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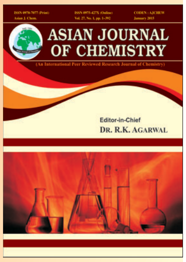

Photocatalytic Hydrogen Production from Aqueous Methanol Using Cu/S-TiO$_2$ Under Visible-Light

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Copper was loaded on the S-doped TiO$_2$ by methods of electroless plating, wet impregnation and chemical reduction, respectively. The physical structure and chemical properties of the prepared Cu/S-TiO$_2$ were characterized by UV-visible, XRD, XPS, EXAFS and FESEM techniques. It was illustrated that copper species loaded by electroless copper plating and wet impregnation method were Cu$_2$O/CuO, while Cu/Cu$_2$O was loaded by chemical reduction method. The Cu/S-TiO$_2$ prepared by electroless plating method showed excellent visible light absorption ability. Moreover, the electroless plated copper on S-TiO$_2$ was highly dispersed, which could facilitate the photogenerated charges capture, transfer and separation. Thus, the catalyst exhibited the highest photocatalytic activity of the three for hydrogen generation and is up to 7.5 mmol h^{-1}g^{-1} cat in methanol solution under visible light and a possible catalytic mechanism was proposed.

Keywords: Photocatalysis, Cu/S-TiO$_2$, Electroless plating, Hydrogen, Methanol solution.

INTRODUCTION

Photocatalytic production of hydrogen using sunlight as the energy input is a valuable sustainable energy technology. In this case, photocatalytic water splitting into hydrogen, a renewable, clean-burning and environmental-friendly fuel for the future energy sources, has been considered as one of significant and attractive solutions to solve the global energy and environmental problems[1]. Titanium dioxide has been widely studied in photocatalyst since the pioneering work by Honda and Fujishima[2]. However, the photocatalytic decomposition of water merely on the TiO$_2$ photocatalyst is ineffective. To improve photocatalytic effciency, one of the effective strategies is to develop metal modified photocatalysts[3-6], such as noble metals or their oxide. Kaneco *et al.*[7] prepared a Pd/TiO$_2$ using simultaneous metal deposition get the hydrogen production of 8 mmol h^{-1}g^{-1} cat. The noble metal loaded TiO$_2$ plays an essential role in the production of H$_2$ by promoting the separation of photoexcited electrons and holes. Although noble metal modified TiO$_2$ is particularly stable and efficient for H$_2$ production under UV excitation, the high cost of Pt, Pa and Au motivate the search for alternative low cost co-catalysts.

Copper-containing TiO$_2$ catalysts are well known for their photocatalytic activity toward CO$_2$ reduction[8-11]. Cu-doped TiO$_2$ as photocatalyst for hydrogen production have also received great attention. Dhanalakshmi *et al.*[12], Sreethawong and Yoshikawa[13] reported that, the capacity of photocatalytic hydrogen production by Cu-loaded TiO$_2$ is higher than that of Pt, Au and Pd. However, the investigation above was all performed under UV light, hydrogen generation ability of the Cu modified TiO$_2$ photocatalysts under visible light have been investigated. Therefore, how to make the Cu doped TiO$_2$ work under visible light will be very significant. Recently, there are documents show that metal sulfide as co-catalyst can achieve the purpose[14,15]. In these case, CdS or CuS as co-catalyst makes the TiO$_2$ work efficiently under visible light. Therein, the state of Cu, S species need to be further sdutied.

As well known, bare TiO$_2$ cannot work in the visible light region because the band gap of TiO$_2$ is 3.2 eV. Usually, addition of nonmetals, metal ions and dye sensitization methods are employed to extend the absorption edge of TiO$_2$ into visible region[16-19]. In order to obtain a photocatalyst with high efficiency and response to visible light, the Cu doped S-TiO$_2$ photocatalyst has been designed in the present work. This study highlights different methods to load Cu that are used in the preparation of Cu/S-TiO$_2$ photocatalysts. A series of factors influencing the activities of Cu/S-TiO$_2$ photocatalysts for H$_2$ evolution have been investigated to understand the functions of Cu and S. Their physicochemical properties were investigated by UV-visible, XRD, XPS, EXAFS, FESEM. We found that Cu/S-TiO$_2$ could significantly enhance the photocatalytic activity of TiO$_2$ for H$_2$ production under visible light and showed the average yield of 7.5 mmol h^{-1}g^{-1} cat within continuous running 6 h.

EXPERIMENTAL

Preparation of S-TiO_2: Titanium isopropylate was dropped to the mixture of thiourea, acetic acid and anhydrous ethanol at 323 K, the molar ratio of titanium isopropylate and thiourea is 1:4. The solution was stirred for 48 h till to get white slurry. After evaporation of ethanol for 48 h at 323 K in the vacuum oven, a yellow powder was obtained. The powder was calcined under air atmosphere for 3 h at 773 K with a heating rate of 2 K/min. Then the vivid yellow S-TiO_2 powder was obtained. Pure TiO_2 was made by the same process without thiourea.

Three Cu doped S-TiO_2 catalysts with the Cu content of 5 wt. % were prepared by electroless plating, wet impregnation and chemical reduction method and were signed as electroless plating (EP), wet impregnation (WI) and chemical reduction (CR), respectively.

Preparation of electroless plating: Plating copper was accomplished in the chemical copper solution, the appropriate amount of S-TiO_2 was added to the solution of HCHO (formaldehyde, as a reducing agent), EDTA·Na4 (ethylene diamine tetra-acetic acid tetra-sodium salt, as a complexing agent) and C_5H_5N (pyridine, as a stabilizer). The temperature and pH of the solution were maintained at 343 K and 12.5. With the vigorous agitation, $CuSO_4$ was added and reduced by HCHO and copper species were deposited on the surface of S-TiO_2. After filtrated several times with distilled water, till the filtrated water close to pH = 7 and then the material was dried at 383 K for 24 h.

Preparation of chemical reduction: S-TiO_2 powder was directly added to the solution of $CuSO_4$ at a ratio of 1 g /10 mL. The copper ions are reduced into metallic copper by formaldehyde solution and deposited on the S-TiO_2, when the temperature and pH of the solution were maintained at 343 K and 12.5. The sample was separated by filtrated several times with distilled water, dried at 383 K for 24 h.

Preparation of wet impregnation: A certain amount of S-TiO_2 powder was added to the solution of $CuSO_4$ (40 mL) at 318 K with vigorous agitation for 1 h. The solution was heated to 353 K and evaporated. Then the powder was dried at 383 K for 12 h and calcined under air atmosphere for 0.5 h min at 673 K.

Characterization of catalysts: UV-visible absorption spectrum were determined on Hitachi U4100 ultraviolet visible spectrophotometer (Japan), using the diffuse reflection method and $BaSO_4$ as a reference to measure all the samples. X-ray diffraction (XRD) was carried on the Bruker D8 advance X ray diffractometer with monochromated high intensity CuK_α radiation and operating at 40 kV/40 mA in the angle range of 5-85°. The surface electronic property was detected by X-ray photoelectron spectrometer (XPS, VG ESCALAB MK2) with an Al K_α source (1486.6 eV), all the binding energies were referenced to the C1s peak at 285 eV of the surface adventitious carbon. Extended X-ray Absorption Fine Structure (EXAFS) measurements at the Cu K-edge of the samples were recorded at room temperature in transmission mode using ion chambers at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (311) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5 Ge V and a current between 150-210 mA. The photon energy was calibrated with the first inflection point of Cu K-edge in Cu metal foil. The surface morphology and surface copper distribution of materials were obtained by Hitachi S-4800 filed emission scanning electron microscope (FESEM, Japan).

Catalytic activity: The hydrogen production from photocatalytic reforming of methanol solution under different wavelength was carried out in a homemade apparatus that have light sources outside the quartz reactor. Different range of wavelengths is obtained through the installation of light filters (420-500 nm). Also, the catalytic activities and stability test were performed using simulated sunlight (Xe lamp) inside the reactor, which was sealed by aluminum foil during the reaction to prevent interference from outside light. All the experiments were run in 300 mL 20(vol) % methanol solution containing 0.2 g of the catalyst at 25 °C. Prior to the irradiation, reaction mixture was evacuated at -10 KPa for 0.5 h and also purged with nitrogen gas for 0.5 h to remove the dissolved oxygen. During the irradiation, the evolved gaseous products were analyzed at every 1 h by a gas chromatography ((Agilent 3000 Mic GC) equipped with TCD detector and the Molsieve /Plot U columns, N_2/He as carrier gases.

RESULTS AND DISCUSSION

Physical structure and chemical properties: The UV-visible absorption spectra of pure TiO_2, S-TiO_2, electroless plating, chemical reduction and wet impregnation were shown in Fig. 1. Only a strong absorption in the UV region could be observed for pure TiO_2, due to the inherent band-gap absorption. The absorption edge of S-TiO_2 shifted to the visible light region, which was owing to the fact that the crystal lattices of S-doped TiO_2 powders are locally distorted by incorporation of S^{4+} species into TiO_2[20]. From the absorption spectra of electroless plating, chemical reduction and wet impregnation samples, it was clear that Cu/S-TiO_2 has a strong absorption between 400 and 800 nm attributed to the presence of Cu species, especially for electroless plating sample.

Fig. 2 is the XRD patterns of as-prepared Cu/S-TiO_2 photocatalysts, with S-TiO_2 as comparison. No characteristic

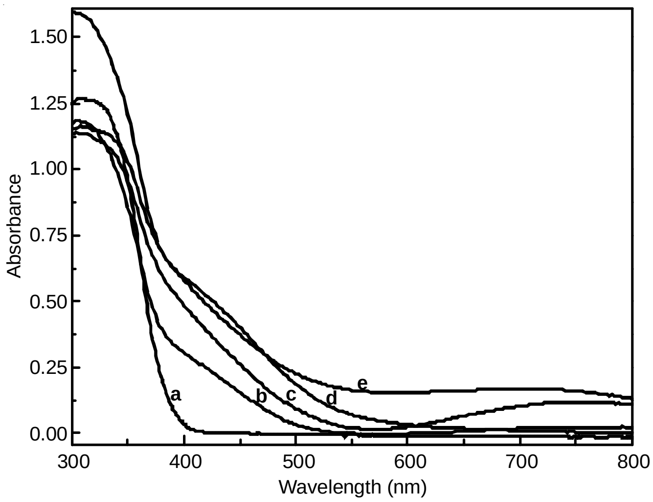


Fig. 1. UV-visible absorption spectra of a: TiO_2, b: chemical reduction, c: wet impregnation, d: S-TiO_2 and e: electroless plating

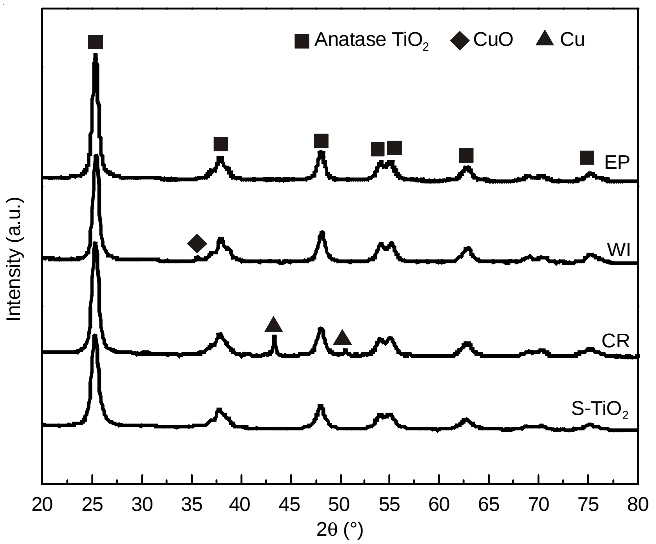


Fig. 2. XRD patterns of electroless plating (EP), wet impregnation (WI) and chemical reduction (CR) and S-TiO_2

peak of Cu was observed in the electroless plating sample. The copper species of chemical reduction and wet impregnation samples were metallic copper and CuO, respectively. Chemical reduction method was carried in formaldehyde solution, Cu^{2+} was reduced into metallic copper by formaldehyde, metallic copper was deposited on the surface of S-TiO_2 and easy to gathered into large metal copper grain. Wet impregnation method was performed at high temperature, easy to cause the CuO agglomerate. The absence of copper peak in the sample of electroless plating indicated the fine dispersion of copper species on the surface of TiO_2.

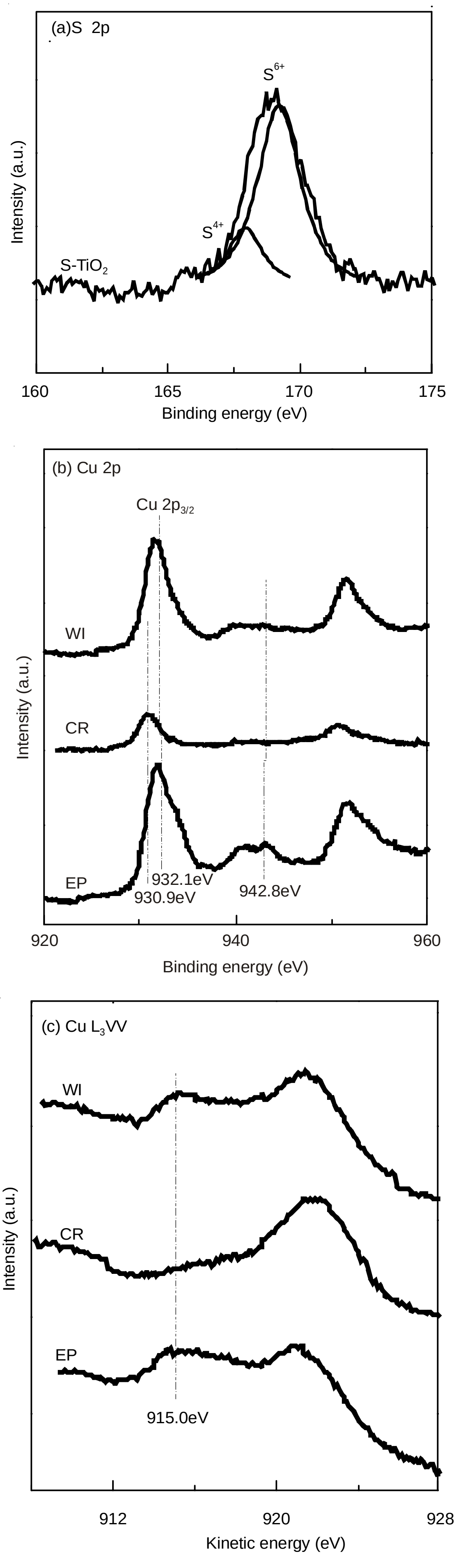
Fig. 3 is the XPS spectra of the Cu/S-TiO_2 photocatalysts, in which the chemical states of Cu and S atoms incorporated into TiO_2 were studied. Fig. 3(a) suggested that S species doped in TiO_2 in the form of S^{6+} and S^{4+} distorted the crystal lattices, which restrained the crystal growing. The binding energy of the Cu $2p_{3/2}$ spin orbital splitting peak around 933 eV together with the characteristic shake-up feature at a binding energy of 942 eV were indicative of Cu^{2+} species, while slightly lower binding energy (around 930 eV) was characteristic of metallic copper. The results point out that the copper species were present as Cu^{2+} in electroless plating and wet impregnation samples as indicated by the shake-up peaks in Fig. 3(b). The binding energy was shifted 1.2 eV to lower energies is evidenced for the XPS spectra corresponding to chemical reduction sample, which indicates the existence of Cu^0 species in this case. From Cu L_3VV Auger spectra (Fig. 3c), the Auger peak corresponding to Cu^+ was observed at 915 eV in the kinetic energy (KE) for electroless plating and wet impregnation samples. A sharp metal copper features diffraction of chemical reduction from XRD pattern proved that the copper formed a big metal crystal cluster. Because of this, the binding energy of Ti 2p (Fig. 3d) photoelectronic peak shift to the lower energies shows that there is interaction between larger copper grain and TiO_2 surface atom, which is also the reason for the phenomenon that Cu $2p_{3/2}$ spin orbital splitting photoelectronic peak combined to lower binding energy.

Fig. 4. and Table-1 showed the EXAFS analysis of Cu/S-TiO_2 photocatalysts. Fig. 4 compares the effects of preparation methods on the FT-EXAFS spectra of Cu/S-TiO_2. The profile of electroless plating is similar to wet impregnation, but very different to chemical reduction sample, especially for the size of peaks around 0.15 and 0.23 nm. The model fitting data shown in Table-1 illustrate that the chemical reduction can be fit with a Cu-O shell and four Cu-Cu shells, the Cu-O shell at 0.192034 nm and Cu-Cu shells at 0.312891 nm can be mapped to the first-shell and second-shell in Cu_2O; the Cu-Cu shells at 0.253770 nm, 0.443696 nm and 0.514370 nm consistent with the first-shell, the third-shell and the fourth-shell coordination of metallic Cu. The low coordination number of the Cu-O at 0.192043 nm indicates that only a small Cu_2O-like bonding is presented. Meanwhile Cu/S-TiO_2 prepared by chemical reduced method contains lots of metallic Cu clusters. The electroless plating shows two Cu-O shells at 0.195301 and 0.138549 nm and two Cu-Cu shells at 0.310155 nm and 0.297913 nm, respectively. The Cu-O shell at 0.195301 nm can be mapped to the first-shell Cu-O in Cu_2O. The Cu-O shells at 0.138549 nm can be mapped to the first-shell Cu-O in CuO. The low coordination number of the Cu-O at 0.138549 nm indicates that only a small CuO-like bonding is presented. The results certify that Cu/S-TiO_2 prepared by electroless plating method has a Cu_2O/CuO structure and the wet impregnation sample

TABLE-1
MODEL FITTING RESULTS OF EXAFS SPECTRA OF Cu/S-TiO_2 PREPARED BY CHEMICAL REDUCTION, WET IMPREGNATION AND ELECTROLESS PLATING

Sample	Bond	Bond distance (nm)	C.N.$^{\alpha}$	σ^2	γ-Factor
CR	Cu-O	0.192043	1.66	0.00588	0.02351
	Cu-Cu	0.312891	13.44	0.03928	
	Cu-Cu	0.253770	3.852	0.00747	
	Cu-Cu	0.443696	14.688	0.01605	
	Cu-Cu	0.514370	12.792	0.01246	
WI	Cu-O	0.194511	3.152	0.00377	0.02779
	Cu-Cu	0.307610	4.476	0.00888	
	Cu-O	0.175654	0.416	0.05264	
	Cu-Cu	0.296192	1.888	0.00434	
EP	Cu-O	0.195301	3.356	0.00449	0.01430
	Cu-Cu	0.310155	7.248	0.01122	
	Cu-O	0.138549	0.46	0.01130	
	Cu-Cu	0.297913	3.624	0.00739	

σ^2 : Mean square displacement, ^{a}Coordination number (C.N.)



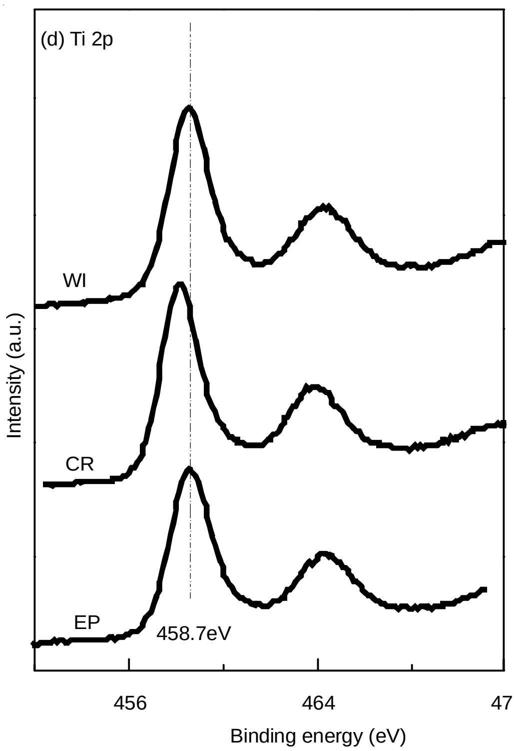


Fig. 3. XPS spectra of electroless plating (EP), wet impregnation (WI) and chemical reduction (CR) samples, (a) S 2p, (b) Cu 2p, (c) Cu L_3VV, d) Ti 2p

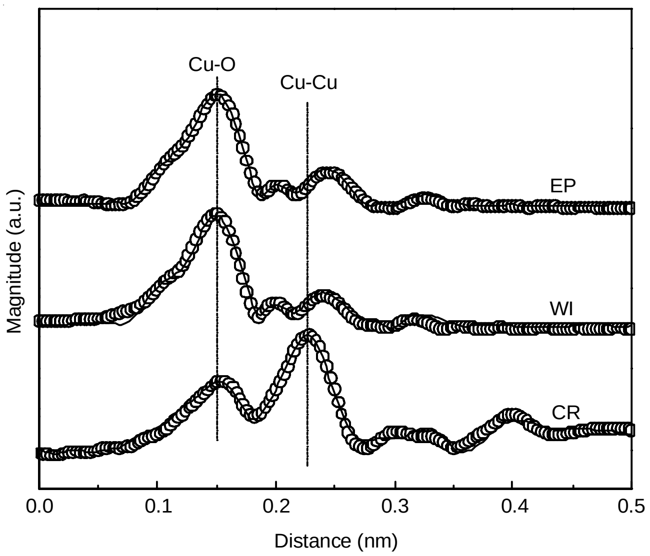


Fig. 4. EXAFS spectra of Cu/S-TiO_2 prepared by chemical reduction (CR), wet impregnation (WI) and electroless plating (EP); (Lines represent experimental data, while symbols represent the model fitting)

has a similar Cu_2O/CuO structure like electroless plating sample.

The characterization results of XRD, XPS and EXAFS show that Cu atoms of electroless plating and wet impregnation samples are in the state of Cu^{2+} and Cu^{+}, while Cu atoms of chemical reduction sample is in the state of Cu^0 and Cu^+. By means of FESEM technique, the copper dispersion state and morphology of as-prepared Cu/S-TiO_2 catalyst have been studied. In the FESEM images of samples (Fig. 5), copper particles appear in the image as characteristic brighter spots. It obviously shows high dispersion of copper species loaded

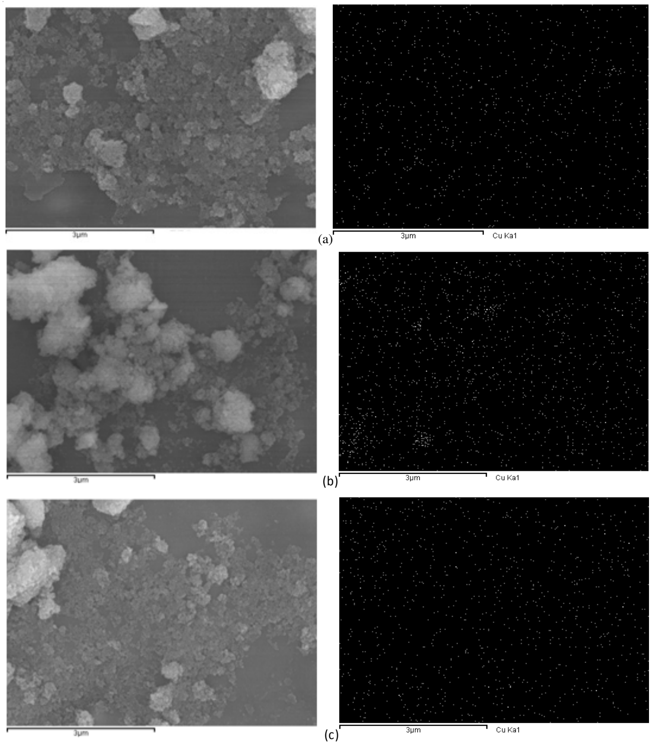


Fig. 5. FESEM images of Cu/S-TiO$_2$, (a) electroless plating (EP), (b) wet impregnation (WI), (c) chemical reduction (CR)

on the surface of S-TiO$_2$ by electroless plating method (Fig. 5a). But the copper species in wet impregnation and chemical reduction show a close aggregation and unevenly distribution (Fig. 5b, 5c).

Photocatalytic reforming of methanol aqueous solution: Fig. 6 showed hydrogen evolution over Cu/S-TiO$_2$ photocatalysts with various wavelengths of radiation. The catalytic activity of S-TiO$_2$ validated that doping S can extend the absorption edge of TiO$_2$ into visible region and the catalytic activity of Cu/S-TiO$_2$ validated that the modification of Cu can prevent fast recombination of electron/hole pairs and hence effectively improve the photocatalytic efficiency of S-TiO$_2$. The yields of hydrogen were significantly lower with the wavelength of 500 nm than with the wavelength of 420 nm and the values obtained by electroless plating sample were the higest for the three Cu/S-TiO$_2$ catalysts.

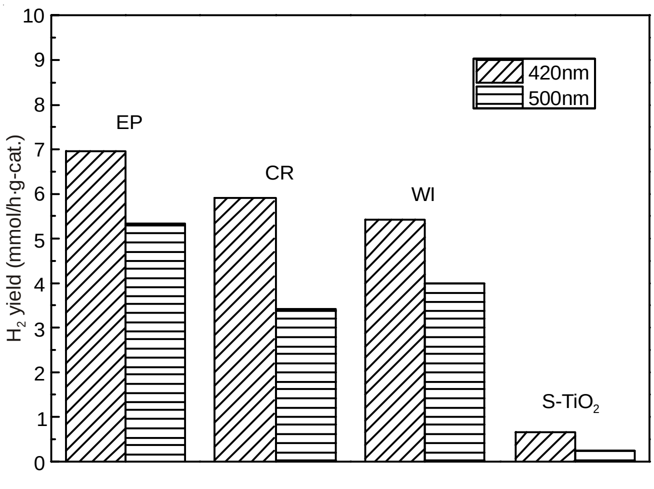


Fig. 6. H$_2$ yield of photocatalytic reforming of methanol solution over electroless plating (EP), chemical reduction (CR), wet impregnation (WI) and S-TiO$_2$ samples with various wavelengths of radiation

Fig. 7 illustrated time courses of hydrogen evolution and cycle stability over prepared Cu/S-TiO$_2$ photocatalysts under the 500 W Xe lamp illumination, with S-TiO$_2$ as comparison. It can be observed that hydrogen could be formed efficiently over three kinds of Cu coated S-TiO$_2$ photocatalysts. This rooted primarily from efficient separation of photo-generated charges and holes in TiO$_2$ by Cu species. It has been proven that different Cu species (CuO/Cu$_2$O/metallic Cu) has different competencies in the capture of electrons[21]. As is known, Cu$_2$O and CuO are p-type semiconductors with smaller band gaps than TiO$_2$[22]. In the initiating stage of photocatalytic reaction, Cu oxides were more inclined to receive electrons from TiO$_2$, as compared to metallic Cu. Considering the initial hydrogen generation rates between electroless plating, chemical reduction and wet impregnation samples, wet impregnation showed a higher activity than electroless plating when they has similar CuO/Cu$_2$O structure. The discrepancy in photocatalytic activities between electroless plating and wet impregnation may relate to the difference of CuO/Cu$_2$O dispersion. The high CuO/Cu$_2$O dispersion of electroless plating may cause inducing period in the initial step of reaction. With the reaction going on, electroless plating sample showed the highest activity, followed by chemical reduction samples, while wet impregnation was the most inferior among the three samples. Considering the final difference of hydrogen generatiohn rates, distribution of Cu in the photocatalysts might play a key role in affecting photocatalytic activities.

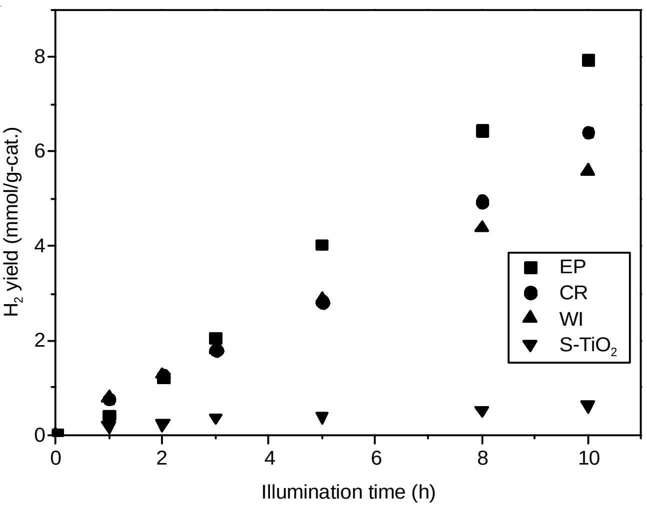
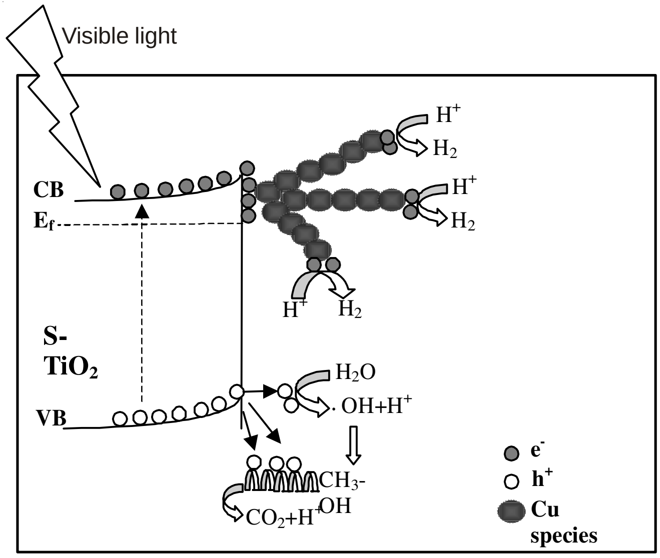


Fig. 7. H$_2$ yield and stability of photocatalytic reforming of methanol solution over electroless plating (EP), chemical reduction (CR), wet impregnation (WI) samples

After irradiation for 10 h under similar reaction conditions, hydrogen evolution rate of electroless plating, chemical reduction, wet impregnation and S-TiO$_2$ were 7.93, 6.57, 5.81 and 0.70 mmol/g-cat, respectively. In the wet impregnation sample, the loaded Cu on the S-TiO$_2$ surface was easy to gather and agglomerate. In this case, photo-generated charges achieved by CuO and Cu$_2$O were soon to recombine with holes, leading to lower life and weaker photocatalytic activity. In electroless plating synthesis, the highly dispersed Cu species interconnect together to form reticulated circuit structure, which could facilitate the photo-generated charges transfer and separation, hence resulting in stable and consistent hydrogen generation throughout the 10 h reaction. After 130 min of reaction, hydrogen generation rate of the electroless plating sample was highest among all three Cu/S-TiO_2 samples. But efficiency of hydrogen generation was observed to abate slightly with time. Decline of hydrogen generation rate may be corresponding with metallic Cu appears. It can be concluded that the dispersion state of Cu in the photocatalysts may be a key factor that would affect hydrogen generation of Cu/S-TiO_2. After six stability cycle tests, though all of the three photo-catalysts' catalytic activity declined slightly, electroless plating ample declined minimum and exhibited excellent catalytic activity, the average H_2 yield can reach 7.5 mmol $h^{-1}g^{-1}$ cat.

A possible reaction mechanism of photocatalytic reforming methanol solution over Cu/S-TiO_2 prepared by electroless plating method is proposed (**Scheme-I**). In the initiating stage of photocatalytic reaction, the mixed copper species of Cu_2O and CuO with smaller band gaps facilitate the light harvest and photoelectron capture. With the reaction progressed, the mixed copper species of Cu_2O and CuO become metallic Cu and Cu_2O compounds by consuming the electrons. Once the metallic Cu appears, a Schottky barrier at the copper/TiO_2 interface can trap the photoelectrons efficiently[23]. Moreover, the copper was highly dispersed on the S-TiO_2 surface of Cu/S-TiO_2 prepared by electroless plating method, which can facilitate the photo-generated electrons transfer and separation, enhance the photocatalytic reduction of H^+. In addition, the methanol and water molecules bond on the TiO_2 surface through their hydroxyl $O^{\bullet}$. The hydroxyl groups are oxidized by photo-generated holes, releasing H^+ and hydroxyl radicals ($^{\bullet}OH$). All of the released H^+ were migrated to the active site of catalyst and then reduced into H_2 by photo-generated charges.



Scheme-I: Mechanism of photocatalytic reforming of methanol solution over Cu/S-TiO_2 prepared by electroless plating method

Conclusion

In this study, Cu/S-TiO_2 photocatalysts for hydrogen generation were successfully synthesized by electroless plating, wet impregnation and chemical reduction methods. The various preparation methods led to different structural and chemical properties of Cu on the surface of S-TiO_2 and both factors were proven to influence their photocatalytic activities. CuO/Cu_2O in the electroless plating sample, exhibited the most excellent properties for hydrogen generation, followed by Cu/Cu_2O in chemical reduction sample. Although wet impregnation sample has the similar chemical state of Cu with electroless plating sample, its photocatalytic activity was low. It was also postulated that distribution of Cu components on the surface of S-TiO_2 was a key factor which influence charge transfer efficiency. In the electroless plating sample, due to the highly dispersion of Cu species and the formation of reticulated circuits, Cu species (CuO/Cu_2O) plated on S-TiO_2 could facilitate the photo-generated charges capture, separation and transfer and enhance its photocatalytic hydrogen evolution.

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