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ARTICLE TYPE

Ortho-Dihydroxyl-9,10-Anthraquinone Dyes as Visible-Light Sensitizers that Exhibit a High Turnover Number for Hydrogen Evolution

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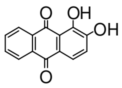
The cheap and organic ortho-dihydroxyl-9,10-anthraquinone dyes, such as Alizarin and Alizarin Red, sensitized Pt/TiO_2 achieved an approximate 10000 TON (TOF ＞250 h^{-1} for the first ten hours) during >80 hours of visible light irradiation (>420nm) when triethanolamine was used as the sacrificial donor. The stability and activity enhancements can be attributed to the highly serviceable two redox reactions involving the 9,10-dicarbonyl and ortho-dihydroxyl groups of the anthracene ring, respectively.

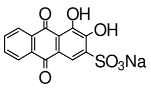
Photocatalytic H_2 evolution using solar energy, especially visible light from the sunlight spectrum, is a promising strategy for environmentally friendly energy production.[1] In this field, feasible catalysts that are efficient in the conversion of visible light in solar energy and are durable under long-time strong irradiation are essential.[2] Specifically, a desirable photocatalyst should have both a high TON (turnover number) and a high TOF (turnover frequency). Because of their excellent visible light absorbing abilities, organic dye sensitized Pt-loaded semiconductors (e.g., dye-Pt/TiO_2) can yield a high hydrogen evolution rate under visible light irradiation.[3-5] For example, NK 2045 sensitized Pt/TiO_2 gave a hydrogen evolution rate of 4200 μmol h^{-1} g^{-1} (catalyst) when triethanolamine (TEOA) was used as the sacrificial reagent.[6] However, the best visible light inorganic photocatalyst without any sensitization, such as $In_{1-x}Ni_xTaO_4$ (x=0–0.2), only reached ~30 μmol h^{-1} g^{-1} under identical irradiation.[7] Furthermore, the dye sensitized photocatalytic hydrogen evolution can be coupled with the semi-reaction of oxygen evolution through Z-scheme system, which is a promising approach for overall water splitting under visible light irradiation.[8] The assembly is expected to not only simplify the photocatalytic water splitting but also can improve the TON and TOF by modification of the organic dyes.[9]

Nevertheless, a common shortcoming of organic dyes, which is instability under long-time light irradiation, causes the TON of hydrogen evolution to be very low when compared with inorganic photocatalysts. Under a strong reductive atmosphere (underlying the H atom in the Pt/oxide system), the conjugated chromophore moiety within most organic dyes is easily hydrogenated and permanently fades. To date, the TON for the organic dyes loaded on Pt/TiO_2 systems is generally less than 150. One strategy has been to cross the classic organic dye Eosin Y on TiO_2 surface via covalence silane-coupling. This raised the TON from approximately 100 to 9000 (the reaction vessel was vacuumized every 7 hours to prevent the suppression of hydrogen evolution).[10] However, this treatment commonly results in a decrease in TOF because of the adverse ET along the σ covalence connection of the dye with the TiO_2. Here, we reported that a kind of 9,10-anthraquinone (AQ) dyes modified with ortho-dihydroxyl groups can achieve as high TON as these dyes covalently linked at Pt/TiO_2 but without any TOF loss.

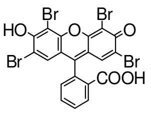
The system for H_2 production was prepared by dispersing Pt/TiO_2 (0.8% Pt w/w) powder into a solution containing the 9,10-AQ dyes, such as Alizarin Red (AR), and the sacrificial donor, triethylolamine (TEOA). The adsorption of the dye on the Pt/TiO_2 quickly reached equilibrium and nearly all of the added dye molecules (>99%) were absorbed by TiO_2 because of the adsorption capacities far from saturation under experiment conditions (Table S1). The absorptions of anthraqinone dyes (AR and Alizarin) sensitized Pt-TiO_2 were measured by UV-Vis diffuse reflectance spectra (Fig.S1).[11] H_2 generation experiments were conducted at room temperature under visible light irradiation (300W Xe lamp, $\lambda > 420$nm, pH=9) (details are shown in the supporting information (SI)). Eosin Y and Coumarin 343 (C-343), which were used as typical sensitizers for H_2 evolution following the reductive and oxidative mechanisms, respectively,[10,12,13] were also compared with the 9, 10-AQ dyes.



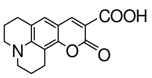
Alizarin



Alizarin red



Eosin Y



Coumarin 343

As shown in Figure1a, when the initial amount of each dye was constant (0.25μmol), the 9,10-AQ dye, AR, exhibited durable activity, and its TON increased to 6342 after 80 hours of uninterrupted irradiation with the 300W Xe lamp. Another 9,10-AQ dye, Alizarin, was employed to produce H_2 under identical conditions, and a TON of 6326 was observed for 92 hours irradiation (Fig. 1a). In addition, the TOF for both dyes was above 250 h^{-1} for the first ten hours, and then it decreased with the inactivation of the dye molecules. If the reaction system was exposed to air for a few minutes after every 6 hours irradiation and then evacuated before the next run, the TON of the AR even increased to approximately 10000 (shown in Fig. 1b and Table S2). To our knowledge, few organic dyes exhibit the ability to steadily produce H_2 with both a high TON and TOF. In contrast, the TON of H_2 evolution for the Eosin Y and C-343 sensitized

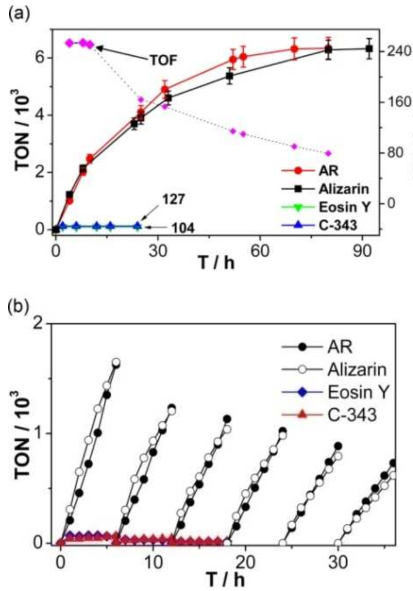


Figure 1. TONs of hydrogen evolution of the dye sensitizers, AR, Alizarin, Eosin Y and C-343 under continuous irradiation. The corresponding TOF of AR is shown in (a) and intermittent irradiation is shown in (b) for the reaction vessels that were exposed to air and then evacuated every 6 hours. In (a), TOF=TON/irradiation time. The hydrogen evolutions of Eosin Y and C-343 were only recorded for three runs in (b) because the amounts of produced hydrogen were below the detection limit. Hydrogen evolution conditions: 100ml 0.6mol/L TEOA aqueous solution, pH=9.0, 100mg Pt/TiO$_2$, 0.25µmol dye, 300W Xe lamp, λ> 420nm.

system only reached 104 and 127, respectively, after 2h irradiation under identical conditions. With the irradiation time extended to 24 hours, no additional H$_2$ accumulation occurred for these two dyes, which is consistent with a previous report of their TONs.[8,10] Corresponding to the TONs of the suspension systems, the photocurrent measurements, based on the dyes sensitized TiO$_2$ working electrodes (prepared by spinning P25 suspension on ITO glasses, details shown in SI), also exhibited a similar trend. Both AR and Alizarin sensitized electrodes retained almost constant photocurrent during four turns, while decreases of approximately 40~50% were observed in the photocurrents for the Eosin Y and C-343 sensitized electrodes over the four runs (see Fig.S2). The 9,10-AQ dyes sharply increased the TON and maintained the photocurrent for several runs, suggesting that their structures were available for long-term stable conversion of optical energy for hydrogen evolution.

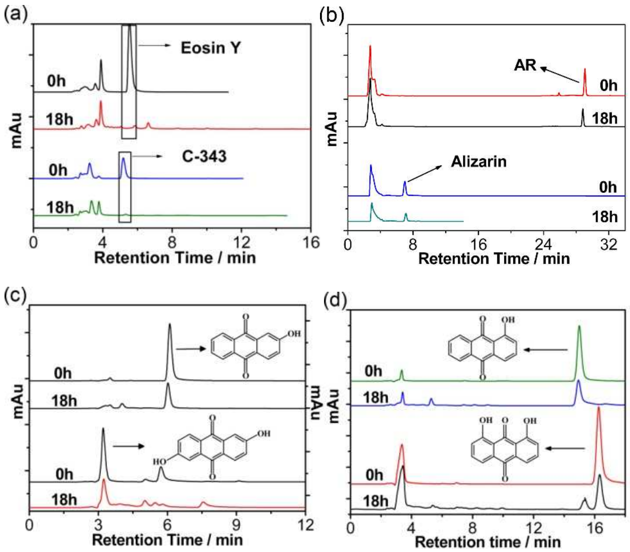
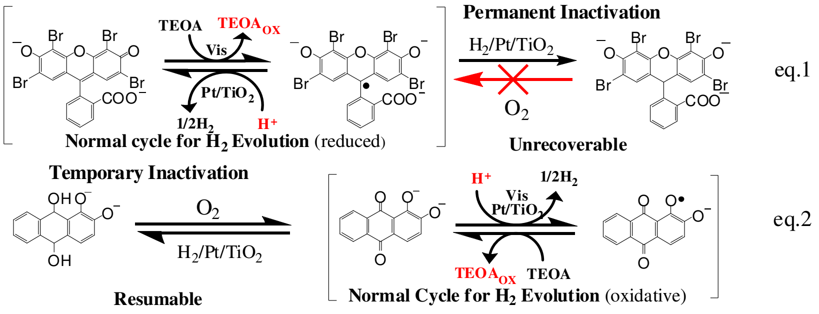


Figure2. HPLC spectra of the dye sensitizers before and after 18h under visible light irradiation: (a) Eosin Y and Coumarin 343; (b)AR and Alizarin; (c) 2-hydroxyl (right Y axis) and 2,6-dihydroxyl AQ; (d) 1-hydroxyl and 1,8-dihydroxyl AQ. The reaction conditions are provided in the supporting information.

To further determine the stability of the dyes mentioned above, we examined the dye molecules in the solution under H$_2$ evolution conditions by using high performance liquid chromatography-mass spectrometry (HPLC-MS) before (upon stirring for 18 hours in the dark for the adsorption/desorption equilibrium) and after 18 hours of irradiation (the experimental details are given in SI) (Fig. 2). Because the same amount of each dye was added initially, the remaining dye in the solution was determined after the separation of the Pt/TiO$_2$ powder. The results showed that most of the Eosin Y disappeared after 18 hours irradiation (Fig. 2a). However, no degradation products from Eosin Y were observed in the HPLC spectra (the wavelength of the UV/Vis detector was fixed at 254nm). Thus, irreversible destruction of the conjugated xanthene ring in the Eosin Y resulted from catalytic hydrogenation under the concomitant environment of H$_2$-Pt/TiO$_2$ (eq.1).[10] Additionally, after 18 hours of irradiation most of the C-343 (<5% left) was transformed into a product with a MW=304 (Fig. 2a). This mass is assigned to a hydroxylated product of C-343. Considering that the added dyes were divided into two portions in the system (free in solution and absorbed by TiO$_2$ particles) during the H$_2$ generation processes, the diffuse reflectance spectra were measured for the Pt/TiO$_2$ catalysts that were separated from the suspension systems irradiated for 18h. No corresponding absorption peaks for the adsorbed Eosin Y and C-343 were found (Fig. S3). Thus, all the added Eosin Y and C-343 were definitely damaged. In contrast, in these 9,10-AQ dye systems, approximately 60% AR or 55% Alizarin including these recovered from AQH$_2$ was undamaged after 18 hours of irradiation (Fig. 2b). The LC-MS results confirmed that the 9,10-AQ dyes were more stable than Eosin Y and C-343 during the hydrogen evolution process. During further

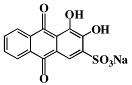
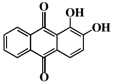
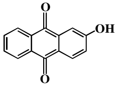
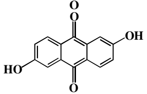
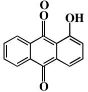
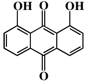


HPLC-MS analysis of the AR system, a few products with MW=321 were detected in the mass spectrum, which were easily identified to anthrahydroquinone (AQH_2) formation (eq.2). Most of the disappeared AQ in the solution was not decomposed and was instead transformed into a steady reduction state, AQH_2, via 2e-reduction coupled with proton transfer. A portion of the 9,10-AQ dyes were temporarily deactivated due to transformation into AQH_2,[14] but the oxidative dehydrogenation easily proceeded under aerobic conditions at room temperature (as eq.2). This process was confirmed by the partial recovery of the colours in the irradiated suspensions of AR and Alizarin after the systems were opened to the air (Fig.S4). Indeed, this was further demonstrated by the improvement of the TON for AR when the reaction suspension was exposed to the air for a few minutes every 6 hours (10000 TON in Table S2 compared to 6300 in Fig. 1a). The presented AQH_2/AQ cycle also coincides with the well-known Riedl-Pfleiderer process.[15] A 9,10-AQ molecule is hydrogenated to the corresponding AQH_2, which is then oxidized by air to the original AQ. Based on the AQH_2/AQ cycle, the 2-alkyl-9,10-AQ is commercially used as a carrier to produce millions of tons of H_2O_2 every year.[16]

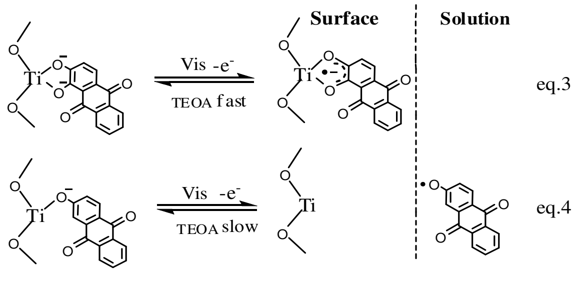
To support the conclusion that the 9,10-AQ framework is universally able to resist hydrogenated deactivation from the H_2-Pt/TiO_2 by the AQH_2/AQ cycle, we selected other hydroxyl substituted 9,10-AQ dyes to observe their stability for H_2 production. As displayed in Fig. 2c and Fig. 2d, all these AQ dyes were >40% was undamaged including these recovered from AQH_2. Although the corresponding AQH_2 was difficult to be detected using HPLC-MS because of their short lifetimes in the air, quick recovery of their colours were easily observed when these systems were opened to the air (Fig. S4) and produced H_2O_2 could be detected through UV-vis spectrum method catalyzed by Horseradish peroxidase (POD) (Fig. S5).[17] The results clearly indicate that the stability and recovery ability are universal characteristics of the 9,10-AQ dyes. In contrast, Eosin Y and C-343 sensitized systems did not return to their initial colors after the 18 hours of H_2 production regardless of introducing dioxygen into the reaction systems (see Fig.S4), suggesting that their conjugated -C=C- bonds were easily broken and difficult to recover via the dehydrogenation reaction with O_2 at room temperature.

Despite their excellent stability, not all the 9, 10-AQ dyes displayed high H_2 generation. Compared with the >250h^{-1} TOF for both AR and Alizarin that have the ortho-dihydroxyl substituent groups, the 2-hydroxyl and 2,6- dihydroxyl substituted 9,10-AQ produced a TOF of approximately 30 h^{-1}(see Table 1). However, 1-hydroxyl and 1,8-dihydroxyl substituted 9,10-AQ exhibited almost no H_2 evolution. These results indicated that only ortho-hydroxyl-modified 9,10-AQ can exhibit high activity for H_2 generation. We aim to explain why the ortho-hydroxyl substituted 9,10-AQ dye, such as AR, Alizarin, kept the highest efficiency of H_2 generation (represented by TOF). Generally, the ortho-dihydroxyl-9,10-AQ dyes attached to the same titanium site of the TiO_2 surface via a bidentate chelating binding mechanism (eq.3),[18] and this coordination linkage was available for the injection of excited electrons into the conduction band (CB) of TiO_2.[18,19] In addition, even in its SQ radical state that is formed through an oxidative mechanism, an ortho-dihydroxyl-9,10-AQ dye can be still bound to the TiO_2 surface by the resonant anion radical (eq.3). In contrast, mono-hydroxyl- or other di-hydroxyl-substituted 9,10-AQ dyes will easily depart from the TiO_2 surface once they are transformed into SQ radicals because their electrically neutral state is unfavourably bounded to the coordination Ti^{4+} site of TiO_2 (eq.4). A bound dye on the TiO_2 surface always exhibits a higher probability of electron injection into the TiO_2 than free dyes once the SQ radicals are quenched by TEOA. The consequences of the rates of generating and quenching SQ radicals must be revealed in the sensitizer recycle rate, i.e., TOF of H_2 generation. Therefore, we systemically researched the properties of these SQ radicals and compared the reactivity of the ortho-hydroxyl-substituted SQ radicals (with TEOA) to other non-ortho-substituted radicals that underwent in situ photo-irradiation ESR experiments (Fig. 3a).

Table 1.The reaction constants with TEOA, intrinsic lifetimes, and the corresponding TOFs of H_2 evolution for the formed semiquinone (SQ) radical.[a]

9,10-AQ dyes	K [b]/10^3·L·mol^{-1}	τ[c]/s	TOF[d]
	5.02	0.76	284
	4.89	1.51	265
	1.01	3.18	30
	1.64	0.64	37
	0.367	1.80	trace
	0.509	3.44	trace

[a] The ESR experimental details are given in the SI. [b] K is the reactive constant of the SQ radicals that react with TEOA. [c] τ is the lifetime of the SQ radicals at the temperature of 243.5K. [d] The TOF for the first 3h.TOF= TON/irradiation time. Hydrogen evolution from 100ml of solution containing 0.25μmol of dye was carried out for 3h using a 300W Xe lamp with a 420nm cut-off filter, pH=9.0.



As our previously reported, the SQ radicals, which are formed via electron injection of the AR dye into the conduction band (CB) of TiO_2, could be easily observed by ESR in a fluoromethylbenzene solvent at room temperature.[20] In the present aqueous solution, all the radicals from these 9,10-AQ dyes were unable to be recorded by ESR at room temperature, but they were successfully observed using a highly sensitive cavity at

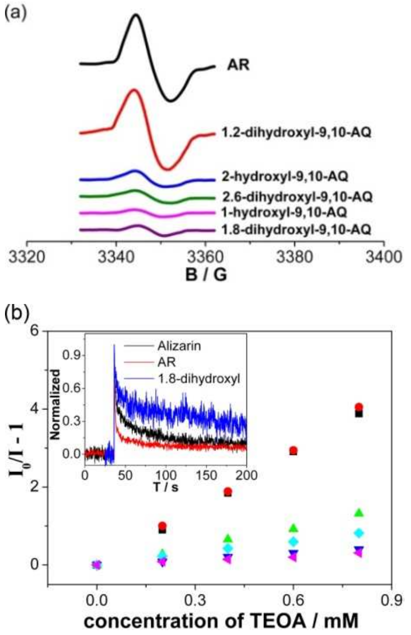


Figure 3.(a) ESR signals of different SQ radicals.(b) The curves of SQ radicals quenched by TEOA. ●: AR; ■: Alizarin (1,2-dihydroxy~); ▲: 2,6-dihydroxyl~;◆: 2-hydroxyl~; ▼: 1,8-dihydroxyl~;○: 1- hydroxyl~. I_0: intensities of organic radicals without TEOA; I: intensities of organic radicals with TEOA of different densities added. $(I_0/I) = K\ [TEOA] +1$. T=243.5K. Inset of Figure 3b shows the signal relaxation of different AQ dye radicals without TEOA.

the temperature of 243.5K (details shown in SI). According to the spectra (shown in Fig.3a), the six AQ dyes yielded a similar radical signal ($g \approx 2.0067$) when they were irradiated by a 532nm laser at 243.5K. The intensities of the signal from AR and Alizarin with the 1,2-dihydroxyl groups are an order of magnitude higher than those of the other systems under identical conditions. This indicated that the excited electron injection from the two ortho-dihydroxyl-AQ dyes to TiO_2 is more efficient than that from other 9,10-AQ dyes. Thus, this result is most likely related to the binding manner between the dye coordination group(s) and the semiconductor interface because these dyes had uniform characteristics including a chromophoric AQ skeleton and anchor group(s) of hydroxyls. Exceptions included their numbers and substituted position.

The intrinsic lifetimes of these AQ radicals were recorded by ESR and are listed in Table 1. When these formed active SQ radicals were quenched with TEOA, the relationship between the ratios of the decrease of radical signal intensities (I_0/I) and the concentrations of TEOA all displayed a linear function as shown in Figure 3b. The reaction constants (K) (listed in Table 1) were consistent with the TOFs of these AQ dyes. The K for the radicals from AR was 5.02×10^3 with a corresponding TOF of 284, whereas the K for the radical from the 1,8-dihydroxyl AQ was ~510 with a corresponding TOF of near zero. Thus, the ET efficiency between the formed SQ radicals and the TEOA electron donor was a key factor for the TOF for H_2 evolution. The 9,10-AQ dyes substituted by the ortho-dihydroxyl provided the most effective ET into the TiO_2 and the biggest K, which resulted in the highest TOF for H_2 evolution among these hydroxyl-substituted AQ dyes.

Conclusions

In summary, 9,10-anthraquinone dyes modified with ortho-dihydroxyl groups are able to operate hydrogen evolution with dramatic high TON (~10000) and without decrease of TOF (＞ $250h^{-1}$), which provides new and useful guidelines for designing better organic dye frameworks that are sensitized for solar energy conversion.

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Notes and references

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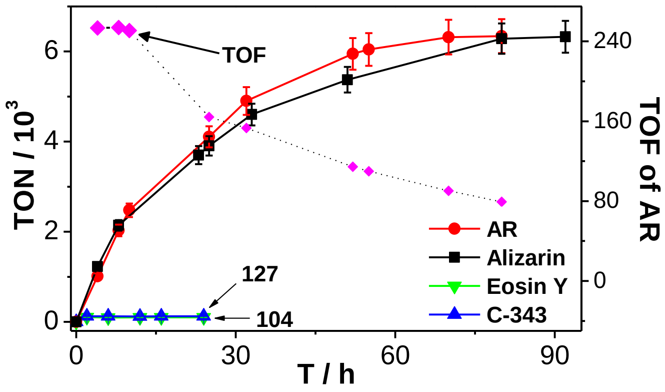

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