>)

Cu<sub>2</sub>O\Au@CeO<sub>2</sub> was firstly synthesized via a template etching method. Under magnetic stirring, 2.5 mL NaCl aqueous solution was added in a beaker containing 200 mL absolute ethanol. Further, 50 mg Cu<sub>2</sub>O\Au was dispersed in the above NaCl solution to obtain well-distributed suspension under ultrasonic dispersion for 15 min. Then, 50 mL ethanol solution containing 0.011 g  $(NH_4)_2Ce(NO_3)_6$  was dropped into the above suspension solution at 45 °C. The obtained final powder was washed and dried (60 °C). Similarly, Cu<sub>2</sub>O@CeO<sub>2</sub> was also obtained under a similar synthesis route using Cu<sub>2</sub>O to replace Cu2O\Au. H-Cu2O\Au@CeO2 was obtained by calcining Cu<sub>2</sub>O\Au@CeO<sub>2</sub> to 300 °C and maintaining it under Ar/H<sub>2</sub> (7%) atmosphere for 10 min, and the resultant product was termed as H-Cu2O\Au@CeO2. As a comparison, Au nanoparticles were also loaded on the outer side of  $Cu_2O(@CeO_2)$ , and the sample was labeled as Cu<sub>2</sub>O@CeO<sub>2</sub>\Au.

## Characterization

The crystal structure of the powder samples was determined using an X-ray diffractometer (D8 Advance), and Cu Ka was the radiation source (40 kV, 44 mA,  $\lambda = 1.5406$  Å). Surface morphology and elemental distributions of the samples were analyzed by scanning electron microscopy-energy-dispersive X-ray spectrometer (SEM-EDS, S-4800, EDAX). Transmission electron microscopy (TEM) was performed using a JEOL 2100 system operated at 200 kV. In order to perform TEM characterization, after ultrasonic dispersion, ethanol suspensions containing catalysts were dropped onto copper grids (400 mesh) coated with carbon. The diffuse reflectance spectra (DRS) were obtained from a UV-2550 UV-vis absorption spectrophotometer equipped with an ISR-240A integrating sphere using BaSO<sub>4</sub> as the reference sample. Raman spectra were obtained from a laser Raman spectrometer (HR800, Horiba) using 632.8 nm excitation wavelength and 1800 L mm<sup>-1</sup> grating. The valence states of the elements were determined on an X-ray photoelectron spectrometer (XPS, VG ESCALABMK II); Al K $\alpha$  (*hv* = 1486.8 eV) was used as the X-ray source. The C 1s peak at 284.6 eV was used as the internal standard. Fluorescence spectra were obtained from the FLS920 fluorescence spectrophotometer (Edinburgh) using a He-Cd laser source, and the excitation wavelength was 320 nm. The metal composition of the optimal catalyst was detected via inductively coupled plasma emission spectrometer (ICP, Optimal 7000).

#### **Electrochemical test**

The electrochemical test was performed on an electrochemical analyzer (BAS100B), and a three-electrode system was applied. Saturated Ag/AgCl was used as the reference electrode, and Pt foil (1 cm  $\times$  1.5 cm) was used as the counter electrode. A Xe lamp (300 W, CEL-HXF-300) was used as the light source; it was equipped with a 400 nm cutoff filter. Here, 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution bubbled with nitrogen gas was used as the electrolyte. Electrochemical impedance spectroscopy (EIS) data was obtained using an electrochemical analyzer (Zahner Elektrik, Germany) over a 100–0.05 Hz frequency range under bias of -0.8 V with sinusoidal perturbations of 10 mV.

#### Photocatalytic performance test

Photocatalytic tests were carried out in a 3 mL quartz vessel. A mixed solution of 1.5 mL deionized water (H<sub>2</sub>O), 15 µL organic reactants, and 15 mg photocatalyst was added into the quartz vessel. Further, oxygen was bubbled through the reactor for 15 min to enhance the oxygen adsorption of the photocatalyst. Then, the vessel was plugged using a rubber stopper. The vessel was maintained at room temperature (20-23 °C) by circulating water through the outer jacket. The samples were collected before and at regular intervals during irradiation, and the catalyst was removed by filtration. The light source was a Xe lamp (300 W, CEL-HXF-300); a 400 nm cutoff filter was employed. The light density was 5.8 mW cm<sup>-2</sup>. After light irradiation, the photocatalyst particles were filtered, and the product was extracted using acetonitrile. It was then analyzed by gas chromatography-mass spectrometry (6890GC-5973MSD, Agilent) after drying with Na2SO4 powder. The electron spin resonance (ESR) spectra were obtained using an A300 ESR spectrometer at room temperature, where DMPO was used as the spin-trap reagent in a methanol solution. Instrument settings conditions: receiver gain,  $1 \times 10^3$ ; time constant, 10.24 ms; modulation amplitude, 3 G; center field, 3507 G; microwave power, 6.35 mW; sweep width, 80 G; sweep time, 42 s.

## Results and discussion

#### Material characterization

X-ray diffraction (XRD) analysis was performed to determine the structures of the catalysts. In Fig. 1A, all the diffraction peaks located at  $36.5^{\circ}$ ,  $42.4^{\circ}$ ,  $60.9^{\circ}$ , and  $73.1^{\circ}$  matched with the cuprite structure Cu<sub>2</sub>O (JCPDS: 05-0667).<sup>40</sup> The diffraction peaks at  $56.3^{\circ}$ ,  $47.5^{\circ}$ ,  $33.1^{\circ}$ , and  $28.6^{\circ}$  correspond to CeO<sub>2</sub> with a fluorite structure (JCPDS: 81-0792).<sup>41</sup> However, Au can-



Fig. 1 (A) XRD patterns and (B) Raman spectra of different samples.

not be identified in the XRD pattern of Cu<sub>2</sub>O\Au@CeO<sub>2</sub> because of its low content. The XRD diffraction peak intensity of H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> is slightly lower than that of Cu<sub>2</sub>O\Au@CeO<sub>2</sub> due to the decrease in the crystallinity after hydrogenation treatment. Moreover, there exists a weak diffraction peak (43.3°) of Cu derived from the partial reduction of Cu<sub>2</sub>O.<sup>42</sup> The Raman spectra in Fig. 1B further confirmed the formation of Cu<sub>2</sub>O and CeO<sub>2</sub> (Fig. 1B). In Fig. 1B, the peak at 459 cm<sup>-1</sup> corresponds to the F<sub>2g</sub> skeletal vibration.<sup>43</sup> However, in the Raman spectrum of H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub>, the peak (459 cm<sup>-1</sup>) corresponding to CeO<sub>2</sub> changes to 465 cm<sup>-1</sup>, which can be attributed to the production of oxygen vacancies (Vo's) originating from the hydrogenation treatment.<sup>44</sup> In optimal H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub>, the molar ratio of Cu:Ce:Au is about 39:18:1 according to the ICP test.

SEM and TEM characterizations were performed to demonstrate the morphology and structure of the catalysts. As shown in Fig. 2A, the outer surface of cubic Cu<sub>2</sub>O is smooth. However, the outer surface of cubic Cu<sub>2</sub>O\Au is rough and uniformly covered by Au nanoparticles (8-10 nm) (Fig. 2B). The TEM image further confirmed the cubic structure of Cu<sub>2</sub>O (Fig. 2C), and uniformly distributed Au nanoparticles on the outer surface of Cu<sub>2</sub>O can also be seen from the inset of Fig. 2D. The diameter of Au nanoparticles is about 8-10 nm. The EDS element mapping results also proved the uniform distribution of Au nanoparticles on the outer surface of Cu<sub>2</sub>O (Fig. S1<sup>†</sup>). From Fig. 3A, it can be seen that rough porous CeO<sub>2</sub> shells were formed on the outside of the Cu<sub>2</sub>O\Au because of the partial sacrifice of Cu<sub>2</sub>O during the etching reaction, and uniform yolk-shell structure nanocubes were observed (Fig. 3B), demonstrating the successful preparation of yolk-shell structure Cu2O\Au@CeO2. Fig. 3C shows the HRTEM image (the box in Fig. 3B); interplanar spacings of 0.31 and 0.19 nm correspond to the (111) and (220) facets of CeO<sub>2</sub>, respectively.<sup>41</sup> After hydrogenation treatment, the



Fig. 2 SEM (A) and TEM (C) images of Cu\_2O; SEM (B) and TEM (D) images of Cu\_2O\Au.



Fig. 3 SEM images of Cu<sub>2</sub>O\Au@CeO<sub>2</sub> (A) and H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> (B). TEM images of Cu<sub>2</sub>O\Au@CeO<sub>2</sub> (C) and H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> (D). HRTEM images of Cu<sub>2</sub>O\Au@CeO<sub>2</sub> (E) and H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> (F).

entire cubic morphology and yolk-shell structure of  $Cu_2O|Au@CeO_2$  were effectively maintained (Fig. 3D and E). The corresponding HRTEM image is shown in Fig. 3F. Apart from the lattice fringe (0.19 nm) of the CeO<sub>2</sub> (220) plane, there exists a thin amorphous CeO<sub>2</sub> surface layer, which is produced from the hydrogenation treatment.<sup>44</sup>

#### Optical and electrochemical properties

The survey XPS spectrum (Fig. S2<sup>†</sup>) confirms the existence of Ce, O, Cu, and Au in H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub>. In Fig. 4A, the peaks assigned to  $Ce^{4+} 3d_{3/2}$  are marked as u''', u'', and u. The peaks corresponding to Ce<sup>4+</sup>  $3d_{5/2}$  are marked as  $\nu''$ ,  $\nu'''$ , and  $\nu$ . Similarly, the peaks attributed to  $Ce^{3+} 3d_{3/2}$  and  $Ce^{3+} 3d_{5/2}$  are marked as u' and v', respectively.<sup>45,46</sup> The deconvolution results reveal the coexistence of Ce<sup>3+</sup> and Ce<sup>4+</sup> in the samples. Moreover, the relative concentration of Ce3+ in H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> is larger than that in Cu<sub>2</sub>O\Au@CeO<sub>2</sub> estimated via the integrated peak area in the spectra through the equation (Fig. S2<sup>†</sup>), implying that the hydrogenation treatment induced the formation of Vo's of Ce<sup>3+</sup>/Ce<sup>4+</sup> redox pairs by causing lattice distortion and charge imbalance in CeO<sub>2</sub>.<sup>46</sup> The peaks of Cu  $2p_{1/2}$  (952.2 eV) and Cu  $2p_{3/2}$  (932.4 eV) are associated with Cu<sup>0</sup> or Cu<sup>1+</sup>.<sup>47</sup> The peaks at 934.1 (Cu 2p<sub>3/2</sub>) and 953.9 eV (Cu  $2p_{1/2}$ ) can be ascribed to  $Cu^{2+}$ .<sup>45</sup> The exis-



**Fig. 4** XPS spectra of (A) Ce 3d, (B) Cu 2p, (C) O 1s, and (D) Au 4f of different samples. Core-level XPS spectra are shown using color maps, and the corresponding deconvoluted peaks are shown using solid lines. The spectra decomposition was executed using the XPS PEAK 41 program with Gaussian functions after the subtraction of a linear background.

tence of satellite peaks at 941.2 and 961.9 eV in the spectra indicates that there is marginal content of the chemical state of  $Cu^{2+}$  oxidation state (CuO).<sup>48</sup> The O 1s spectra are shown in Fig. 4C. The two deconvoluted peaks at around 529.3 and 531.4 eV are related to lattice oxygen and hydroxyl-type oxygen species/molecular water, respectively.<sup>49</sup> In the Au 4f XPS spectrum (Fig. 4D), the peaks at 84.0 and 87.7 eV can be attributed to metallic Au atoms in the composite catalysts.<sup>50</sup>

UV-vis absorption spectra are employed to investigate the optical properties of the photocatalysts. In Fig. 5A, steep absorption edges can be found at 450 and 635 nm in the absorption spectra of CeO<sub>2</sub> and Cu<sub>2</sub>O, respectively. When compared with CeO<sub>2</sub>, the increased visible light absorption of Cu<sub>2</sub>O\Au@CeO<sub>2</sub> mainly comes from the introduction of Cu<sub>2</sub>O. Meanwhile, the existence of Au and Cu nanoparticles can exhibit localized surface plasmon resonance (SPR) effect. Moreover, H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> exhibited the strongest visible light absorption among these samples because of the existence of surface defects generated from hydrogenation.

Surface defects such as the existence of Vo's were confirmed by ESR test (Fig. S3<sup>†</sup>). For Cu<sub>2</sub>O@CeO<sub>2</sub>\Au, weak absorption at about 550 nm can be found from its UV-vis absorption spectrum, which originated from the SPR effect of Au nanoparticles. The direct optical bandgaps of CeO<sub>2</sub> and Cu<sub>2</sub>O were measured by plotting the graph of  $(ahv)^2$  versus photon energy (*hv*) (Fig. 5B). Here, *a* is the optical absorption coefficient, and *hv* can be calculated as hv = 1240/wavelength. The direct optical bandgaps of CeO<sub>2</sub> and Cu<sub>2</sub>O were 2.87 and 1.95 eV, respectively, measured by extrapolating the linear region of the square of the absorption curve to the *x*-axis. These values are in good agreement with the reports of CeO<sub>2</sub> (2.8– 3.0 eV) and Cu<sub>2</sub>O (2.0–2.2 eV).<sup>46,51</sup>

Photoluminescence is an important characterization technique to analyze the behavior of photogenerated carriers.<sup>52</sup> Published on 03 October 2018. Downloaded by Kaohsiung Medical University on 11/11/2018 12:38:37 AM.



**Fig. 5** (A) UV-vis absorption spectra and (B) calculated bandgaps of different catalysts; steady state (C) and transient state (D) photo-luminescence spectra of the different catalysts.

In Fig. 5C, the steady state photoluminescence spectra show emission bands at around 427 and 465 nm, originating from the defects within the Ce 4f and O 2p levels, respectively.<sup>53</sup> Obviously, these composite catalysts including Cu<sub>2</sub>-O@CeO2\Au showed relatively lower photoluminescence intensity than pure CeO<sub>2</sub>. In particular, H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> showed the lowest photoluminescence intensity. It indicates that the inhibited photoinduced charge recombination in the composites was because of the existence of proper surface defects (Vo's) and the synergy between Cu<sub>2</sub>O, Au, and CeO<sub>2</sub>. Moreover, the transient state photoluminescence spectroscopy tests (Fig. 5D) also prove that the average fluorescence lifetime of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> is the longest in these catalysts (Table S1<sup>†</sup>). Hence, this H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> Z-scheme yolkshell system is better than an ordinary heterojunction structure.

Transient photocurrent tests were implemented to demonstrate the accelerated photoinduced charge transfer and separation of different samples. As evident from Fig. 6A, the H– Cu<sub>2</sub>O\Au@CeO<sub>2</sub> electrode showed higher photocurrent density than Cu<sub>2</sub>O, Cu<sub>2</sub>O@CeO<sub>2</sub>, and Cu<sub>2</sub>O\Au@CeO<sub>2</sub>. The results indicate that the Z-scheme structure and proper surface defects in H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> could generate additional charge carriers, thereby promoting their effective separation. Similarly, EIS tests were also performed. In Fig. 6B, the smallest arc size can be observed for the H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> electrode, suggesting the lowest interfacial charge transfer resistance (Rct), resulting in the highest charge transfer and separation efficiency. This agrees with the photoluminescence spectra and transient photocurrent results.<sup>54</sup>

#### Photocatalytic activities

A series of organic synthesis reactions of imines from amines were performed to evaluate the photocatalytic activity of cata-



Fig. 6 (A) Photocurrent response of different samples with and without visible light irradiation under bias of 0.4 V versus NHE. (B) Nyquist plots of different samples. Supporting electrolyte is 0.1 M  $Na_2SO_4$ .

lysts in deionized water. The N-benzylidene benzylamine derived from benzylamine under aerobic oxidation was first studied. A high yield (88.0%) and good selectivity (96.5%) to N-benzylidene benzylamine product were obtained in the presence of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> after 5 h visible light irradiation. However, when using Cu<sub>2</sub>O\Au@CeO<sub>2</sub>, Cu<sub>2</sub>O@CeO<sub>2</sub>\Au, Cu<sub>2</sub>O@CeO<sub>2</sub>, CeO<sub>2</sub>\Au, and CeO<sub>2</sub> as the photocatalysts in an oxygen atmosphere, despite having similar selectivity, relatively low yields of 72%, 56.2%, 41.3%, 40.3%, and 21.6% are obtained, respectively. The significantly enhanced photocatalytic activity of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> arise from several factors. Firstly, the enhanced photoinduced charge separation and transfer rate in Z-scheme Cu<sub>2</sub>O@CeO<sub>2</sub> composites can accelerate the photocatalytic organic reaction rate. Secondly, significantly enhanced visible light absorption of the composites because of hydrogenation can indeed contribute toward the generation of additional photogenerated charge carriers. Meanwhile, hot electrons can be produced from Au nanoparticles during visible light irradiation, and some hot electrons can leap into the conduction band of Cu<sub>2</sub>O to participate in the catalytic reactions. Thirdly, the Vo's (generated from the formed Ce<sup>3+</sup> after hydrogenation) can also provide a higher carrier concentration and promote enhanced carrier separation,<sup>43</sup> which can be proven by photochemical and photoelectrochemical tests. Moreover, the porous CeO<sub>2</sub> shell and hollow interlayer can also promote the reactants transfer. In addition, the relatively high adsorption capacity (Table S2<sup>†</sup>) of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> contributes toward the enhancement of photocatalytic activity.

In photocatalytic tests, some control experiments were also carried out. The photocatalytic tests of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> with different Au contents confirmed that the moderate content of Au can make H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> exhibit optimal photocatalytic activity (Fig. S4<sup>†</sup>). The same organic reaction occurring in air and under de-aerated conditions showed relatively low yields of 69% and 15% (Fig. 7B), respectively. Meanwhile, the control experiments also indicated that there was a very low conversion rate under dark or no catalyst conditions (Fig. 7B). Meanwhile, when compared with the reported catalysts, the catalyst in this work still achieves satisfying conversion and selectivity (Table S3<sup>+</sup>). The results verified that the oxidative reactions could be driven under the existence of a catalyst, molecular oxygen, and light irradiation. The effect of substrate concentration on the photocatalytic reactions (Fig. S5<sup>†</sup>) was also studied. It can be seen that the conversion rate and yield increased with the benzylamine concentration up to 90 mM; it then decreased at higher concentrations. This can be attributed to the fact that when the concentration is less than or equal to 90 mM, more benzylamine molecules can reach the surface active sites of the catalysts and participate in the oxidation reaction, leading to a higher conversion rate (Fig. S5A<sup>†</sup>) and yield (Fig. S5B<sup>†</sup>). When the benzylamine concentration is too high, some of the benzylamine molecules cannot reach the surface



Fig. 7 (A) Time course of benzylamines yield over various photocatalysts: a) Cu<sub>2</sub>O, b) CeO<sub>2</sub>, c) CeO<sub>2</sub>\Au, d) Cu<sub>2</sub>O@CeO<sub>2</sub>, e) Cu2O@CeO2\Au, f) Cu2O\Au@CeO2, g) H-Cu2O\Au@CeO2. Reaction conditions: 15 mg photocatalysts, 1.5 mL H<sub>2</sub>O, 15  $\mu$ L substrates, visible light ( $\lambda$  > 400 nm), illumination time is 5 h, oxygen atmosphere, room temperature (20-23 °C); (B) time course of benzylamines yield over H-Cu2O\Au@CeO2 under different reaction conditions: (a) no photocatalysts, (b) dark, (c) N<sub>2</sub> atmosphere, (d) air; (C) photocatalytic oxidation of benzylamines over H-Cu2O\Au@CeO2 using different trapping agents: isopropanol (IPA) for 'OH, benzoquinone (BQ) for 'O2, and ammonium oxalate (AO) for h<sup>+</sup>; (D) ESR spectra of DMPO-'O2 in H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> dispersion under different conditions: a) reaction conditions: 15 mg photocatalysts, 1.5 mL methanol dispersion, 15 µL of substrates under visible light irradiation  $(\lambda > 400 \text{ nm})$ , illumination time is 2 h, oxygen atmosphere, room temperature (20-23 °C), b) no photocatalysts, c) dark.

of the catalyst and participate in the reaction, so the conversion rate and yield decrease. However, the selectivity exhibits no obvious change (Fig. S5C†). The aerobic oxidation reactions of some other amines were also carried out. The experimental results are listed in Table 1. Obviously, the aerobic oxidation of amines was realized. Moreover, higher yields can be obtained from benzylamines containing electron-donating groups such as OCH<sub>3</sub> and CH<sub>3</sub> in comparison to benzylamines with electron-withdrawing groups (*e.g.*, Cl), which is in agreement with a previous report.<sup>55</sup> In addition, for the *para*-substituted benzylamines, a higher reaction rate can be provided in comparison to the *ortho* and *meta* isomers due to steric effects.

To reveal the underlying cause of the dramatic enhancement in activity and corresponding intrinsic mechanism of photocatalytic aerobic oxidation of amines, radical scavenger tests were performed. Isopropanol (IPA), benzoquinone (BQ), and ammonium oxalate (AO) were selected as the trapping agents of 'OH, 'O2-, and h+, respectively.56 As shown in Fig. 7C, the introduction of BQ and AO led to a significant decrease in the benzylamine conversion, demonstrating that  $O_2^-$  and h<sup>+</sup> act as the main active species. The significantly important role of 'O<sub>2</sub><sup>-</sup> in the photocatalytic reaction was further confirmed by ESR measurements. As presented in Fig. 7D, four obvious signals assigned to DMPO- $O_2^-$  can be observed when H-Cu2O\Au@CeO2 acts as the catalyst under visible light illumination, indicating that  $O_2^-$  can be generated from H-Cu2O\Au@CeO2.57 The control experiments show that 'O<sub>2</sub><sup>-</sup> signal cannot be found in the absence of H- $Cu_2OAu()CeO_2$  or under dark conditions. Meanwhile, the weak ESR signal of DMPO-'OH adduct can be found (Fig. S6<sup>†</sup>). This indicated that only a small quantity of 'OH radicals were produced in this photocatalytic system. The above ESR and radical trapping tests confirmed the synergistic effects of  $h^+$  and  $O_2^-$  in the photocatalytic reaction.

The improved photocatalytic activity of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> can be elucidated from the formation of the Z-scheme band structure system (Fig. 8). According to the XPS valence spectra (Fig. S7<sup>†</sup>), the valence band (VB) positions of CeO<sub>2</sub> and Cu<sub>2</sub>O were located at 2.44 and 0.63 V, respectively. As evident from Fig. 5B, the bandgaps of CeO<sub>2</sub> and Cu<sub>2</sub>O were 2.74 and 1.95 eV, respectively. Therefore, the conduction band (CB) positions of CeO<sub>2</sub> and Cu<sub>2</sub>O were located at about -0.30 and -1.32 V versus NHE, respectively. The designed schematic diagram of the energy band structure of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> is shown in Fig. 8. In the Z-scheme H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> system, Cu<sub>2</sub>O and CeO<sub>2</sub> can be simultaneously excited under visible light irradiation. Photoinduced electrons from the CB of CeO<sub>2</sub> could transfer to the VB of Cu<sub>2</sub>O via metallic Au to recombine with the holes. This combination process was very fast. Hence, the charge carriers' separation efficiency was considerably enhanced. Electrons in the CB of Cu<sub>2</sub>O were captured by  $O_2$ , so  $O_2^-$  was produced. The h<sup>+</sup> in the VB of CeO<sub>2</sub> directly oxidized H<sub>2</sub>O to form 'OH radicals. Therefore, the produced predominant active species  $O_2^-$  and  $h^+$  could effectively oxidize various amines to their corresponding

 $\label{eq:table_transform} \begin{array}{l} \mbox{Table 1} & \mbox{Photocatalytic oxidation of a series of benzylic amines over $H-Cu_2O\Au@CeO_2$. Reaction conditions: 15 mg $H-Cu_2O\Au@CeO_2$, 1.5 mL $H_2O$, 15 mL $H_2O$, 16 mL $H_2O$, 16 mL $H_2O$, 16 mL $H_2O$, 17 mL $H_2O$, 17 mL $H_2O$, 18 mL $H_2O$, 18 mL $H_2O$, 18 mL $H_2O$, 19 mL $H_2O$, 10 mL $H_2O$$ 

				Conversion	Selectivity (%)	
Entry	Substrate	Product	By-product	(%)	N-Benzylidene benzylamines	Benzaldehydes
1	NH <sub>2</sub>			91.2	96.5	13.5
2	NH <sub>2</sub>	p C P P		91.9	94.8	15.2
3	Cl NH2	CI CI		71.6	69.5	30.5
4	NH <sub>2</sub>			90.4	61.0	39
5	NH <sub>2</sub>			75.4	56.8	43.2

imines. Meanwhile, a small number of generated hot electrons could jump to the CB of Cu<sub>2</sub>O and then be captured by the molecular oxygen to yield superoxide radicals ( $O_2$ ). Moreover, the Vo's on H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> can accelerate the photoinduced charge separation and improve the photocatalytic performance. Conversely, in a traditional type-II heterostructure model (Fig. S8<sup>†</sup>), the electrons in the CB of Cu<sub>2</sub>O and Au jump to that of  $CeO_2$ , and the h<sup>+</sup> in the VB of  $CeO_2$ would leap to that of  $Cu_2O$ . However,  $O_2^-$  could not be produced because CeO<sub>2</sub> has a more positive CB-edge potential (-0.30 V) than  $O_2/O_2^-$  (-0.33 V). Similarly, 'OH radicals cannot be produced because Cu<sub>2</sub>O has a more negative VB (+0.63 V). However, the production and significant role of  $O_2^{-}$  and 'OH were verified in the active species trapping experiments (Fig. 7C). Therefore, a Z-scheme structure mechanism is reasonable. The above experiment results showed that the produced  $h^+$  and  $O_2^-$  species should exert a synergistic catalytic role on the photocatalytic reaction. The photocatalytic reaction mechanism was also proposed (Fig. 8). The electrons (e<sup>-</sup>) in the CB of  $Cu_2O$  reacted with  $O_2$  to produce  $O_2^-$ . The h<sup>+</sup> in the VB of CeO<sub>2</sub> oxidized the anchored amine to produce the cation radical complex.58 Meanwhile, the hydrogen atoms



Fig. 8 Photocatalytic reaction mechanism of imines derived from amines under aerobic conditions over  $H-Cu_2O\setminus Au@CeO_2$ .

can be extracted by  $O_2^-$  from the amine radial cations to generate imine intermediates, and the hydrolysis of imine intermediates leads to the formation of intermediate benzaldehyde and ammonia gas, which were proven by the GC-MS (Fig. S9†) and ion chromatography test results (Fig. S10†). Then, benzaldehyde molecules are transferred to the primary amines to produce the corresponding imines (Table 1).

The photocatalytic cycling stability of H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> was also tested. After six reaction cycles, only a slow decrease in the photocatalytic activity can be found (Fig. S11<sup>†</sup>). Meanwhile, conversion and selectivity have no obvious decrease after the reusability test (Fig. S12<sup>†</sup>), indicating the excellent active stability of the H-Cu<sub>2</sub>O/Au@CeO<sub>2</sub> catalyst. Furthermore, the different characterizations (XRD, Raman, XPS, SEM, and TEM) of the H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> catalyst after the tests were done (Fig. S13-S16<sup>†</sup>). The results show that the catalyst has relatively high morphology and structural stability. In addition, the H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> catalyst can be applied to other organic synthesis reactions. For example, the photocatalytic synthesis of aromatic aldehyde from the corresponding aromatic alcohol derivatives were also achieved (Table S4<sup>†</sup>). This suggests that the H-Cu<sub>2</sub>O\Au@CeO<sub>2</sub> catalyst may have wide applications in photocatalytic organic syntheses.

## Conclusions

In summary, we have developed a H–Cu<sub>2</sub>O\Au@CeO<sub>2</sub> Z-scheme yolk–shell structure photocatalyst. The prepared H– Cu<sub>2</sub>O\Au@CeO<sub>2</sub> catalysts can significantly enhance the charge separation efficiency and maintain strong oxidation/reduction capabilities. The transformation of amines into imines was realized with high productivity and excellent selectivity under aerobic oxidation conditions. Besides, the composite catalysts showed potential performance in other organic reactions and possessed excellent stability without compromising on the photocatalytic efficiency. More detailed studies were also performed to clarify the factors that determine the catalytic activity and applications to some other oxidation reactions. This synthesis strategy can contribute toward fabricating Z-scheme catalysts yielding both high oxidation and excellent reduction ability.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

We thank the financial support from the National Natural Science Foundation of China (51772079, 51672073 21771061), Natural Science Foundation of Heilongjiang Province of China (B2017009).

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