

Ternary CdS/Au/3DOM-SrTiO₃ Composites with Synergistic Enhancement for Hydrogen Production from Visible-light Photocatalytic Water Splitting

Authored by

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Abstract

New ternary composites based on three dimensionally ordered macroporous (3DOM) SrTiO₃ (CdS/Au/3DOM-SrTiO₃) were prepared and used as photocatalysts in visible light ($\lambda > 420$ nm) photocatalytic water splitting for hydrogen evolution. Through optimizing the pore size of 3DOM-SrTiO₃ materials and the loading amounts of Au and CdS, CdS/Au/3DOM-SrTiO₃(300), templated by 300 nm sized poly(methyl methacrylate) colloids, was found to exhibit a remarkably enhanced photocatalytic hydrogen evolution rate (2.74 mmol/h•g), which was 3.2 times as high as that of CdS/Au/C-SrTiO₃ catalyst based on commercial SrTiO₃. This notably enhanced photocatalytic performance was mainly attributed to the slow photon enhancement effect of 3DOM-SrTiO₃(300) material, which significantly promoted the light harvesting efficiency of ternary composite for the slow photon region of 3DOM-SrTiO₃(300) was well matched with the optical absorption band of photocatalyst. Further depositing Pt nanoparticles on CdS/Au/3DOM-SrTiO₃(300) composite as a co-catalyst, an extraordinarily high hydrogen evolution rate (up to 5.46 mmol/g•h) and apparent quantum efficiency (42.2% at 420 nm) were achieved because of the synergistic effect of efficient carrier separation, Au SPR effect, and slow photon effect. Furthermore, these ternary CdS/Au/3DOM-SrTiO₃ composite photocatalysts were very stable and could be easily recycled four times in visible light photocatalytic water splitting experiments without any loss in activity.

Keywords

Three-dimensionally ordered macroporous material; CdS/Au/3DOM-SrTiO₃; Ternary composite; Hydrogen production from water splitting; Slow photon effect.

1. Introduction

Since photocatalytic water splitting into hydrogen by TiO_2 was discovered by Fujishima and Honda in the early 1970s^[1], hydrogen production from water splitting has become one of the most promising strategies in scientific and technological research for utilizing renewable solar energy to solve the issues of energy crisis and environmental pollution^[2-5]. However, because of the low quantum yield and light harvesting efficiency of conventional photocatalysts, especially in the visible light range, it is still a huge challenge to develop a highly efficient catalyst for photocatalytic water splitting.

Perovskite strontium titanate (SrTiO_3), one of the most important *n*-type semiconductors, has been widely investigated owing to its efficient photocatalytic properties, structural flexibility, good stability and low cost^[6-12]. However, the wide band gap of SrTiO_3 (ca. 3.2 eV) makes it unsuitable to be motivated by visible light, leading to a low solar energy conversion efficiency. Combination of SrTiO_3 with narrow band-gap semiconductors would be an effective approach to address this issue^[13-15]. In this respect, cadmium sulfide (CdS) has been regarded as an ideal candidate because of its narrow band gap (2.4 eV) and more negative conduction band edge than the reduction potential of H^+ to H_2 ^[16-19]. Meanwhile, the obtained heterostructured photocatalysts were found to be able to facilitate the spatial separation of photogenerated electron-hole pairs, further improving their charge utilization efficiency^[20-22].

On the other hand, depositing noble metal, such as Au, in between two

semiconductors to form a ternary composite, could further increase their photocatalytic performance due to the facilitated transfer of photogenerated carriers^[23, 24]. Moreover, the surface plasmon resonance (SPR) of metal nanoparticles arising from the collective oscillation of electrons in the metallic nanostructure could also improve the performance of photocatalysts through hot electron transfer^[25-31]. Many researchers had attempted to fabricate the ternary composites using two semiconductors and one noble metal, such as Au/CdS/TiO₂^[23, 32-37], Au/CdS/WO₃^[38, 39], Pt/CdS/TiO₂^[40-45], and Au/CdS/ZnO^[46-48]. However, improving the light harvesting efficiency through a special nanostructure design is still an attractive research field.

In the last decade, three-dimensionally ordered macroporous (3DOM) materials with an inverse opal structure have received much attention in photocatalysis field. A series of 3DOM semiconductors including TiO₂^[49-51], WO₃^[52, 53], InVO₄^[54-56], BiVO₄^[57-59], and g-C₃N₄^[35] have been fabricated and applied in the degradation of organic pollutants and the production of hydrogen and/or oxygen from water splitting. Notably improved photocatalytic performances were achieved over these 3DOM photocatalysts because of their slow photon effect as a photonic crystal, which could significantly enhance the photon-matter interaction, and further improve the light energy conversion efficiency of semiconductor^[60-63].

Recently, we reported the 3DOM-SrTiO₃ materials with notably improved catalytic performance for hydrogen evolution via water splitting compared with solid-state SrTiO₃ under UV-Vis light irradiation^[64]. In order to further extend their

visible light absorption and develop a highly efficient visible-light-driven photocatalyst, herein, we designed and fabricated a novel form of catalysts: CdS/Au/3DOM-SrTiO₃ ternary composites. The influences of CdS/Au composite ratio and pore size of 3DOM-SrTiO₃ were investigated. An extraordinarily excellent efficiency for visible-light-driven photocatalytic hydrogen evolution can be expected over these ternary CdS/Au/3DOM-SrTiO₃ composites because of the synergistic effect of slow photon effect, efficient charge separation and hot electron transfer enhancement.

2. Experimental

2.1 Materials

Tetrabutyl titanate [Ti(OBu)₄], cadmium nitrate tetrahydrate [Cd(NO₃)₂•4H₂O], gold(III) chloride hydrate (HAuCl₄•4H₂O), and chloroplatinic acid hexahydrate (H₂PtCl₆•6H₂O) were purchased from Aladdin. Acetic acid (CH₃COOH) and methanol (CH₃OH) were acquired from Concord Technology (Tianjin) Co., Ltd. Strontium nitrate [Sr(NO₃)₂] was purchased from Tianjin Bodi Chemical Co., Ltd. Citric acid monohydrate (C₆H₈O₇•H₂O), trisodium citrate dihydrate (Na₃C₆H₅O₇•2H₂O), sodium sulfite (Na₂SO₃), and sodium sulfide hydrate (Na₂S•9H₂O) were obtained from Tianjin Guangfu Fine Chemical Research Institute. Commercial SrTiO₃ (C-SrTiO₃) was provided by Energy Chemical. All of the reagents were of analytical grade and used as received.

2.2 Characterization

The X-ray powder diffraction (XRD) patterns of the photocatalysts were

obtained on the Bruker D8 X-ray diffractometer with Cu K α radiation operating at 40 kV and 40 mA over 2θ range of 10°-90°. The JEOL JSM-7500F field-emission scanning electron microscope (SEM) was employed in order to observe the morphology of samples. The images of high-resolution transmission electron microscopy (HRTEM) were acquired using a Philips Tecnai G2 F30 instrument. Diffuse-reflectance UV-vis (DR UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrophotometer with the integral sphere in the measurement range from 200 nm to 800 nm. Photoluminescence (PL) spectra were carried out employing an Edinburgh Instrument FLS 920P fluorescence spectrophotometer. The online gas chromatography (GC) analysis in photocatalytic hydrogen evolution experiments was performed on a FL9790II gas chromatograph equipped with a thermal conductive detector (TCD) and a carbon molecular sieve column, using argon as the carrier gas. The photocurrent-time characteristic, electrochemical impedance spectroscopy (EIS) and Mott-Schottky measurement of these photocatalysts were carried out on a CHI 660D electrochemical workstation in a standardized three-electrode-configuration. The photocatalyst on a FTO glass was used as the working electrode. And a platinum plate and an Ag/AgCl electrode were served as the counter electrode and reference electrode, respectively.

2.3 Synthesis of 3DOM-SrTiO₃

The poly methyl methacrylate (PMMA) colloidal crystal templates with average diameters of 200 nm, 300 nm, and 400 nm, and the 3DOM-SrTiO₃ materials with different pore sizes were synthesized according to our previous reports^[53, 64]. More

specifically, firstly, the precursor solution was prepared as follows. 10 mL of acetic acid was added to 0.01 mol of $\text{Ti}(\text{OBU})_4$ under stirring, followed by the dropping of 10 mL of deionized water. Then, 10 mL of $\text{Sr}(\text{NO}_3)_2$ solution (1 mol/L) and 10 mL of citric acid solution (2 mol/L) were consecutively added into this mixture at room temperature and the precursor solution was obtained. Secondly, the PMMA colloidal crystal template was placed into this precursor solution. After 2 h, the impregnated colloidal crystal template was filtrated to remove the redundant precursor solution. The sample was dried in a vacuum oven at 50 °C for 12 h and then calcined in air using tube furnace at 650 °C for 4 h. According to the diameters of PMMA microspheres (200, 300, and 400 nm), the as-synthesized 3DOM-SrTiO₃ materials were named as 3DOM-SrTiO₃(200), 3DOM-SrTiO₃(300) and 3DOM-SrTiO₃(400), respectively.

2.4 Synthesis of ternary CdS/Au/3DOM-SrTiO₃ composites

The synthesis procedure of ternary CdS/Au/3DOM-SrTiO₃ composites is shown in Scheme 1.

Au nanoparticles were decorated on the surface of 3DOM-SrTiO₃ through a chemical deposition method, and the typical synthesis procedure was described as follows. 0.15 g of 3DOM-SrTiO₃ was dispersed into 75 mL of deionized water, and a certain amount of H₂AuCl₄ solution (10 g/L) was added into this mixture at 110 °C under vigorous stirring for 0.5 h. Then, 1.5 mL of trisodium citrate aqueous solution (0.034 mol/L) was added to the flask twice every 15 min. After stirring for 1 h, the mixture was cooled down to room temperature. The purple Au/3DOM-SrTiO₃ solid

sample was collected by centrifugation and washed with deionized water for once. The nominal Au loading amount in Au/3DOM-SrTiO₃ samples was 0.5%, 1.0%, 1.5%, or 2.0% in weight.

CdS/Au/3DOM-SrTiO₃ composites were fabricated through a deposition-precipitation method. Au/3DOM-SrTiO₃ was dispersed into 12 mL of Cd(NO₃)₂•4H₂O aqueous solution under vigorous stirring for 0.5 h, and then Na₂S aqueous solution was dropwise added. After stirring for 0.5 h, the obtained precipitate was collected by centrifugation, washed with deionized water for several times, and dried at 50 °C for 12 h. The obtained samples were marked as CdS/Au/3DOM-SrTiO₃(200), CdS/Au/3DOM-SrTiO₃(300), and CdS/Au/3DOM-SrTiO₃(400). The nominal CdS loading amount in CdS/Au/3DOM-SrTiO₃ samples was 5%, 15%, or 20% in weight.

Because Au nanoparticles were deposited on the surface of 3DOM-SrTiO₃ through trisodium citrate reduction, the obtained Au nanoparticles were covered by citrate ions. Then these citrate ions could prior capture Cd²⁺ and further lead to the coverage of CdS on the surface of Au nanoparticles. This process has been reported by Zhao et al.^[35].

For comparison, commercial SrTiO₃ was used to prepare the ternary composite under the same synthesis procedure with CdS/Au/3DOM-SrTiO₃. And the obtained photocatalyst was marked as CdS/Au/C-SrTiO₃.

2.5 Photocatalytic hydrogen evolution experiments

The photocatalytic performance of as-prepared composite photocatalysts was

determined by the hydrogen evolution experiments at room temperature under visible light irradiation. In a typical process, 0.1 g of photocatalyst and 100 mL of water containing Na₂SO₃ (0.10 M) and Na₂S (0.10 M) as the sacrificial reagents were added in a 150 mL quartz flask under stirring. After the reaction system was thoroughly degassed, the flask was irradiated by a 300W Xe lamp (CEL-HXUV300) with a UV cut-off filter ($\lambda > 420$ nm). The generated hydrogen was monitored by online GC.

3. Results and Discussion

3.1. Characterization of as-synthesized CdS/Au/3DOM-SrTiO₃ composites

The as-synthesized CdS/Au/3DOM-SrTiO₃ photocatalysts were characterized by XRD, SEM, TEM, and DR UV-Vis.

The XRD patterns of CdS/Au/3DOM-SrTiO₃ and CdS/Au/C-SrTiO₃ are shown in Figure 1. The characteristic diffraction peaks of 3DOM-SrTiO₃ for three CdS/Au/3DOM-SrTiO₃ samples can be well indexed to the (100), (110), (111), (200), (211), (220) and (310) crystal planes of pure cubic perovskite phase (JCPDS No. 35-0734). Except the diffraction peaks of 3DOM-SrTiO₃, the weak and wide diffraction peak at about 26.5° (marked with ◆) on the patterns of CdS/Au/3DOM-SrTiO₃ could be resulted from overlapped diffraction peaks of the (100), (002), and (101) planes of the greenockite structured CdS, suggesting the presence of CdS. The diffraction peak of Au (111) at 38.1° is also observed from Figure 1, corroborating the successful deposition of Au nanoparticles on the surface of 3DOM-SrTiO₃. In addition, the XRD peak intensities of CdS/Au/3DOM-SrTiO₃ photocatalysts are modestly weaker than those of CdS/Au/C-SrTiO₃ indicating a

lower crystallinity of 3DOM-SrTiO₃.

The morphology of the as-synthesized 3DOM-SrTiO₃ and ternary CdS/Au/3DOM-SrTiO₃ composites were visualized through SEM, and the related images are shown in Figure 2. Clearly, the well-ordered inverse opal structure can be observed for all the 3DOM-SrTiO₃ materials with different pore sizes, and the average pore diameters of 3DOM-SrTiO₃(200), 3DOM-SrTiO₃(300), and 3DOM-SrTiO₃(400) can be determined as 120 nm, 185 nm, and 245 nm, respectively, from Figure 2(a) to 2(c). After decorating CdS/Au nanoparticles, the highly ordered periodic 3DOM structures were still maintained, and the CdS/Au nanoparticles were mainly dispersed into the macropores of 3DOM-SrTiO₃ as seen in Figure 2(e) to 2(g). Furthermore, it is found from Figure 2(d) and 2(h) that the commercial SrTiO₃ is made up of micro-sized particles with an average size of 500 nm, and the CdS/Au nanoparticles are mainly accumulated on the surface of SrTiO₃ in the CdS/Au/C-SrTiO₃ composite. SEM-EDS elemental mapping images of these CdS/Au/3DOM-SrTiO₃ composites are shown in Figure S1 of Supplementary Materials.

The TEM and HRTEM images, and EDS elemental mapping of the CdS/Au/3DOM-SrTiO₃(300) composite are depicted in Figure 3. The inverse opal structure of 3DOM-SrTiO₃(300) can also be clearly observed in the TEM image in Figure 3(a). The average size of the Au nanoparticles is ~20 nm. Moreover, as shown in Figure 3(b) and 3(c), the existence of Au and CdS in the ternary composite is directly confirmed through the measure lattice spacing corresponding to the CdS(002) and Au(111) planes. In addition, the EDS elemental mapping in a selected area

indicated that Au nanoparticles were covered by CdS, which further confirmed the heterojunction structure of ternary CdS/Au/3DOM-SrTiO₃(300) composite. More HRTEM images of CdS/Au/3DOM-SrTiO₃ composites are given in Figure S2 of Supplementary Materials.

Figure 4 shows the DR UV-Vis spectra of 3DOM-SrTiO₃(300), CdS/3DOM-SrTiO₃(300), Au/3DOM-SrTiO₃(300) and CdS/Au/3DOM-SrTiO₃(300) samples. The optical absorption edge of 3DOM-SrTiO₃(300) locates at around 380 nm. Au/3DOM-SrTiO₃(300) exhibits a broad absorption peak at 550 nm, corresponding to the SPR absorption of Au nanoparticles. Because of the combination of CdS, both CdS/3DOM-SrTiO₃(300) and CdS/Au/3DOM-SrTiO₃(300) show a strong response in the range of 400~600 nm. It is worthy to note from Figure 4 that the absorption edge of the ternary CdS/Au/3DOM-SrTiO₃(300) composite has an obvious redshift compared with other specimens, which can be attributed to the synergistic influence of CdS and Au.

3.2. Effect of Au and CdS loading amount on the efficiency of photocatalytic hydrogen evolution

In order to optimize the constituent of the ternary CdS/Au/3DOM-SrTiO₃ composites, the influence of Au and CdS loading amount on the photocatalytic efficiency of CdS/Au/3DOM-SrTiO₃ has been investigated. A series of CdS/Au/3DOM-SrTiO₃(300) composites with different mass percentages of Au (0.5%, 1.0%, 1.5%, and 2.0%) and CdS (5%, 15% and 20%) were synthesized and used in the visible light photocatalytic water splitting. It can be found from Figure 5, the

hydrogen evolution rate over CdS/Au/3DOM-SrTiO₃(300) obviously increases as the Au loading amount increases from 0.5 wt% to 1.0 wt%, suggesting the more efficient transfer of photogenerated carrier with increasing the Au loading amount. However, with further increase of the Au loading amount from 1.0 wt% to 2.0 wt%, the hydrogen evolution rate of CdS/Au/3DOM-SrTiO₃(300) catalyst slightly decreases, which could be attributed to the increased particle size of Au nanoparticles. In addition, as shown in Figure 5, the highest hydrogen evolution rate could be obtained when the loading amount of CdS is 15 wt% in CdS/Au/3DOM-SrTiO₃(300). Consequently, in this work, the optimized loading amounts of CdS and Au are found to be 15 wt% and 1.0 wt%, respectively.

3.3. The slow photon effect on the efficiency of photocatalytic hydrogen evolution

To study the influence of inverse opal structure on the photocatalytic activity of ternary CdS/Au/3DOM-SrTiO₃ composites, the specimens with different pore sizes and CdS/Au/C-SrTiO₃ were evaluated in the visible light photocatalytic water splitting for hydrogen evolution and the results are shown in Figure 6(a). It can be clearly observed that all the CdS/Au/3DOM-SrTiO₃ catalysts exhibit notably higher photocatalytic hydrogen evolution rates than CdS/Au/C-SrTiO₃. It indicates that the inverse opal structure of 3DOM-SrTiO₃ can remarkably enhance the photocatalytic activity of these ternary composites, which can be mainly attributed to the following reasons. Firstly, the three dimensionally interconnected pore channels can facilitate the diffusion and mass transfer of aqueous solution containing S²⁻ and SO₃²⁻, which can eliminate the photogenerated holes. Secondly, the skeletal wall thickness of

3DOM-SrTiO₃ is nano-sized, which can shorten the diffusion length of photogenerated carriers so as to prevent carriers' recombination. Finally, and most importantly, the 3DOM-SrTiO₃ materials possess an amazing slow photon effect, which increases the interaction between photons and the catalyst, leading to the enhancement of light-energy conversion efficiency.

As described in Figure 6(a), among these ternary CdS/Au/3DOM-SrTiO₃ composites, CdS/Au/3DOM-SrTiO₃(300) exhibits the highest hydrogen evolution rate, up to 2.74 mmol/g•h, which is 3.2 times as high as that of CdS/Au/C-SrTiO₃ catalyst. Meanwhile, the hydrogen evolution rates of CdS/Au/3DOM-SrTiO₃(200) and CdS/Au/3DOM-SrTiO₃(400) are 1.76 mmol/g•h and 2.14 mmol/g•h, respectively.

A photocurrent generation measurement for CdS/Au/3DOM-SrTiO₃ and CdS/Au/C-SrTiO₃ catalysts was performed under visible light irradiation, and the results are shown in Figure 6(b). All the samples show strong sensitivity to visible light irradiation and there is a dramatic rise for the photocurrent from the off illumination to the on illumination. In addition, the photocurrent response of CdS/Au/3DOM-SrTiO₃ is remarkably higher than that of CdS/Au/C-SrTiO₃, which indicates the notably enhanced separation efficiency of photogenerated carriers over the CdS/Au/3DOM-SrTiO₃ composites. Among these ternary CdS/Au/3DOM-SrTiO₃ composites, CdS/Au/3DOM-SrTiO₃(300) exhibits the highest photocurrent response, which is well consistent with the results of photocatalytic hydrogen evolution experiments.

In order to concretely analyze the influence of slow photon effect in the

CdS/Au/3DOM-SrTiO₃ catalysts, the stop-bands of 3DOM-SrTiO₃ materials were calculated using the modified Bragg's law as described in Eq.(1)^[57, 64, 65]. In this equation, λ is the wavelength of the photonic stop-band, D is the pore size derived from the inverse opals, n_{SrTiO_3} and n_{Water} are the refractive index of SrTiO₃ and water, respectively, f is the SrTiO₃ phase volume percentage, which is generally given as 0.26, θ is the incident angle of light, which is in the range of 0-90° due to a varied and wide range of the incident angle under light irradiation for the photocatalysts in the reaction solution. Therefore the calculated stop-band of 3DOM-SrTiO₃(300) ($D=185$ nm) is in the range of 407~507 nm, while for 3DOM-SrTiO₃(200) ($D=120$ nm) and 3DOM-SrTiO₃(400) ($D=245$ nm), the stop-band ranges are about 264~329 nm and 533~663 nm, respectively.

$$\lambda = 2\sqrt{\frac{2}{3}}D\sqrt{n_{\text{SrTiO}_3}^2 f + n_{\text{water}}^2 (1-f) - \sin^2 \theta} \quad \text{Eq. (1)}$$

According to the related literatures^[34, 66, 67], the group velocity of light could dramatically reduce at the edges of stop-band and result in the appearance of slow photons. Especially, the red-edge of stop-band for inverse opals is thought to be more important in photocatalysis because of the relative higher refractive index of skeletal material. In the present work, because of the varied incident angle in the range of 0-90°, the stop-bands of these 3DOM-SrTiO₃ materials were variable in a wide range^[68, 69]. It would result in a wide slow photon region at the red-edges of stop-band, and this slow photon region was partially overlapped with its stop-band. Figure 7(a) depicts the UV-Vis spectra of these CdS/Au/3DOM-SrTiO₃ composites. It can be found that the CdS/Au/3DOM-SrTiO₃ composites exhibit a strong absorption at the

wavelength from 400 to 500 nm, which was exactly overlapped with the slow photon region of 3DOM-SrTiO₃(300) material. However, the slow photon region of 3DOM-SrTiO₃(200) is in the range of ultraviolet light and the slow photon region of 3DOM-SrTiO₃(400) oversteps the absorption region of these CdS/Au/3DOM-SrTiO₃ composites.

In order to further prove the influence of slow photon effect on the hydrogen evolution efficiency upon CdS/Au/3DOM-SrTiO₃ catalysts, the controlled experiments over these composites were carried out under the certain wavelength light irradiation, including 435 nm, 475 nm, 550 nm, and 578 nm. It can be found from Figure 7(b) that CdS/Au/3DOM-SrTiO₃(300) exhibits the highest photocatalytic hydrogen evolution rate under irradiation of 435 nm and 475 nm light. The result can be attributed to the proper slow photon region of 3DOM-SrTiO₃(300), which could significantly increase the photon-matter interaction and further improve the photocatalytic performance of CdS/Au/3DOM-SrTiO₃(300). When the water splitting experiments were carried out under the irradiation of 550 nm or 578 nm light, CdS/Au/3DOM-SrTiO₃(400) exhibits slightly higher hydrogen evolution rates compared with the other two catalysts because of the overlap between incident light wavelength and slow photon region of 3DOM-SrTiO₃(400). It is a direct experimental evidence for the slow light enhancement effect on these ternary CdS/Au/3DOM-SrTiO₃ composites and also directly proves the conclusion that the overlap of slow photon region with the electronic absorption band would significantly improve the photocatalytic performance of CdS/Au/3DOM-SrTiO₃ composites.

3.4. The roles of Au nanoparticles in ternary CdS/Au/3DOM-SrTiO₃ composites

Besides the slow photon effect of 3DOM-SrTiO₃ materials, the efficient separation of photogenerated carriers and the SPR effect of Au nanoparticles in these ternary CdS/Au/3DOM-SrTiO₃ photocatalysts are also important factors in enhancing the photocatalytic performance. In order to comprehend the roles of Au in ternary composites, 3DOM-SrTiO₃(300) and binary composites, including Au/3DOM-SrTiO₃(300) and CdS/3DOM-SrTiO₃(300), were used as photocatalysts in water splitting experiments. In this experiment, CdS/3DOM-SrTiO₃(300) was prepared through a deposition-precipitation method similar with that of CdS/Au/3DOM-SrTiO₃(300), except that Au/3DOM-SrTiO₃(300) was replaced by 3DOM-SrTiO₃(300).

It is evident from Figure 8(a) that 3DOM-SrTiO₃(300) is inactive in this visible-light-driven photocatalytic water splitting experiment due to its wide band gap. While Au/3DOM-SrTiO₃(300) exhibits a very slight activity (1.86 μmol/g•h), which could be assigned to the SPR effect of Au nanoparticles^[23, 30, 70]. As for CdS/3DOM-SrTiO₃(300), a considerable hydrogen evolution rate (0.44 mmol/g•h) is obtained under visible light irradiation because of the heterojunction structure between CdS and 3DOM-SrTiO₃(300) that extended the light absorption of 3DOM-SrTiO₃(300) and promoted the carrier separation efficiency. Compared with the three former photocatalysts, ternary CdS/Au/3DOM-SrTiO₃(300) composite furnished the highest photocatalytic hydrogen evolution rate (2.74 mmol/g•h). This excellent performance of CdS/Au/3DOM-SrTiO₃(300) could be attributed to the

synergistic effect of two factors. On the one hand, the SPR effect of Au nanoparticles could improve the performance of CdS/Au/3DOM-SrTiO₃ through hot electron transfer^[25-30]. On the other hand, the presence of Au nanoparticles between CdS and 3DOM-SrTiO₃ could obviously facilitate the transfer and separation of photogenerated carriers.

In order to verify these two roles of Au nanoparticles in ternary CdS/Au/3DOM-SrTiO₃ composites, a series of controlled experiments and characterizations were carried out in present work. Firstly, the SPR effect of Au nanoparticles can be observed from the DR UV-Vis characterization of obtained photocatalysts (as shown in Figure 4). The obvious absorption peaks centered at 550 nm in the DR UV-Vis spectra of Au/3DOM-SrTiO₃(300) and CdS/Au/3DOM-SrTiO₃(300) can be associated with the SPR effect of Au nanoparticles. Taking into account of the absorption edge of binary CdS/3DOM-SrTiO₃(300) composite located at 550 nm, a series of controlled water splitting experiments over binary CdS/3DOM-SrTiO₃(300) and ternary CdS/Au/3DOM-SrTiO₃(300) composites under the certain wavelength (including 435, 550, and 578 nm) light irradiation were carried out to investigate the SPR effect of Au nanoparticles. It can be found from Figure 8(b), the hydrogen evolution rate of CdS/Au/3DOM-SrTiO₃(300) was 2 times as high as that of CdS/3DOM-SrTiO₃(300) when the radiation wavelength was 435 nm. However, when the radiation wavelength was 550 nm, the hydrogen evolution rate of CdS/Au/3DOM-SrTiO₃(300) was 20 times higher than that of CdS/3DOM-SrTiO₃(300). Further increasing the radiation

wavelength to 578 nm, the hydrogen evolution efficiency ratio of CdS/Au/3DOM-SrTiO₃(300) to CdS/3DOM-SrTiO₃(300) reached up to 46 times. The notably enhanced photocatalytic performance of CdS/Au/3DOM-SrTiO₃(300) under the light irradiation with wavelength of 550 and 578 nm can be derived from the contribution of Au SPR effect in ternary CdS/Au/3DOM-SrTiO₃ composites.

Secondly, the facilitated charge transfer and separation derived from Au nanoparticles can be confirmed through the PL and EIS measurements of 3DOM-SrTiO₃(300), CdS/3DOM-SrTiO₃(300), and CdS/Au/3DOM-SrTiO₃(300) materials. Figure 9(a) depicts the PL spectra of these samples. It can be seen that 3DOM-SrTiO₃(300) exhibited the highest intensity in the PL emission spectrum. After loading CdS, the intensity of PL emission spectrum arising from the recombination of free carriers obviously decreased, which indicated that the separation efficiency of electron-hole pairs was enhanced over the binary CdS/3DOM-SrTiO₃(300) composite. When Au nanoparticles were introduced between CdS and 3DOM-SrTiO₃(300) to form the ternary CdS/Au/3DOM-SrTiO₃(300) composite, the PL emission intensity decreased to the lowest level compared with 3DOM-SrTiO₃(300) and CdS/3DOM-SrTiO₃(300), implying the notably improved separation efficiency of photogenerated electron-hole pairs in ternary composite.

To further verify the efficient charge transfer in ternary composite, the EIS characterization of 3DOM-SrTiO₃(300), CdS/3DOM-SrTiO₃(300), and CdS/Au/3DOM-SrTiO₃(300) were carried out and the results are shown in Figure 9(b). The EIS Nyquist plot of CdS/Au/3DOM-SrTiO₃(300) exhibited the smallest diameter

of semicircle compared with 3DOM-SrTiO₃(300) and CdS/3DOM-SrTiO₃(300), suggesting that CdS/Au/3DOM-SrTiO₃(300) provided more efficient charge transfer across the interface of the electrode and the electrolyte. The results of PL and EIS characterization indicated that the presence of Au nanoparticles in ternary CdS/Au/3DOM-SrTiO₃(300) composite can significantly improve the transfer and separation of photogenerated carriers.

3.5. The photogenerated carriers transfer mechanism of ternary CdS/Au/3DOM-SrTiO₃ photocatalysts

In order to investigate the transfer process of photogenerated carriers for ternary CdS/Au/3DOM-SrTiO₃(300) composite under visible light irradiation, two Pt nanoparticles decorated CdS/Au/3DOM-SrTiO₃(300) samples were prepared according to the reported method^[31]. It should be noted that the loading position of Pt nanoparticle in these two samples was different. Scheme 2 depicts the synthesis procedure of these Pt deposited CdS/Au/3DOM-SrTiO₃(300) photocatalysts. For the first sample, marked as CdS/Au/3DOM-SrTiO₃(300)/Pt, Pt nanoparticles (0.7wt%) were photodeposited on the surface of 3DOM-SrTiO₃(300) using methanol as the sacrificial agent under UV light irradiation before the combination of Au and CdS. For the second sample, named as Pt/CdS/Au/3DOM-SrTiO₃(300), Pt nanoparticles (0.7wt%) were in situ photodeposited on the surface of CdS via a UV-Vis light driven Z-scheme process over CdS/Au/3DOM-SrTiO₃(300) photocatalyst^[33, 34, 38]. As seen in Figure 10, the decoration of Pt nanoparticles can significantly increase the hydrogen evolution rate of the CdS/Au/3DOM-SrTiO₃(300) composite. Especially by using the

CdS/Au/3DOM-SrTiO₃(300)/Pt catalysts, an extraordinarily high hydrogen evolution rate was achieved (up to 5.46 mmol/g•h) in visible light photocatalytic water splitting. The apparent quantum efficiency (AQE) value of CdS/Au/3DOM-SrTiO₃(300)/Pt composite for hydrogen evolution was calculated by the following equation (2) under 420 nm wavelength light irradiation, and the calculated AQE_{420nm} value was 42.2%. Compared with the ever reported similar catalysts based on SrTiO₃^[31, 71-80], this is a remarkably enhanced hydrogen evolution efficiency under the similar visible-light-driven water splitting conditions (the detailed comparison was described in Supplementary Materials).

$$\text{AQE} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \quad \text{Eq. (2)}$$

In addition, CdS/Au/3DOM-SrTiO₃(300)/Pt exhibited higher hydrogen evolution rate compared with Pt/CdS/Au/3DOM-SrTiO₃(300) (5.46 vs. 4.72 mmol/g•h). It has been well known that Pt nanoparticles, as a co-catalyst, can provide trapping sites for the photogenerated electrons. The higher activity of CdS/Au/3DOM-SrTiO₃(300)/Pt implies that the photogenerated electrons might move from CdS to 3DOM-SrTiO₃(300) by a cascade of energy states. In other words, more active sites for reducing H⁺ to H₂ are generated on the surface of 3DOM-SrTiO₃(300) instead of CdS. Therefore, it is logical to deduce that a favorable electron transfer pathway is CdS→Au→3DOM-SrTiO₃(300).

According to the above results, a graphic mechanism for the photocatalytic hydrogen generation process over the ternary CdS/Au/3DOM-SrTiO₃ composites under visible light irradiation is illustrated in Figure 11. The redox potential of

conduction bands (CB) and valence bands (VB) of as-synthesized 3DOM-SrTiO₃(300) and CdS semiconductor materials were detected through Mott-Schottky measurement as described in Figure S3 of Supplementary Materials. When the CdS/Au/3DOM-SrTiO₃ composites were irradiated under visible light, the electrons and holes were generated on the CB and VB of CdS, respectively. Because of the more negative CB redox potential of CdS, the photogenerated electrons could transfer from the CB of CdS to that of 3DOM-SrTiO₃ through the conducting of Au nanoparticles. At the same time, the plasmon-induced electrons in Au nanoparticles were generated under the visible light irradiation. The plasmon-induced hot electrons migrate to the interface between Au and 3DOM-SrTiO₃, and then also transfer to the CB of 3DOM-SrTiO₃. The photogenerated electrons in the CB of 3DOM-SrTiO₃ reacted with H⁺ in water to produce H₂, and the photogenerated holes existed in the VB of CdS can oxidize the S²⁻/SO₃²⁻ ions to S₂²⁻/SO₄²⁻.

3.6. Photocatalytic stability of the ternary CdS/Au/3DOM-SrTiO₃ composites

The stability of the as-synthesized ternary CdS/Au/3DOM-SrTiO₃ photocatalysts was evaluated in a cycling visible light water splitting experiment using CdS/Au/3DOM-SrTiO₃(300) as a model catalyst and Na₂S/Na₂SO₃ as scavengers. Obviously, CdS/Au/3DOM-SrTiO₃(300) exhibits good stability in visible-light-driven water splitting hydrogen evolution experiments (Figure 12). At the fourth cycling experiment, the hydrogen evolution rate still remained more than 2.65 mmol/g•h. The used CdS/Au/3DOM-SrTiO₃(300) catalyst after 4th recycle were characterized through XRD and SEM. The results are shown in Figure S4 and Figure

S5 of Supplementary Materials. It can be found that the 3DOM structure and the crystallinity of used CdS/Au/3DOM-SrTiO₃(300) catalyst were well maintained after 4th recycle.

4 Conclusions

In summary, a series of promising ternary composite photocatalysts with inverse opal structure (CdS/Au/3DOM-SrTiO₃) had been successfully fabricated and well demonstrated by the characterization of XRD, SEM, TEM, DR UV-Vis, and photoelectrochemical measurement. These ternary CdS/Au/3DOM-SrTiO₃ composites exhibited excellent performance in visible light photocatalytic water splitting for hydrogen evolution. Because of the synergistic enhancement of slow photon effect, efficient charge separation, and Au SPR effect, CdS/Au/3DOM-SrTiO₃(300) exhibited a notably enhanced hydrogen evolution rate (2.74 mmol/g•h) under visible light irradiation. With further deposition of Pt nanoparticles as co-catalyst, an extraordinarily high hydrogen evolution rate of up to 5.46 mmol/g•h was achieved. Apart from these, the charge transfer mechanism in the ternary CdS/Au/3DOM-SrTiO₃ composites had been proposed in the present work. Moreover, these CdS/Au/3DOM-SrTiO₃ photocatalysts were found to be stable and could be recycled for four times without obvious loss in activity.

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Figure 1. Powder XRD patterns of (a) CdS/Au/C-SrTiO₃, (b) CdS/Au/3DOM-SrTiO₃(200), (c) CdS/Au/3DOM-SrTiO₃(300), and (d) CdS/Au/3DOM-SrTiO₃(400).

Figure 2. SEM micrographs of (a) 3DOM-SrTiO₃(200), (b) 3DOM-SrTiO₃(300), (c) 3DOM-SrTiO₃(400), (d) C-SrTiO₃, (e) CdS/Au/3DOM-SrTiO₃(200), (f) CdS/Au/3DOM-SrTiO₃(300), (g) CdS/Au/3DOM-SrTiO₃(400), and (h) CdS/Au/C-SrTiO₃.

Figure 3. TEM image (a), HRTEM images (b, c) and HAADF-STEM-EDS elemental mapping (d) of CdS/Au/3DOM-SrTiO₃(300).

Figure 4. DR UV-vis spectra of CdS/Au/3DOM-SrTiO₃(300), CdS/3DOM-SrTiO₃(300), Au/3DOM-SrTiO₃(300), and 3DOM-SrTiO₃(300).

Figure 5. The efficiencies of hydrogen evolution over CdS/Au/3DOM-SrTiO₃(300) with different Au and CdS loading amounts under visible light irradiation ($\lambda > 420$ nm).

Figure 6. The efficiencies of hydrogen evolution (a) and photocurrent-time (I-t) curves (b) over the CdS/Au/C-SrTiO₃ and CdS/Au/3DOM-SrTiO₃ composites with different pore sizes.

Figure 7. (a) DR UV-Vis spectra of CdS/Au/3DOM-SrTiO₃ composites. (b) The efficiencies of hydrogen evolution over CdS/Au/3DOM-SrTiO₃ under the certain wavelength light irradiation.

Figure 8. The efficiencies of hydrogen evolution over (a) unary, binary, and ternary photocatalysts based on 3DOM-SrTiO₃(300) and (b) CdS/3DOM-SrTiO₃(300) and

CdS/Au/3DOM-SrTiO₃(300) under the certain wavelength light irradiation.

Figure 9. (a) PL spectra and (b) EIS Nyquist plots of 3DOM-SrTiO₃(300), CdS/3DOM-SrTiO₃(300), and CdS/Au/3DOM-SrTiO₃(300).

Figure 10. The efficiencies of hydrogen evolution over Pt decorated CdS/Au/3DOM-SrTiO₃(300) composites and the Pt free composite as a reference.

Figure 11. Illustration of photogenerated carrier transfer mechanism for CdS/Au/3DOM-SrTiO₃ catalyst under visible light irradiation.

Figure 12. Cycling tests of CdS/Au/3DOM-SrTiO₃(300) for visible light photocatalytic hydrogen evolution from water splitting.

Scheme 1. The synthesis procedure of ternary CdS/Au/3DOM-SrTiO₃ composites.

Scheme 2. The synthesis procedure of Pt deposited CdS/Au/3DOM-SrTiO₃(300) photocatalysts.

Figure 1.

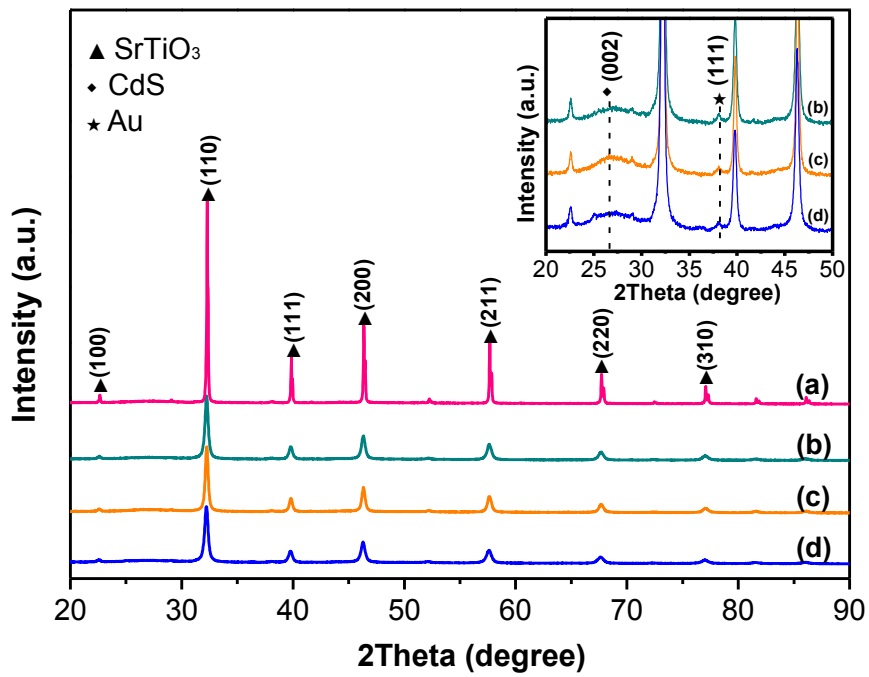


Figure 2.

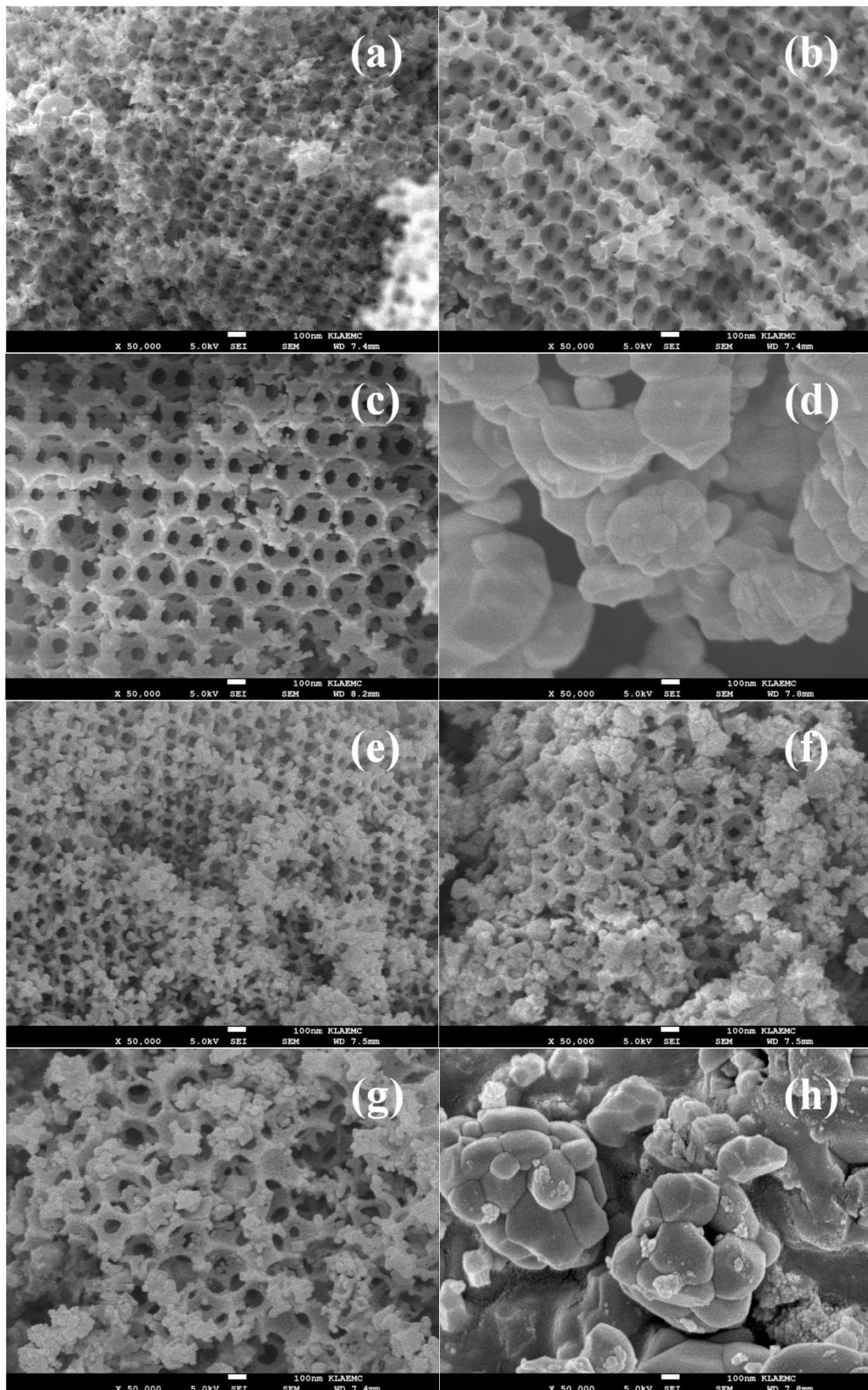


Figure 3.

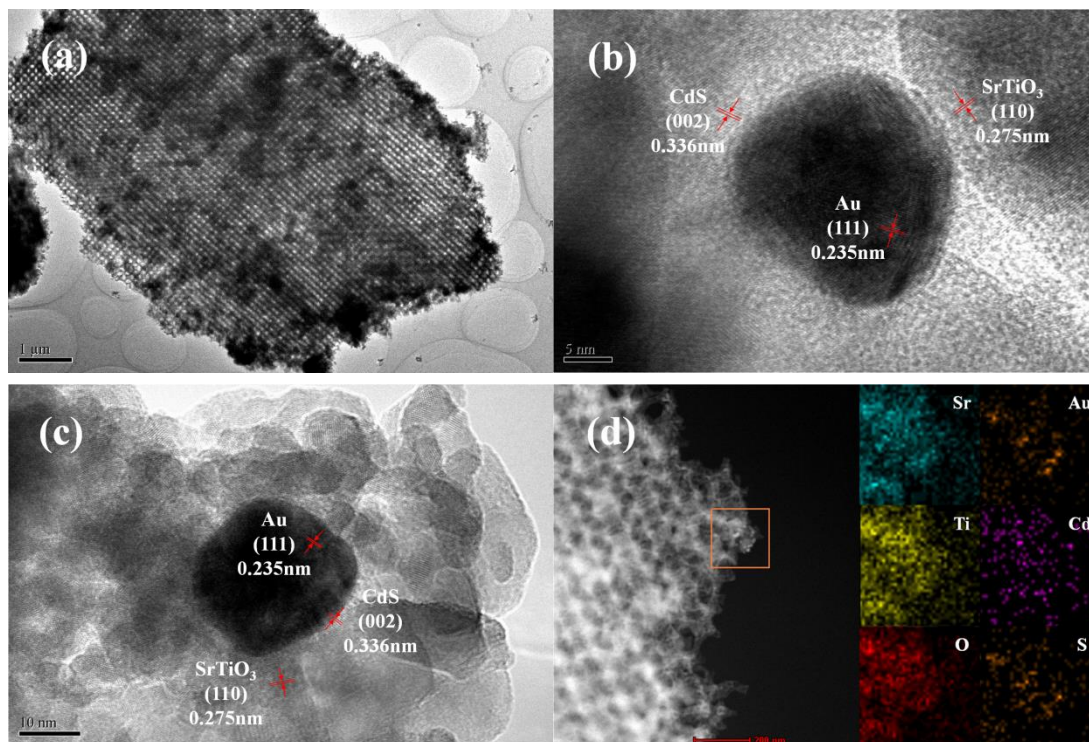


Figure 4.

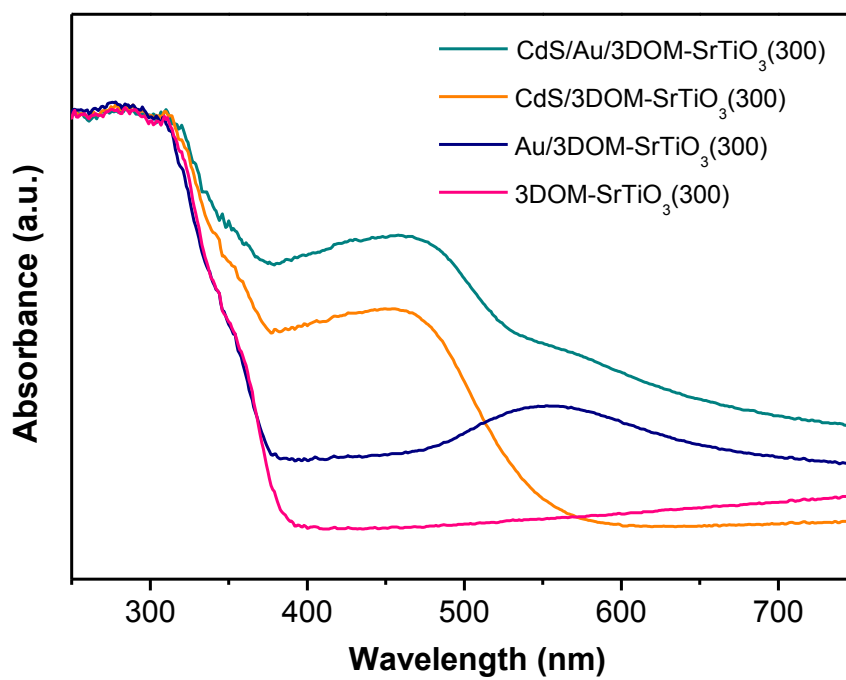


Figure 5.

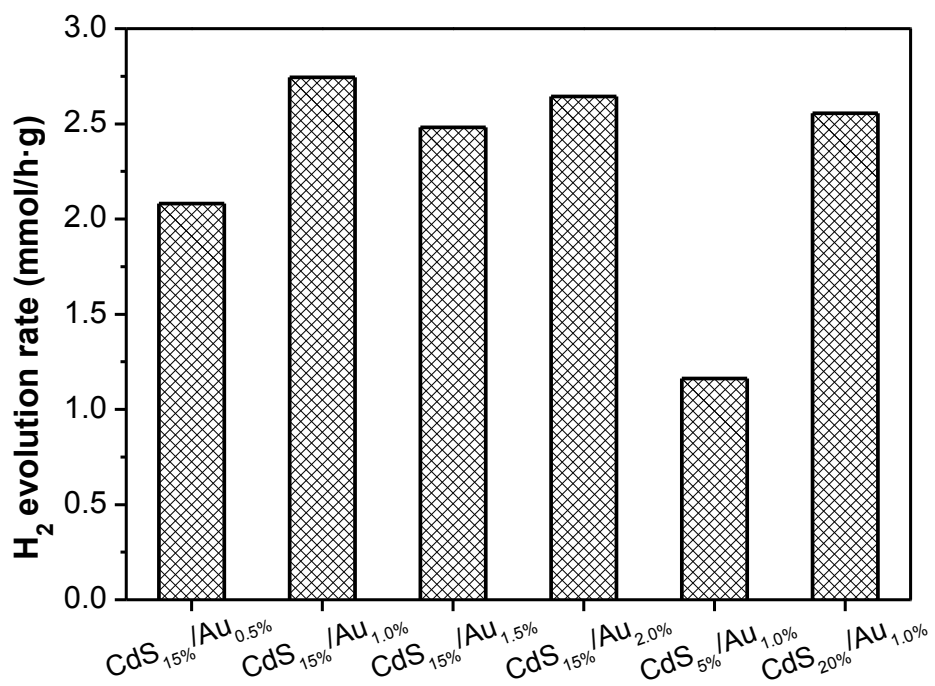


Figure 6.

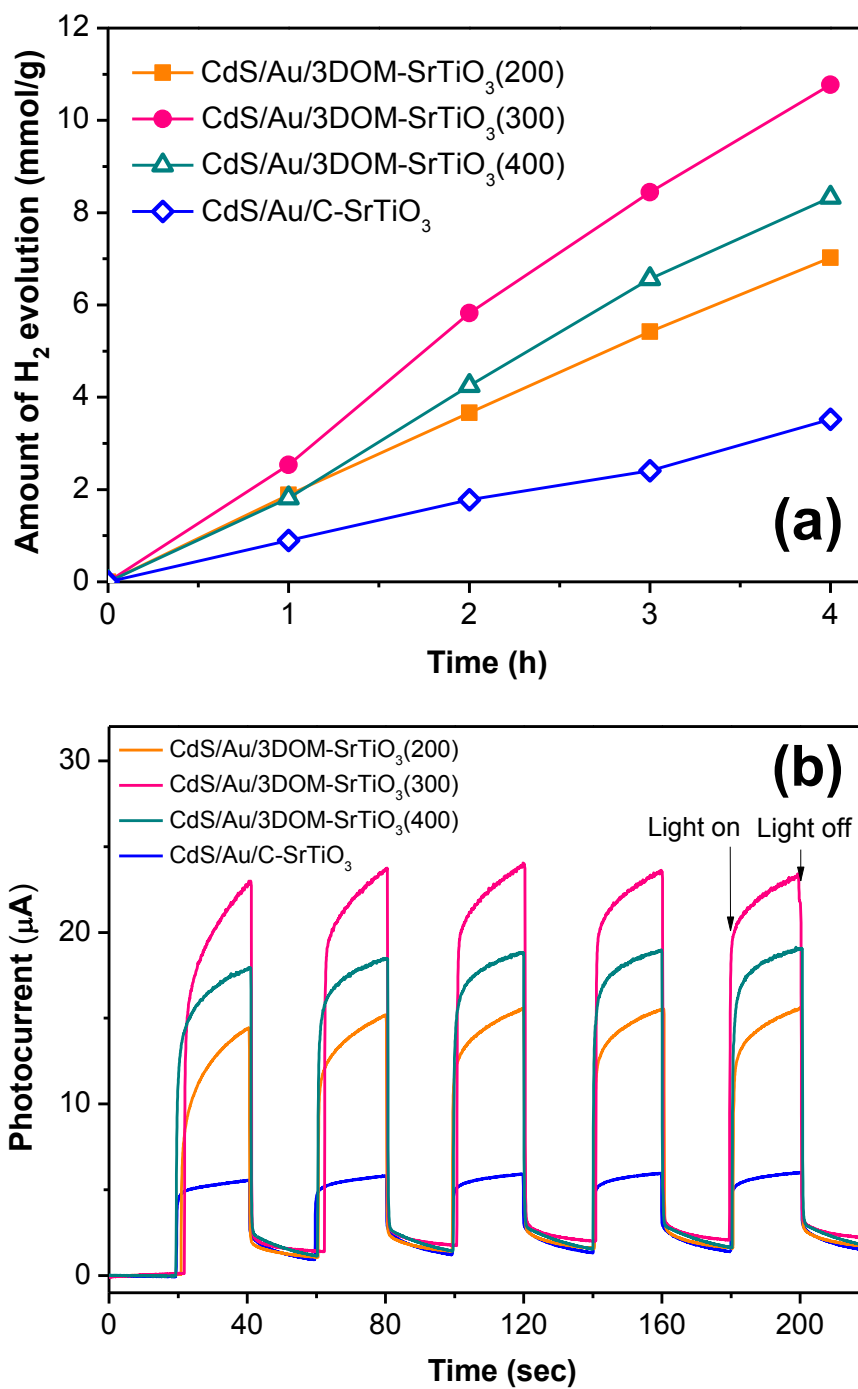


Figure 7.

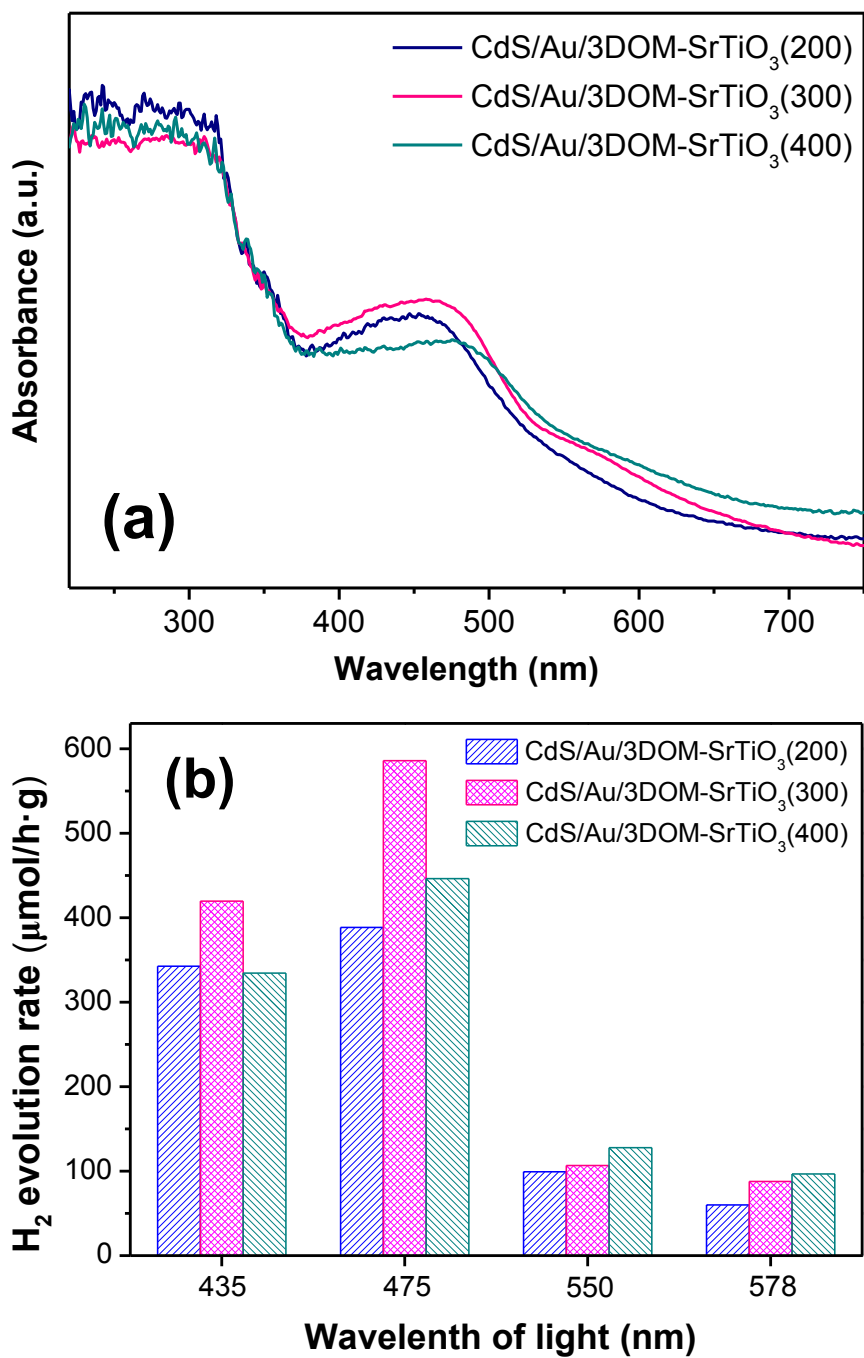


Figure 8.

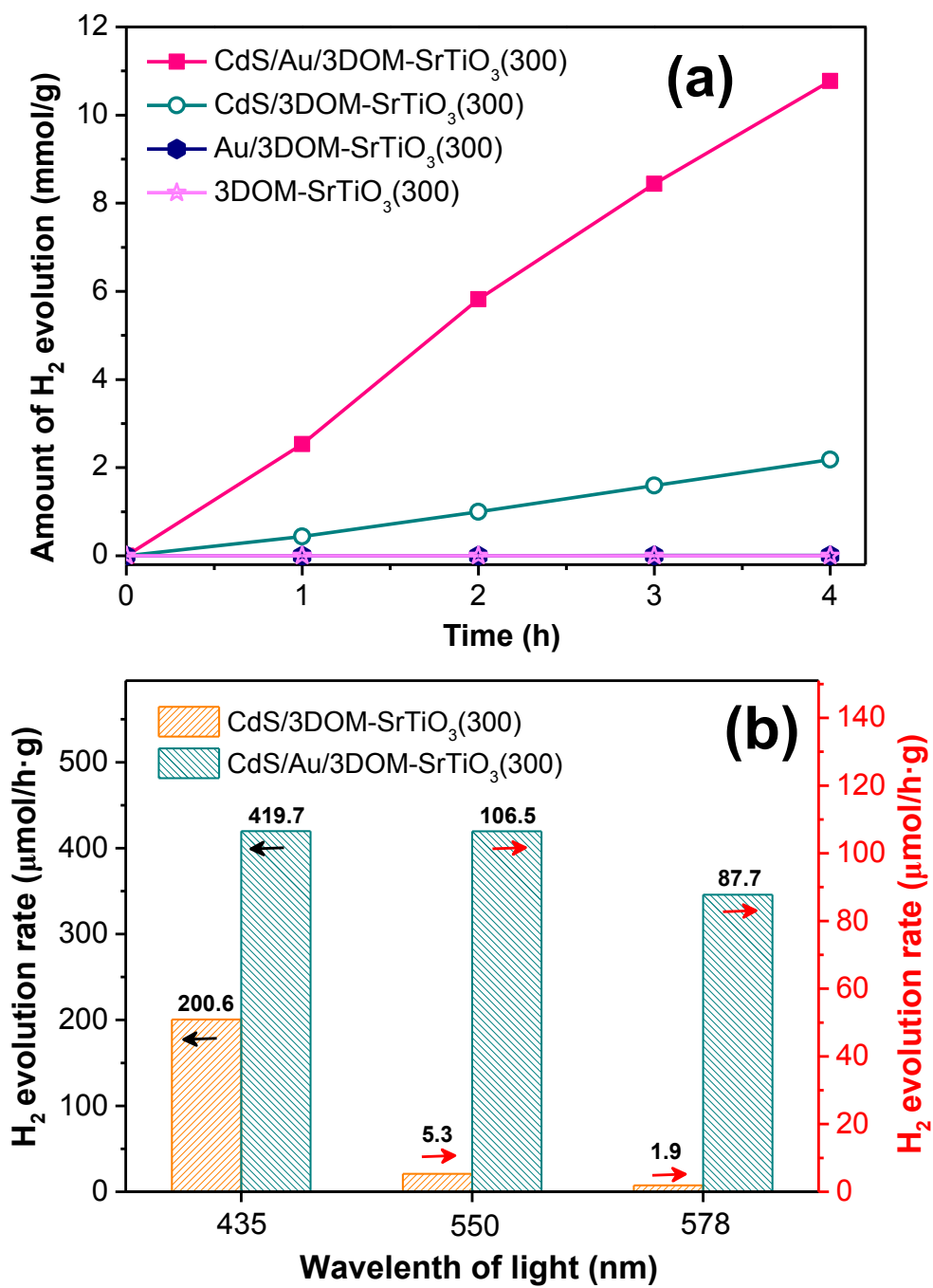


Figure 9.

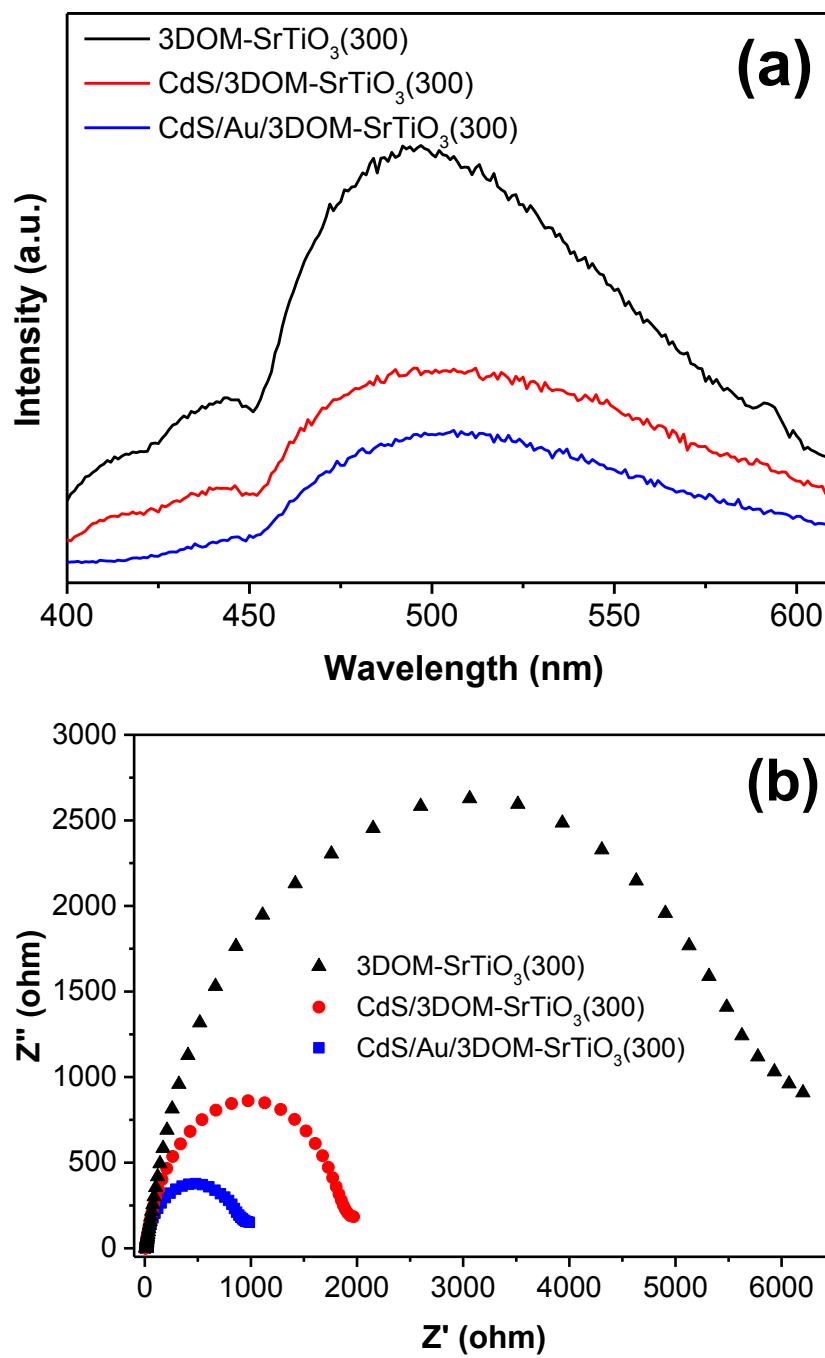


Figure 10.

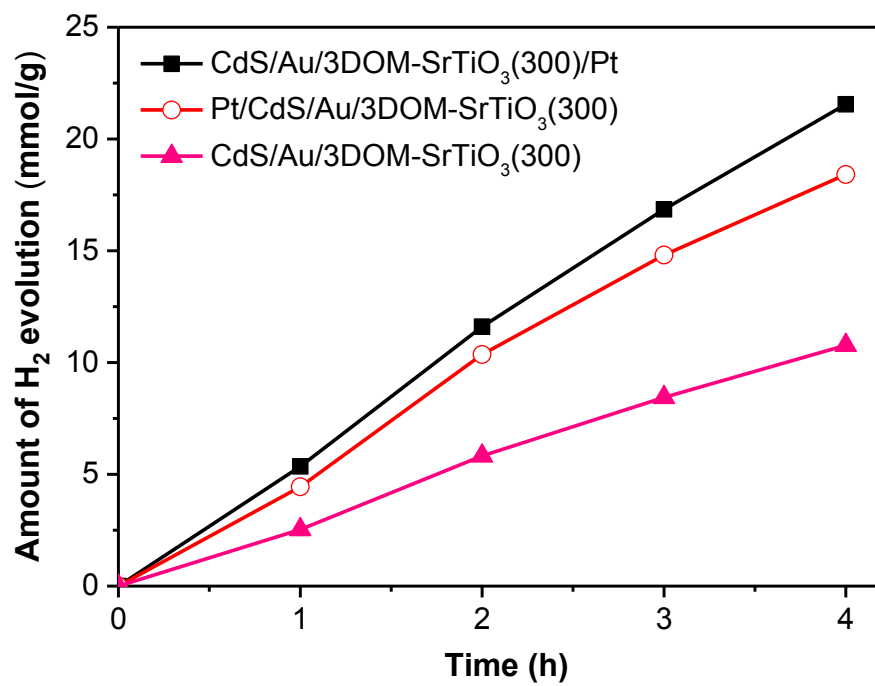


Figure 11.

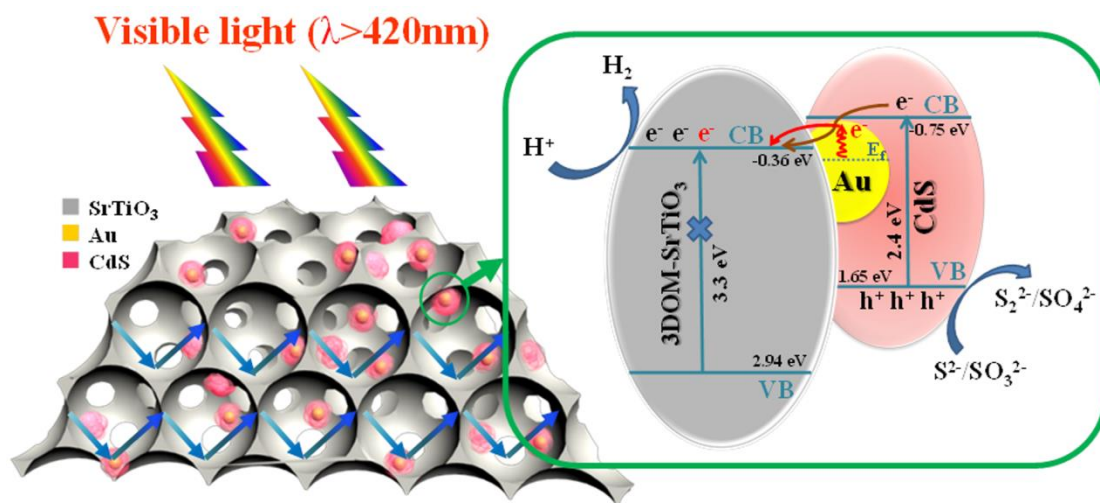
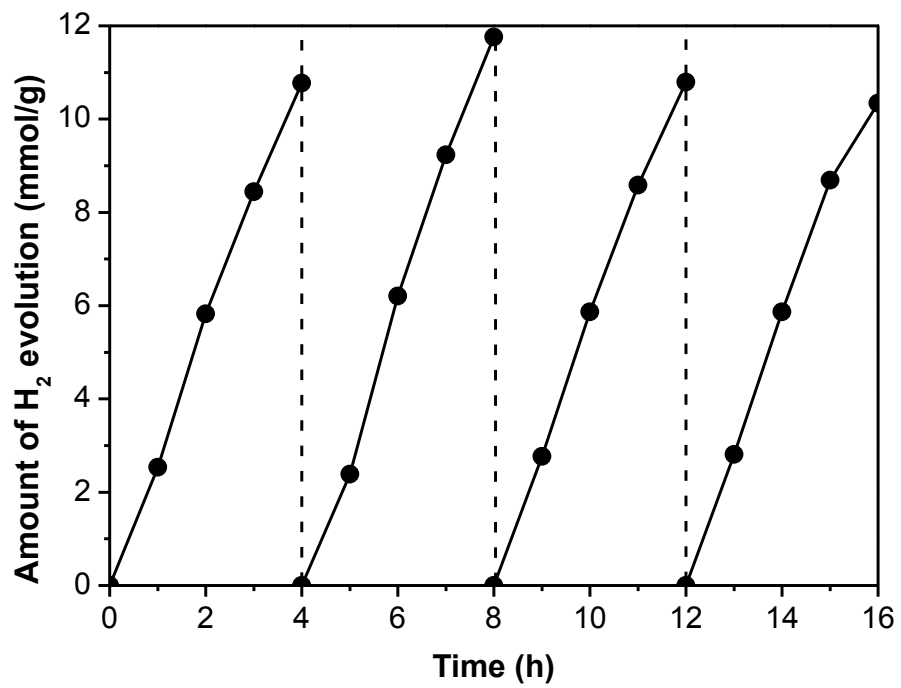
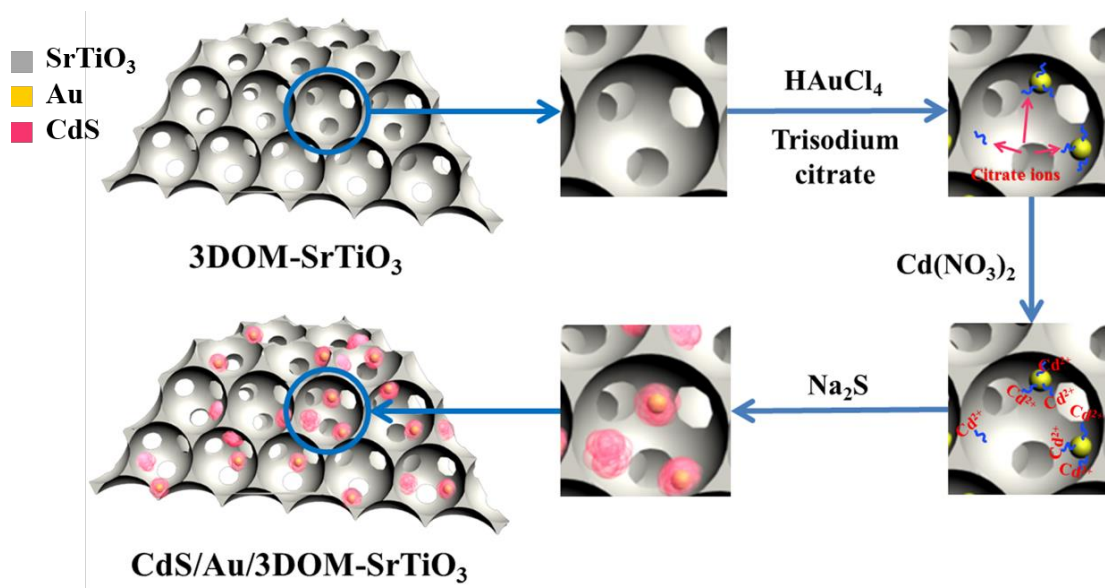


Figure 12.



Scheme 1.



Scheme 2.

