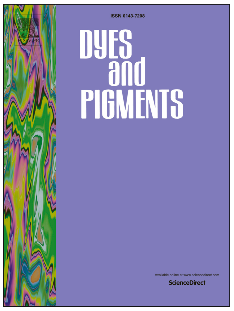

The investigation of novel D-π-A type dyes (MK-3 and MK-4) for visible light driven photochemical hydrogen evolution

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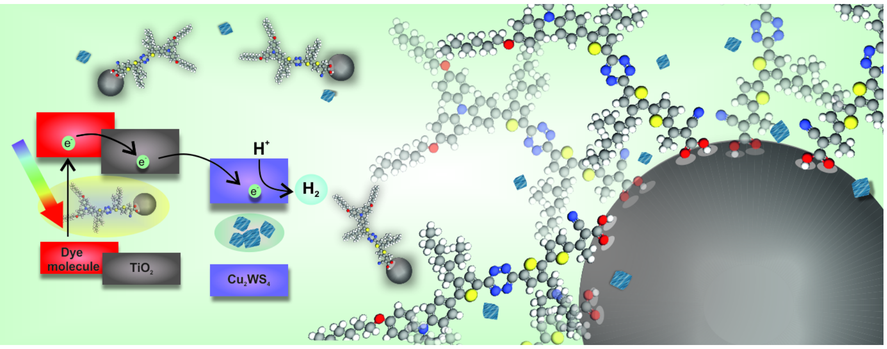
e^-
e^-
H^+
e^-
H_2
Dye molecule
TiO_2
Cu_2WS_4

The investigation of novel D-π-A type dyes (MK-3 and MK-4) for visible light driven photochemical hydrogen evolution

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Abstract: Two novel donor-π-acceptor (D-π-A) semiconductor organic dyes have been synthesized for the photochemical hydrogen evolution reaction (HER) to sensitize TiO_2 for the first time. The molecular structures of D-π-A semiconductor organic dyes, which are entitled as MK-3 and MK-4, have been characterized by NMR spectroscopy method; and also electrochemical and optical properties have been investigated by cyclic voltammetry and UV-

Vis absorption techniques, respectively. Amount of dye loading on TiO_2 surface has been investigated by EDX method. The HER activities have been explored in the presence of triethanolamine (TEOA) as a electron donor reagent under sunlight (solar simulator illumination limited by cut-off filter $\lambda \geq 420$ nm) in the absence and presence of co-catalysts (Pt and Cu_2WS_4). Transient photocurrent densities of MK-3/TiO_2 and MK-4/TiO_2 electrodes have been reached to 110 µA cm^{-1} and 275 µA cm^{-1}, respectively. The photocatalytic HER activities have been relatively enhanced in the presence of the Pt or Cu_2WS_4 co-catalysts (dye/TiO_2/Cu_2WS_4 or dye/TiO_2/Pt) when compared to only dye/TiO_2. The HER rates have been found as 427, 1277, 675, 682, 1027 and 795 $\mu molg^{-1}h^{-1}$ for the MK-3/TiO_2, MK-3/TiO_2/Pt, MK-3/TiO_2/Cu_2WS_4, MK-4/TiO_2, MK-4/TiO_2/Pt and MK-4/TiO_2/Cu_2WS_4, respectively. The differences of photochemical activities of MK-3/TiO_2 and MK-4/TiO_2 have been stated taking into account dye molecule structures. Moreover, the HER mechanism have been described by using electrochemical band energy levels of dyes, TiO_2 and Cu_2WS_4 co-catalyst.

Keywords: photocatalysis, solar energy conversion, hydrogen evolution, D-π-A organic dyes

1. INTRODUCTION

The production of cheap, renewable and environmentally friendly fuel hydrogen by using solar energy has attracted much attention due to the increasing energy crisis. The sun's energy converts to hydrogen via photoelectrochemical and photocatalytic reaction systems from water in the presence of semiconductor photocatalysts. Until now, large-scale photocatalytic HER systems have been thoroughly examined by using a myriad of catalysts including metal oxides, chalcogenides, oxynitrides, metal free catalysts, sulfides, phosphides, borides, carbides [1]. The most commonly used TiO_2 photocatalyst possess huge potential hydrogen-generating capabilities from water splitting. Beside this advantage, hydrogen production efficiency of a bare TiO_2 still remains limited owing to the wide band gap, the high recombination of electron-hole pairs and the fast-backward reaction [2-4]. These obstacles can be decreased by dye sensitization and using co-catalyst for the absorption visible light and the minimization of recombination rates, respectively [4]. Currently, semiconductor donor-π-acceptor (D-π-A) structured semiconductor organic dyes have been aroused interest in photovoltaic and photocatalytic conversion applications due to the properties of configurable electrochemical band levels, absorption and high intermolecular charge transfer (ICT) performance [5-8]. These D-π-A structures have been composed of π-electron-poor (electropositive) acceptor (A) groups and π-electron-rich donor (D) groups linked by a π bridge, which make possible the separation of electrons and holes to reduce the recombination events [9-13]. Photocatalytic HER by D-π-A dye, which are consisted of triphenylamine based donor group, sensitized TiO_2 have been investigated by changing hydrophilic and steric effect, the amount of loading dye, spacer length and the amount of anchoring groups of dyes [14-19]. D-π-A structured semiconductor organic dyes have also been employed in the covalently functionalized p-type photocathodes and the modification of graphene/Pt electrodes [20-24]. Konieczna *et al.* have been explored that ionic structures of semiconductor D-π-A sensitizers displayed higher photochemical HER activity than that of the neutral D-π-A sensitizers [25]. We have shown that the photocatalytic HER activity by different D-π-A dye (changing electron donating groups) sensitized TiO_2 is decreased by the addition of donor groups because of the steric effect of dyes on TiO_2 [26]. In addition, effect of additional π group has been reported by our group and founded out D-π-A structure is efficient than D-A structure [27]. D□π□A conjugated polymeric photocatalyst have also been used on photocatalytic HER under UV–Vis light irradiation ($\lambda > 300$ nm) [28]. The HER activities of phenothiazine based D-A type organic semiconductor dyes sensitized TiO_2

photocatalyst have been also investigated by Tiwari *et al.* under solar irradiation [29, 30]. Besides, both the photocatalytic HER and the photovoltaic application of two D□A□π□A structured semiconductor organic dyes have been investigated under limited light (420 nm$<\lambda<$780 nm) illumination. It has been shown that both high photocatalytic HER activity and photoelectric conversion efficiency have been observed due to the absorption properties of the dyes with high molar extinction coefficient [31]. Dye sensitized photocatalytic HER studies are generally performed by using co-catalyst in order to decrease charge recombination rates and photocorrosion, and to increase stability of reactions and photogenerated charge transport efficiency, and to host active sites. Co-catalysts for the photocatalytic HER are usually consisted of platinum group noble metals (PGMs) such as Pt, Pd, Ru or Ir [7]. Metal sulfide based catalysts like WS_2 and MoS_2 have been attracted great attentions as an alternative to PGMs. Transition metal doping or alloyed structures are given rise to enhance the photocatalytic activities of MS_2 (M = Mo and W) [26, 32, 33].

In this study, we have reported first time in the literature the synthesis of two D-π-A type semiconductor organic dyes, which are entitled **MK-3** (*(2E) -3- [5 '- {6- [5- (4- {bis [4-(hexyloxy) phenyl] amino} phenyl) -4- (2-ethylhexyl) -2-thienyl] -1,2 , 4,5-tetrazin-3-yl} -2,2'-bithien-5yl] -2-cyanoacrylic acid*) and **MK-4** (*(2E)-3-{5-[5-{6-[5-(4-{bis[4-(hekzilloks)phenyl]amino}phenyl)-4-(2-ethylhexyl)-2-thienyl]-1, 2,4,5-tetrazin-3-yl -3-(2-ethylhexyl)-2-thienyl]-2-furyl}-2-cyanoacrylic acid*), for the visible light sensitization of TiO_2. The molecular structures of MK-3 and MK-4 have been clarified by NMR spectroscopy and elemental analysis methods. The electrochemical and optical properties of these dyes have been clarified by the cyclic voltammetry and UV-Vis absorption spectroscopy methods, respectively. Dye loading rates on TiO_2 surface has been also calculated by EDX method. The photoelectrochemical and the photocatalytic activities of MK-3/MK-4 sensitized TiO_2 photocatalysts on the HER have been investigated. The photoelectrochemical HER performance of dye sensitized electrodes has been surveyed by chronoamperometry and linear sweep voltammetry (LSV) methods in the aqueous TEOA/Na_2SO_4 solution. The photocatalytic HER activities have been examined in the aqueous TEOA solution as the sacrificial electron donor medium. Cu_2WS_4 has also used as the co-catalyst and its catalytic activity has compared to *in situ* photodeposited Pt. MK-3/TiO_2, MK-3/TiO_2/Cu_2WS_4, MK-3/TiO_2/Pt, MK-4/TiO_2, MK-4/TiO_2/Cu_2WS_4 and MK-4/TiO_2/Pt have produced 427, 675, 1277, 682, 795 and 1027 $\mu molg^{-1}h^{-1}$, respectively. The differences of HER rates among the dye sensitized TiO_2 photocatalysts explicated by structural differences of D-π-A organic dye. Moreover, the HER mechanism has been clarified by the energy band levels of the Cu_2WS_4 co-catalyst, TiO_2, and each photosensitizer D-π-A dyes.

2. EXPERIMENTAL SECTION

2.1. Optical and electrochemical experiments

Optical measurements were performed by using a UV-Vis absorption spectrophotometer (Shimadzu UV-1800) and Perkin Elmer LS-50B luminescence spectrometer. Molar absorption coefficients were calculated according to literature [34]. The electrochemical characterizations were performed by electrochemical working station (CH Instruments 760D) in three-electrode cell in acetonitrile solution. Glassy carbon, platinum wire and Ag/AgCl electrodes were used as working electrode, counter electrode and reference electrode, respectively. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as supporting electrolyte.

2.2. Dye sensitization process

TiO_2 has been calcined to detract adsorbed and water organic pollutants from the surface for 45 minutes at 450 ºC. This step is important to generation of binding region between the surface of dye molecules and TiO_2. Then the prepared TiO_2 and donor-π-acceptor dye solutions (10^{-2} mM) have been mixed and stirred for a while under the darkness (half a day to overnight). After the binding process, the solution was filtered and precipitate was rinsed extensively with tetrahydrofuran (THF) and ethanol, respectively. In a similar method, for the photoelectrochemical reaction, TiO_2 coated FTO electrodes (Dyesol MS001630-1) have been immersed into the MK-3 or MK-4 solutions (10^{-5} M) in THF and washed with ethanol to remove unbinding molecules of dye. Finally, the prepared photocatalyst and TiO_2/electrodes were dried at room temperature and ready for use in the photocatalytic and photoelectrochemical hydrogen production reaction.

2.3. Photoelectrochemical and photocatalytic hydrogen evolution measurements

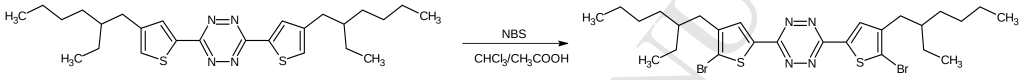
Photoelectrochemical treatment was carried out in a three-electrode cell for linear sweep voltammetry and chronoamperometry, which includes dye-coated FTO (Dyesol MS 001630, 0.4 cm × 0.7 cm, ca. 10 μm in thickness) as a working electrode, Ag/AgCl and platinum served as the reference and counter electrodes, respectively, in combination with redox electrolyte solution of TEOA/Na_2SO_4. Photocatalytic hydrogen evolution was performed in a single compartment Pyrex glass reaction cell under visible light irradiation ($\lambda \geq 420$ nm, Solar Light XPS-300™). MK-3/TiO_2 or MK-4/TiO_2 hybrid photocatalysts, Cu_2WS_4 or Pt co-catalysts were dispersed in solutions containing TEOA (0.33M) electron donor into the reaction-cell in the nitrogen gas filled glovebox. Then reaction-cell was plugged up with septa and ultrasonic treatment was applied for homogeneous distribution. Subsequently, photocatalytic HER test was initiated in the visible light and the evolved hydrogen gas was analysed by gas chromatograph using Shimadzu GC-2010 Plus, thermal conductivity detector (TCD) and argon as the carrier gas.

3. RESULTS AND DISCUSSION

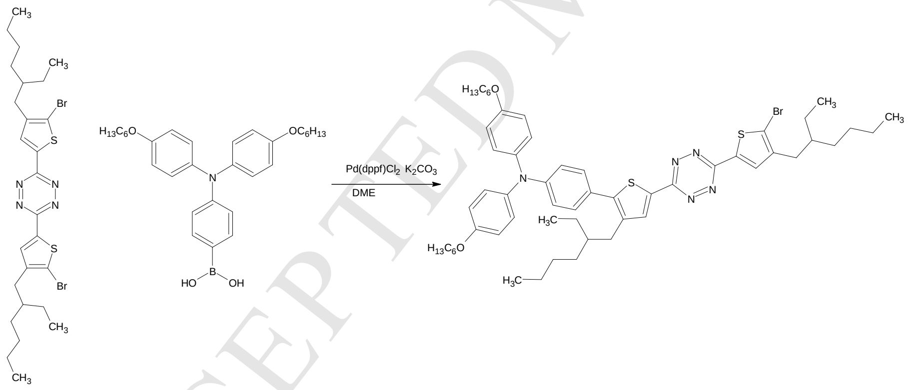
3.1. Synthesis route, optical and electrochemical properties of organic dyes

The synthetic routes of MK-3 and MK-4 dyes are depicted in Scheme 1. 3,6-bis [4-methylthien-2-yl]-stetrazine (1) was synthesized by using previous literature [35, 36]. 5 '-{6-

[5-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-4-(2-ethylhexyl)-2-thienyl] 1,2,4,5-tetrazin- 3-yl} -3'- (2-ethylhexyl) 2,2'-bithiophene-5-carbaldehyde **(4)** and 5-[5-{6-[5-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-4-(2-ethylhexyl)-2-thienyl]-1,2,4,5-tetrazin-3-yl}-3-(2-ethylhexyl)-2-thienyl]-2-furaldehyde **(5)** were synthesized by Suzuki reaction between the 4-[5-{6-[5-Bromo-4-(2-ethylhexyll)-2-thienyl]-1,2,4,5-tetrazin-3-yl}-3-(2-ethylhexyl)-2-thienyl -*N*,*N*-bis[4-(hexyloxy)phenyl]aniline **(3)** and the boronic acids (5-formyl-2-furanboronic acid 5-formyl-2-thienylboronic acid). Molecules **(4)** and **(5)** were converted by Knoevenagel condensation reaction to MK-3 and MK-4 dyes. The synthetic process, structural and elemental characterization of MK-3 and MK-4 are given in the SI in detail (Figure S1-10).



(1) **(2)**



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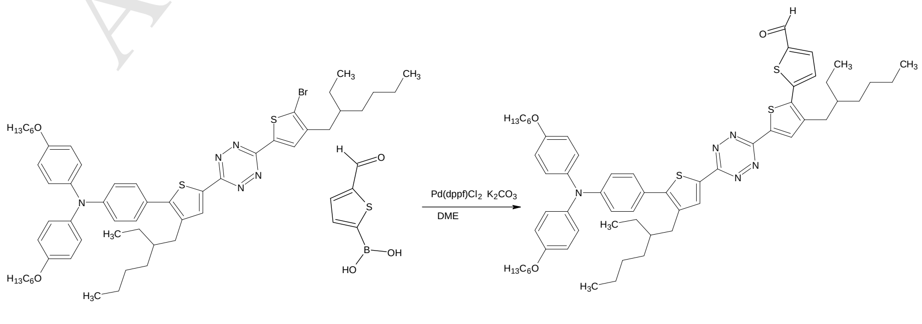

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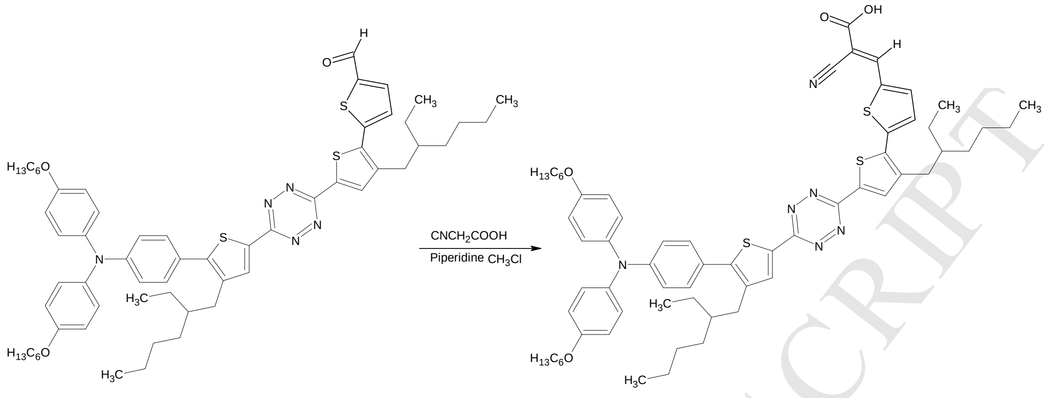
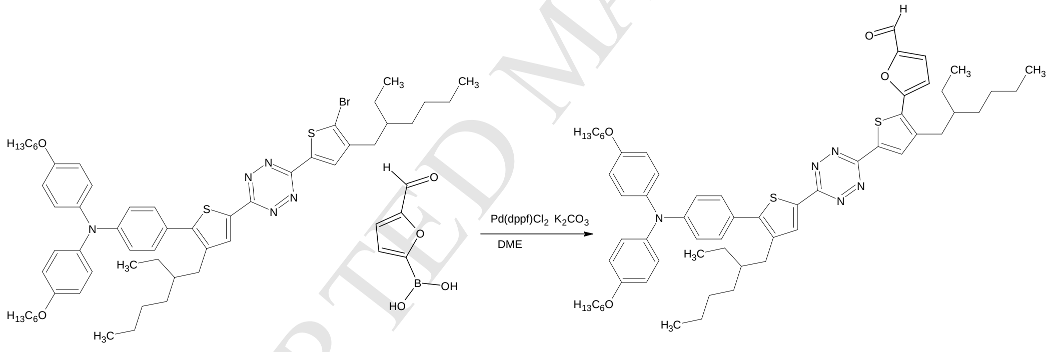
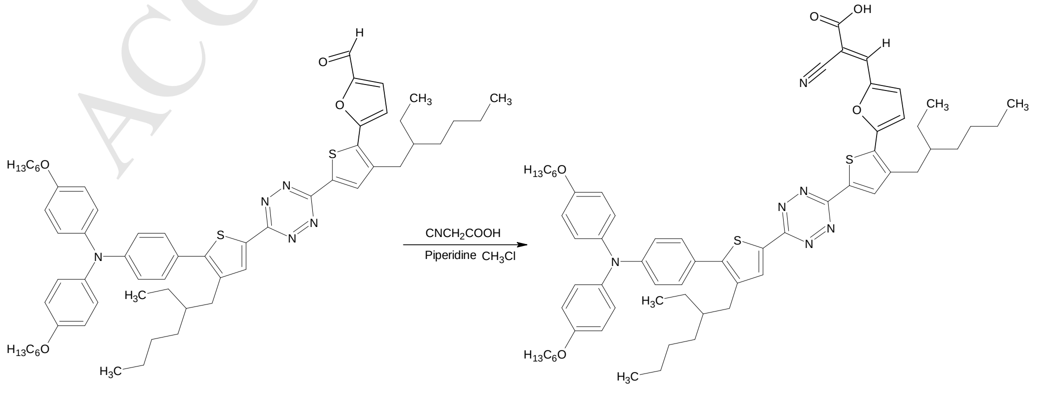

CNCH$_2$COOH
Piperidine CH$_3$Cl

MK-3


Pd(dppf)Cl$_2$ K$_2$CO$_3$
DME

(5)


CNCH$_2$COOH
Piperidine CH$_3$Cl

MK-4

Scheme 1. Synthetic pathway of the MK-3 and MK-4 dyes.

Binding ratios between TiO_2 and MK-3/MK-4 dyes have been found out from the energy dispersive X-ray spectroscopy (EDX) data's. EDX spectra and of dye sensitized TiO_2 have been displayed in the figure S11 (see SI). Elemental analysis obtained from EDX spectra of dye sensitized TiO_2 have been given in the Table 1. The binding ratio between TiO_2 and dye has been calculated from N/Ti ratio because of the common elements in the each sample. N/Ti ratios have been turned out to be $3.25x10^{-3}$ and $3.16x10^{-3}$ for the MK-3/TiO_2 and MK-4/TiO_2, respectively. It is obvious that the dye contents are quite similar in both photocatalyst. The corresponding SEM images of MK-3/MK-4 sensitized TiO_2 have also been given in the supporting information as the figure S12.

Table 1. EDX spectra data's of dye sensitized TiO_2

	Element	**Normal (%wt)**	**Normal (%wt)**	**Atom (%atom)**	**Error (%)**
MK-3	Titanium	49.06	56.34	**30.73**	1.4
	Oxygen	32.62	37.46	61.16	37.2
	Carbon	1.92	2.21	4.80	0.4
	Nitrogen	0.05	0.05	**0.10**	0.1
	Sulfur	3.43	3.94	3.21	0.2
	Total	87.08	100	100	
MK-4	Titanium	49.46	53.94	**28.45**	1.4
	Oxygen	38.02	41.54	65.57	24.5
	Carbon	1.64	1.78	3.75	0.3
	Nitrogen	0.04	0.04	**0.09**	0.2
	Sulfur	2.48	2.70	2.13	0.1
	Total	91.63	100	100	

When the optical properties of dyes are examined, sharp absorption peaks at 426 nm and 286 nm for MK-3, and a weak peak at 362 nm while a sharp peak at 282 nm for MK-4 was observed as shown in Figure 1a-b. The first peaks at 286 and 282 nm for the MK-3 and MK-4, respectively, are originated from localized π-π* transitions. The second peaks at 426 and 362 nm for the MK-3 and MK-4, respectively, are arise from delocalized π-π* transitions thanks to intermolecular charge transfer (ICT) properties between the donor and acceptor groups [37]. Using the UV-Vis absorption spectra, the molar absorption coefficients were calculated for MK-3 and MK-4 dyes as 2142 M^{-1} cm^{-1} (426 nm) and 2570 M^{-1} cm^{-1} (365 nm) [34]. The photoluminescence emission spectra of MK-3 and MK-4 have been given in the supporting information as the figure S13. Maximum emission peaks of MK-3 and MK-4 have been 575 nm and 538 nm, respectively. The electrochemical behaviour of dyes was investigated by the cyclic voltammetry. In cyclic voltammograms as shown in Figure 1c-d, the oxidation potentials which originated from triphenylamine groups (donor moieties) were found to be 0.86 V and 0.83 V for MK-3 and MK-4, respectively. The reduction peaks, which are thought to belong to π groups in the molecules, are found to be -0.79 V and -0.83 V for MK-3 and MK-4, respectively. Finally, the peaks observed in -1.54 V and -1.25 V are pointed out the acceptor group (the cyanocarboxylic acid) of MK-3 and MK-4 dyes, respectively (Table 2).

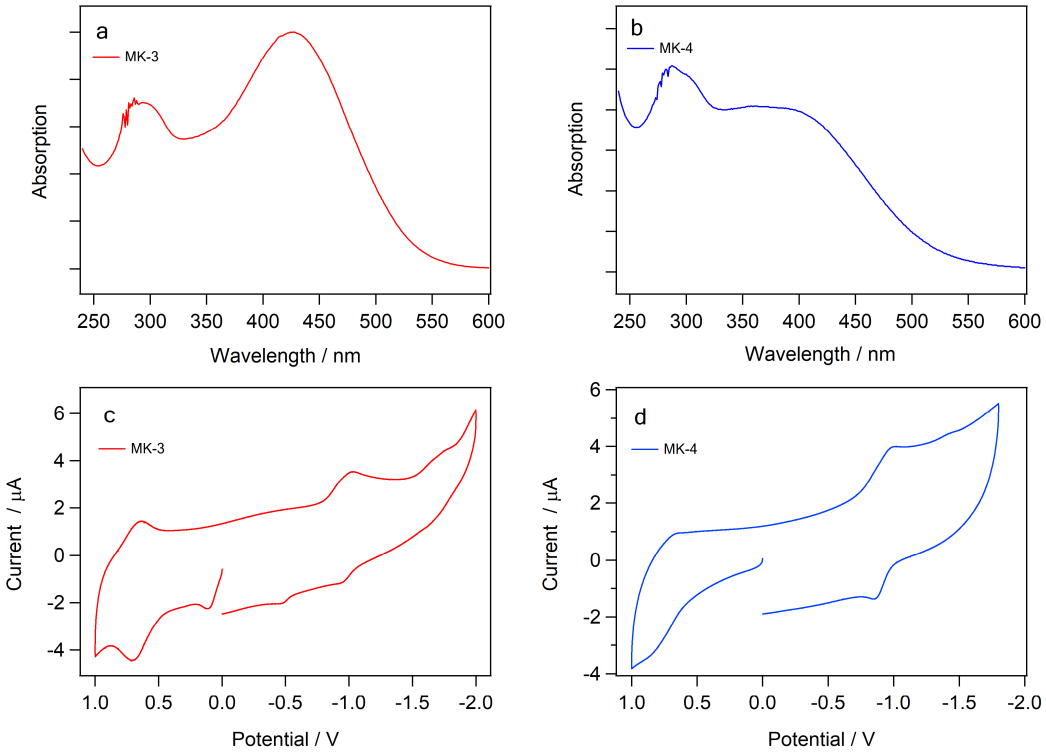


Figure 1. Absorption spectrums **(a-b)** and cyclic voltammograms **(c-d)** of MK-3 (red line) and MK-4 (blue line)

Table 2. Optical and electrochemical parameters of MK-3 and MK-4 dyes

Dyes	**Wavelength (λ) / nm**	**Molar Absorption Coefficients (ε) / M^{-1} cm^{-1}**	**Oxidation Potentials / V**	**Reduction Potentials / V**
MK-3	426	2142	0.86	-0.79 / -1.54
MK-4	362	2570	0.83	-0.83 / -1.25

3.2. Photochemical Hydrogen Evolution Reactions

Photoelectrochemical (PEC) hydrogen evolution characteristics of MK-3/MK-4 sensitized TiO2 electrodes have been carried out in the aqueous electrolyte solution (Na_2SO_4/TEOA) containing of a three-electrode setup with Pt counter electrode, Ag/AgCl reference electrode and dye sensitized TiO_2 working electrodes under solar simulator (Solar

Light XPS-300^{TM}) illumination limited by cut-off filter ($\lambda \geq 420$ nm). PEC experiments, which are consisted of chronoamperometry and linear sweep voltammetry (LSV) techniques, have been performed by open/close of irradiation. LSV studies have been recorded from 0.5 V to -0.5 V, under light/dark cycles. The dye sensitized electrodes display very stable behavior in this potential frame (Figure 2a). Then, PEC experiments have been studied by the chronoamperometric method during 350 second with 50 second light off and 50 second light on at the 0 V potential as shown in figure 2b. MK-3/MK-4 sensitized TiO_2 electrodes display enhancing transient photocurrent density when compared to non-sensitized TiO_2 electrode due to the photogenerated electron-hole separation efficiency of D-π-A organic dyes [38]. Transient photocurrent densities for MK-3/TiO_2 and MK-4/TiO_2 photoelectrodes have been attained to 110 and 275 µA cm^{-1}, respectively, while non-sensitized TiO_2 electrode reached to 1 µA cm^{-2} [39]. These comparable photocurrent values of MK-3/TiO_2 and MK-4/TiO_2 could be cleared up by differences of intermolecular charge transfer properties [5].

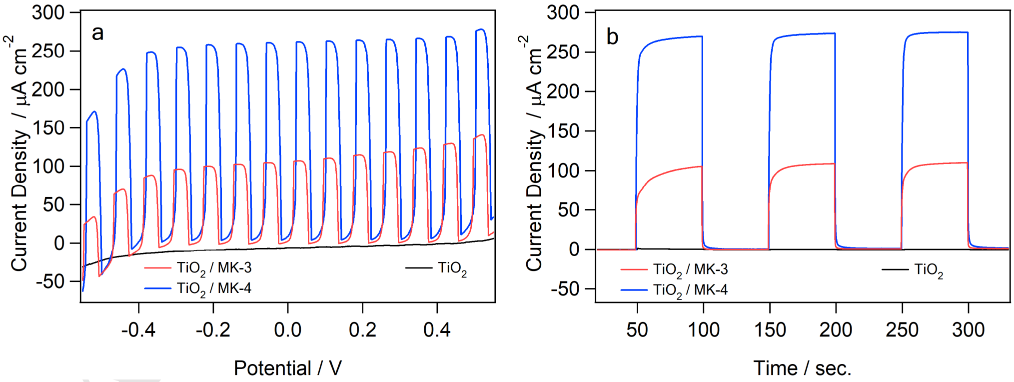


Figure 2. Photoelectrochemical response of TiO_2 (black line), TiO_2 / MK-3 (red line) and TiO_2 / MK-4 (blue line) by **(a)** LSV (at a scan rate of 100 mV s^{-1}) and **(b)** chronoamperometry techniques in the TEOA (5%) and Na_2SO_4 (0.1 M) solution at pH 9.

In addition, photoactivities of MK-3 and MK-4 dyes have been investigated by photocatalytic HER using dye/TiO_2 (10 mg) and aqueous TEOA (5%) solution as a photocatalyst and sacrificial electron donor, respectively, under solar simulator illumination (light limited by cut-off filter $\lambda \geq 420$ nm). First of all, optimal pH studies have been carried out under changing pH from 7 to 10. Among these pH values, the best HER activity has been shown at pH 9 according to the hourly evolved hydrogen amount (Figure S14 in SI). HER rates have been decreasing remarkably at more acidic or basic conditions. TEOA is protonated under pH values of 7, which leads to weakened giving electron of TEOA as a sacrificial electron donor agent. Hydrogen generation rates thermodynamically become unfavorable at strong alkaline media. These results have been also in accordance with the previous published papers using TEOA sacrificial electron donor [17, 26, 27, 40-43]. HER rates at the pH 9 have been found 427 $\mu molg^{-1}h^{-1}$ and 682 $\mu molg^{-1}h^{-1}$ for the MK-3/TiO_2 and MK-4/TiO_2, respectively. The differences of HER rates according to pH can be explained by electron donor roles of TEOA. The acidic pH of solution is inhibited the ability of electron donation due to the protonation of TEOA. The increasing pH of alkaline TEOA solution is lead to decrease in the HER rates because the driving force of HER from water (H^+/H_2) is become more negative at high pH [44-46]. The HER activities of dye sensitized TiO_2 have been also explored in the absence and presence of co-catalysts (Pt and Cu_2WS_4). Pt co-catalyst has been obtained by the reduction of H_2PtCl_6. The other co-catalyst ternary metal sulfide Cu_2WS_4 as an alternative to Pt has been supplied from our previous published papers [26, 47] and used as the PGM-free co-catalyst. The HER rates have been found as 427, 675, 1277, 682, 795 and 1027 $\mu molg^{-1}h^{-1}$ for the MK-3/TiO_2, MK-3/TiO_2/Cu_2WS_4, MK-3/TiO_2/Pt, MK-4/TiO_2, MK-4/TiO_2/Cu_2WS_4 and MK-4/TiO_2/Pt, respectively. The evolved amounts of H_2 have been figured out after 8 hour of photocatalytic HER for MK-3/TiO_2, MK-3/TiO_2/Cu_2WS_4, MK-3/TiO_2/Pt, MK-4/TiO_2, MK-4/TiO_2/Cu_2WS_4 and MK-4/TiO_2/Pt as the

2071, 3170, 15780, 3740, 4200 and 4972 μmolg^{-1}, respectively (Figure 3a-b). When using only TiO_2, Cu_2WS_4 or TiO_2/Cu_2WS_4, there is no H_2 evolved in the same conditions. This results shows that light is absorbed by only dye molecules. Photoelectrochemical and photocatalytic HER results in accordance with each other. The differences of HER rates using D-π-A organic dye sensitized TiO_2 have been related to structural variation of MK-3 and MK-4 dyes. The strong acceptor groups of the MK-3 and MK-4 are displayed similar properties for cyanocarboxylic acid that attached on the TiO_2 surface. On the other hand, the thiophene (MK-3) and furan (MK-4) spacers linked to this strong acceptor can be distinguished from their different electronegativity effect. Here, the electronegativity of the oxygen in the furan group is higher value than the sulphur in the thiophene group, so that intramolecular electron transfer activity and the photoactivity are more effective.

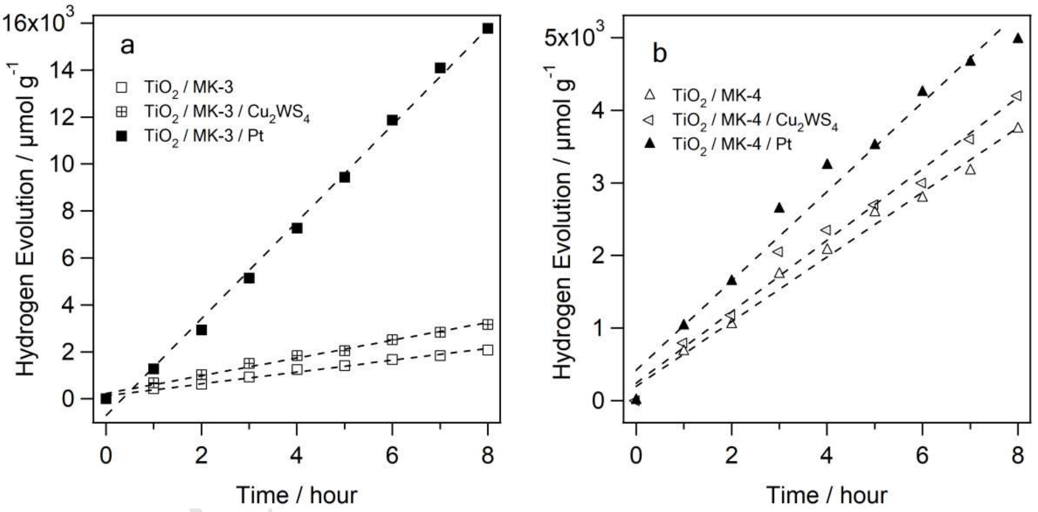


Figure 3. Photocatalytic hydrogen evolution activities of **(b)** TiO_2 / MK-3, TiO_2 / MK-3 / Cu_2WS_4, TiO_2 / MK-3 / Pt and **(c)** TiO_2 / MK-4, TiO_2 / MK-4 / Cu_2WS_4, TiO_2 / MK-4 / Pt (10 mg TiO_2 / dye; 20 ml TEOA (5%), pH=9).

3.3. The mechanism of Hydrogen Evolution Reaction

The mechanism of HER has been proceeded by electron transfer mechanism as displayed in the figure 4. This mechanism is taken place in three step: (i) Photons are absorbed by dyes and electrons excited from HOMO level to LUMO. (ii) Then, the photogenerated electrons are injected to conduction band (CB) energy level of TiO_2. These photogenerated electrons can be transfused to CB of co-catalyst in the presence of Cu_2WS_4, which is thermodynamically favorable since the CB of Cu_2WS_4 is located between CB of TiO_2 and redox level of H_2O/H_2 [26]. (iii) Finally, photogenerated electrons on the CB are reduced the water to produce H_2 gas, and holes on the oxidative state of the dye molecules are refilled with electrons by sacrificial electron donor TEOA to regenerate photocatalytic HER at the same time. Herewith, HER reaction is readily cycled according to electrochemical band levels of each component.

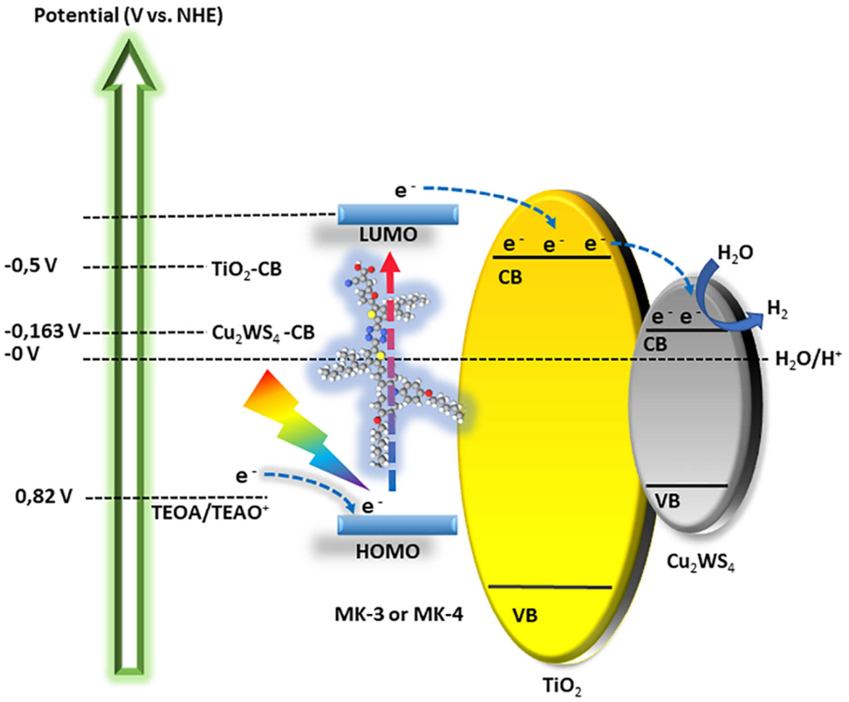


Figure 4. The proposed mechanism of HER by using dye sensitized TiO_2 as the photocatalyst in the presence of Cu_2WS_4 as the co-catalyst.

4. CONCLUSIONS

In conclusion, the photochemical HER has been investigated by using tetrazine based novel D-π-A type MK-3 and MK-4 dyes for the sensitization of TiO_2 photocatalyst in the absence and presence of co-catalysts (Pt or Cu_2WS_4). The photochemical HER differences can be attributed to the structural variation of MK-3 and MK-4 dyes. The thiophene (MK-3) and furan (MK-4) spacers linked to cyanocarboxilic acid acceptor give rise to the different electronegativity effect. MK-4 dye causes the more photoactivity for the HER due to the high electronegativity of the furan spacer group. In addition, photocatalytic activities of dye sensitized TiO_2 have been increased by addition of Cu_2WS_4 or Pt co-catalysts. The photoactivities shows that these D-π-A dyes (MK-3 and MK-4) may be used different solar energy conversion applications such as dye sensitized solar cells.

ASSOCIATED CONTENT

Supporting Information Available. Detailed synthesis, structural and elemental characterization of dyes, EDX spectra and SEM images of dye sensitized TiO_2, photoluminescence emission spectra of dyes and pH dependency of photocatalytic HER rates are given in Supporting Information.

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Figure and Scheme Captions

Figure 1. Absorption spectrums **(a-b)** and cyclic voltammograms **(c-d)** of MK-3 (red line) and MK-4 (blue line)

Figure 2. Photoelectrochemical response of TiO_2 (black line), TiO_2 / MK-3 (red line) and TiO_2 / MK-4 (blue line) by **(a)** LSV (at a scan rate of 100 mV s^{-1}) and **(b)** chronoamperometry techniques in the TEOA (5%) and Na_2SO_4 (0.1 M) solution at pH 9.

Figure 3. Photocatalytic hydrogen evolution activities of **(b)** TiO_2 / MK-3, TiO_2 / MK-3 / Cu_2WS_4, TiO_2 / MK-3 / Pt and **(c)** TiO_2 / MK-4, TiO_2 / MK-4 / Cu_2WS_4, TiO_2 / MK-4 / Pt (10 mg TiO_2 / dye; 20 ml TEOA (5%), pH=9).

Figure 4. The proposed mechanism of HER by using dye sensitized TiO_2 as the photocatalyst in the presence of Cu_2WS_4 as the co-catalyst.

Scheme 1. Synthetic pathway of the MK-3 and MK-4 dyes.

Table 1. EDX spectra data's of dye sensitized TiO_2

Table 2. Optical and electrochemical parameters of MK-3 and MK-4 dyes

- Tetrazine based two novel D-π-A organic dyes are synthesized for the first time
- First time MK-3 and MK-4 D-π-A dyes are used on photochemical hydrogen evolution
- Photoactivity differences are explained by changing spacer group
- HER rates are clarified by structural and optical properties of dyes