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Enhanced photocatalytic H_2 generation on noble metal modified TiO_2 catalysts excited with visible light irradiation

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Abstract Photocatalysts were prepared by the deposition of noble metal nanoparticles (Au, Pt, Rh or Ru) on different commercially available titanias. The photocatalytic performance of these catalysts was studied for the evolution of H_2 during excitation with visible light. Experiments were carried out in irradiated suspensions containing various organic compounds. Noble metal nanoparticles can promote the lowering of the overvoltage of H^+ reduction. The noble metal nanoparticles were deposited onto the TiO_2 surface by in situ chemical reduction in a quantity of 1 wt%. Three aspects were considered: (i) the photocatalytic performance of different bare TiO_2 deposited with Pt; (ii) the effect of the deposition of Au, Pt, Rh or Ru nanoparticles onto the TiO_2 surface; and (iii) choosing the most suitable H_2 production supporting organic compound. The rate of H_2 evolution proved to be strongly dependent on the quality of TiO_2 powder and the presence of different organics. The applied noble metal was also an efficiency determining factor during these photocatalytic reactions. With the best combination of the above mentioned circumstances, we achieved promising results to be able to effectively harvest the energy of sunlight.

Keywords TiO_2 · Photocatalytic H_2 production · Noble metals · Visible light · Oxalic acid

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Introduction

There is a steadily increasing demand for clean and environmentally friendly energy resources. The production of H_2 is of great importance to meet future needs. The combustion of gaseous H_2 results only in the formation of water (without CO_2 emission), while relatively high energy becomes available. The use of heterogeneous photocatalysis may offer a sustainable solution for the indirect storage of solar energy via producing H_2 gas from water [1, 2]. TiO_2 photocatalysts can be excited with UV photons, though in most cases, bare TiO_2 has low efficiency for direct photocatalytic water splitting when irradiating them with visible light. While natural sunlight contains only $\sim$4% UV irradiation, the quantity of visible photons comprises nearly 40%. For practical purposes, this high-intensity photon flux should be harvested effectively. The overvoltage of H_2 evolution and the recombination rate of electron-hole pairs can be lowered by depositing noble metal co-catalyst particles onto the TiO_2 surface [3]. Numerous publications have reported on the use of Pd [4, 5], Pt [6–9], Ru [10], Rh [4], Au [11, 12] and Ag [13] to enhance the photocatalytic performance of TiO_2. These nanoparticles can readily be synthesized and precipitated from their precursors through applying chemical reducing agents [14, 15]. From the aspect of cost-effectiveness, a noble metal content of 1 wt% [16–18] or below [5, 8, 19] is considered optimal and sufficient for a significant increase in photocatalytic activity. Higher quantities of noble metal particles on TiO_2 can block the active sites. Several other factors also may influence the overall rate of H_2 production, e.g. the surface properties and particle size of the catalyst and the reaction temperature. A noteworthy increase in reaction rate is observed in the presence of easily oxidizable organic compounds (especially water–alcohol mixtures) rather than using only pure water [6, 8, 20–27]. These electron donors (sacrificial reagents) react irreversibly with the photoinduced holes, resulting in suppressed electron-hole recombination and O_2/H_2 back-reaction rates. As the organic content of the suspension is completely mineralized, the H_2 evolution rate falls back dramatically. In the study published by Yang et al. [4], different alcohols were compared for photocatalytic H_2 production. Over Pt–TiO_2, the evolution of molecular hydrogen showed the following trend: methanol $\approx$ ethanol $>$ propanol $\approx$ isopropanol $>$ n-butanol. Despite alcohols are the most investigated compounds in this area of photocatalysis, some carboxylic acids may serve as suitable hole scavengers, e.g. formic acid [28], chloroacetic acid [9] or oxalic acid [29].

In terms of environmental benefit, a combination of the disposal of organic industrial waste products with the production of gaseous H_2 would be highly advantageous. Although huge efforts have been devoted to increasing the performance of noble metal deposited TiO_2, the process still needs to be improved to make it suitable for industrial application. The aim of the present work was to find optimized reaction circumstances and developed photocatalytic processes through which to harvest the energy of sunlight efficiently. The main objective was to compare the H_2 evolution rates of the photocatalysts during excitation with visible light. Three different factors that can be crucial in photocatalytic H_2 evolution were considered: the roles of different TiO_2 bare catalysts, the type of the noble metal nanoparticles on the TiO_2 surface, and the nature of the organic sacrificial agent present during the photocatalytic reaction. Widely used titanias and common organic compounds were compared in an effort to optimize the reaction rates.

Materials and methods

Catalyst preparation

Six commercially available TiO_2 photocatalysts were used as bare catalysts: Aeroxide P25 (TiO_2–P25, Evonik Industries), Aldrich anatase (TiO_2–AA, Sigma-Aldrich Co.), Aldrich rutile (TiO_2–AR, Sigma-Aldrich Co.), Kronos vlp 7000 (TiO_2–VLP7000, Kronos-Titan GmbH), Nanomaterials rutile (TiO_2–NR, US Research Nanomaterials Inc.) and Sumitomo TP-S201 anatase (TiO_2–TP-S201, Sumitomo Chemical Inc.) (Table 1). TiO_2 photocatalysts modified with 1 wt% (m_M/m_{TiO_2}) noble metal (Au, Pt, Rh or Ru) were prepared. This particular noble metal content was selected because photocatalytic activity is often optimal at around 1 wt% noble metal loading. Noble metal nanoparticles were deposited onto the TiO_2 surface by in situ chemical reduction. The concentration of the TiO_2 suspension was 5 g/L, while the quantity of noble metal precursor ($HAuCl_4$, H_2PtCl_6, $RhCl_3$ or $RuCl_3$) was calculated to result in the desired noble metal loading on the photocatalyst. Trisodium citrate ($c_{citrate,\ final} = 1.25 \times 10^{-4}$ M) was utilized to stabilize the growth of the noble metal nanoparticles and to achieve a nearly monodisperse size distribution. Finally, freshly prepared, ice-cold $NaBH_4$ solution was added as a reducing agent ($c_{NaBH_4,\ final} = 3 \times 10^{-3}$ M). The suspensions were thermostated at 20 °C during the reaction. The syntheses were carried out for 1 h in the dark. The catalysts were then washed by centrifugation, and the particles were resuspended in oxalic acid solution (1.0×10^{-3} M) to improve the sedimentation and to eliminate the residual chloride and sodium ions. The final suspensions were used fresh for the photocatalytic tests without any further purification.

All the syntheses and photocatalytic experiments were carried out in *Millipore MilliQ* ultrapure water as medium.

Table 1 Properties of the investigated commercially available TiO_2 powders

Name	Anatase (wt%)	Rutile (wt%)	BET (m^2/g)	Average particle size (nm)
Aeroxide P25 (TiO_2–P25)	90	10	50	26.8
Aldrich anatase (TiO_2–AA)	100	–	9.9	>85
Aldrich rutile (TiO_2–AR)	4	96	2.7	315
Kronos VLP7000 (TiO_2–VLP7000)	100	–	297	7.8
Nanomaterials rutile (TiO_2–NR)	–	100	n.a.	30
Sumitomo TP-S201 (TiO_2–TP-S201)	100	–	80	17.3

The average particle size of the bare catalysts were determined by XRD measurements

Characterization of the catalysts

Diffuse reflectance spectroscopy (DRS)

The UV–VIS reflection spectra ($\lambda = 300$–800 nm) of the photocatalyst powders were measured with a JASCO-V650 spectrophotometer equipped with an integration sphere (ILV-724). The possible electron transitions were evaluated by plotting $dR/d\lambda$ vs. λ, where R is the reflectance and λ is the wavelength. DRS measurements were carried out with TiO_2 powders in a cuvette.

Transmission electron microscopy (TEM)

The average size of the noble metal nanoparticles deposited on the TiO_2 surface was calculated from TEM images recorded with a 100 kV *Phillips CM 10* instrument. The catalyst samples were investigated immediately after preparation.

H_2 production measurements

The freshly prepared, washed catalyst was suspended in a 50 mM solution of the hole scavenger organic compound, which was poured into a glass reactor (total volume: 150 mL). The VIS photoexcitation was achieved through the surrounding ten 15 W lamps (400–480 nm, $\lambda_{max} = 425$ nm). The light emitted by the lamps contained a minimal amount of a 380–400 nm UV component, which was completely filtered out through the use of 0.1 M $NaNO_2$ solution circulating in the reactor mantle. The well-stirred suspension ($c_{catalyst} = 1$ g/L) was purged with N_2 carrier gas at a flow rate of 50 mL/min to ensure O_2-free conditions. The reactor was connected through a PTFE tube to a *Hewlett Packard 5890* gas chromatograph fitted with a 5 Å molecular sieve column and a thermal conductivity detector. Gas samples were taken with a 2 mL sampling valve to provide high fidelity for the measurements. The rate of H_2 evolution was calculated with regard to the GC calibration (carried out with certified 5% H_2:N_2 gas) and the N_2 flow rate.

Results and discussion

Photocatalytic H_2 production using different types of TiO_2

There are numerous types of commercially available TiO_2 catalysts on market. As a consequence of the differences in the production methods, these catalysts differ considerably in particle size, crystalline phase, specific surface area and other specific surface properties, all features which may influence the photocatalytic performance appreciably. We investigated six widely used TiO_2 catalysts from the aspect of their suitability for photocatalytic H_2 production during irradiation with visible light. Under the reaction circumstances described above, the photocatalytic activity of pure TiO_2 is negligible, whereas the photocatalytic properties of Pt deposited TiO_2 is emphasized frequently. Thus, Pt nanoparticles were chemically reduced onto the TiO_2 surface at a level of 1 wt% to enhance the rate of H_2 evolution. The syntheses were carried out in a similar way for all the TiO_2 catalysts. During the photocatalytic tests, the reaction mixture contained an initial concentration of 50 mM oxalic acid as sacrificial reagent. In the case of Pt–TiO_2–AR, substantially higher initial rates of H_2 production were detected, which had diminished to a steady-state level after the first 2 h of irradiation (Fig. 1a).

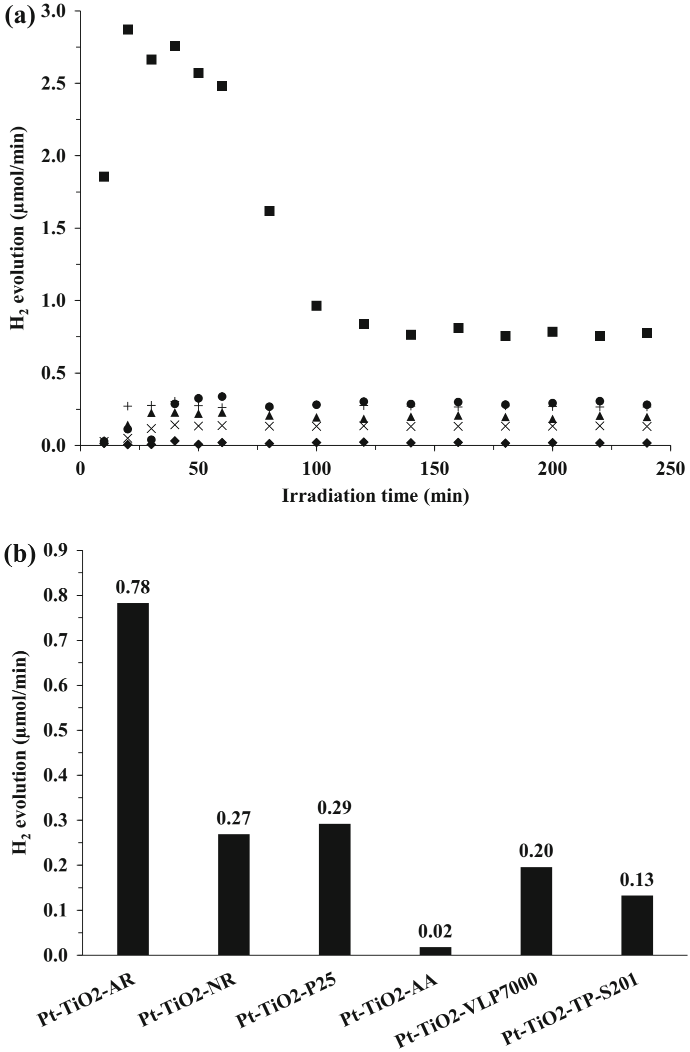

Fig. 1 **a** H_2 evolution from oxalic acid solution ($c_{initial} = 50$ mM) using Pt deposited on (*filled square*) TiO_2–AR, (*filled circle*) TiO_2–P25, (*plus*) TiO_2–NR, (*filled triangle*) TiO_2–VLP7000, (*times*) TiO_2–TP-S201 or (*filled diamond*) TiO_2–AA catalysts (1 g/L)—VIS irradiation (400–480 nm, $\lambda_{max} = 425$ nm). **b** Average H_2 evolution rates (120–240 min of irradiation) on the use of different commercially available bare TiO_2 photocatalysts deposited with 1 wt% Pt (1 g/L) in the presence of 50 mM oxalic acid—VIS irradiation (400–480 nm, $\lambda_{max} = 425$ nm)

According to our previous measurements, this significant decrease also can be observed in H_2 production rates when the Pt–TiO_2 catalyst is irradiated with UV light [30]. It was confirmed by TEM measurements that the average particle diameter and size distribution of platinum does not change considerably during irradiation. Furthermore, it was proven by ICP measurements that the detachment and dissolution of Pt from the TiO_2 surface is negligible (below 2 ppb in the solution phase from the total concentration of 10,000 ppb). Raising the carrier gas flow rate causes an elongated maximum of H_2 production, while low N_2 flow rate (25 mL/min) resulted in the complete disappearance of the initial maximum values in the investigated time frame. At the later stages of the experiments ($t > 50$ min), the steady state H_2 evolution rates were nearly identical. A possible explanation of the phenomenon can be that in the first period of irradiation, the hydrogen generation is regulated by the varying potential of H-electrode established by the dissolution of hydrogen in Pt [31]. At higher carrier gas flow rates, this process is limited. Therefore, the overpotential of hydrogen evolution can remain in an optimal range for a longer timeframe, while with lower N_2 flow the equilibrium redox potential can be achieved faster.

In view of the shape of the H_2 evolution curves, the steady-state results were averaged and compared for the 120–240 min period of the measurements (Fig. 1b). The H_2 evolution rate was appreciably better using Pt–TiO_2–AR than with the other commercially available TiO_2 based samples.

During visible light excitation, considerable H_2 evolution was observed only in the cases of the rutile-containing catalysts. The DRS spectra of these catalysts clearly reveal that Pt–TiO_2–AR is more easily excited with photons above 400 nm, while Pt–TiO_2–NR and Pt–TiO_2–P25 are more likely to absorb photons in the near UV (<400 nm) according to the dR/λ vs. λ plots (Fig. 2). The effect is possibly due

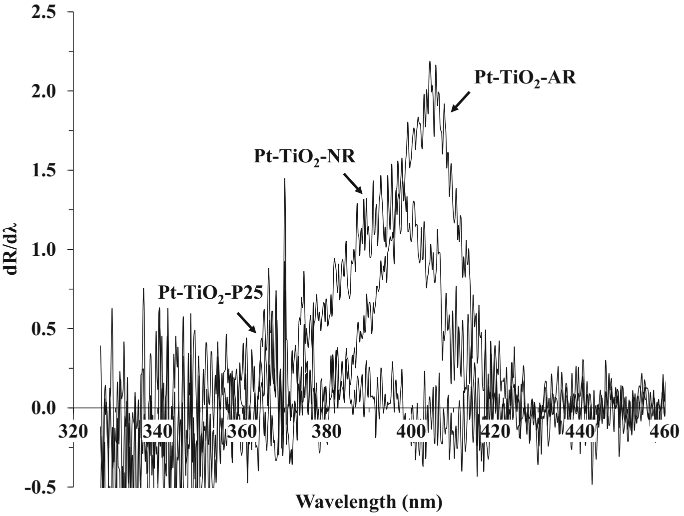

Fig. 2 Reflectance as a function of irradiation wavelength for Pt-modified rutile-containing TiO_2 photocatalysts (DRS measurements). *Peaks* represent the band gap energies of each catalyst

to that the size reduction of a semiconductor crystal is accompanied with band gap widening—in the literature, the so called blue shift. When having semiconductor crystals with lower particle size (but the same crystalline phase), higher absorbed quantum energy is required to excite electrons from the valence band into the conduction band, and this results in absorption edge shift [32].

Effect of different noble metal nanoparticles deposited on TiO_2–AR

For further photocatalytic experiments, TiO_2–AR was chosen as bare catalyst and 1 wt% Au, Pt, Rh or Ru nanoparticles were deposited onto the TiO_2 surface by the identical chemical reduction synthesis method. The average diameters of the

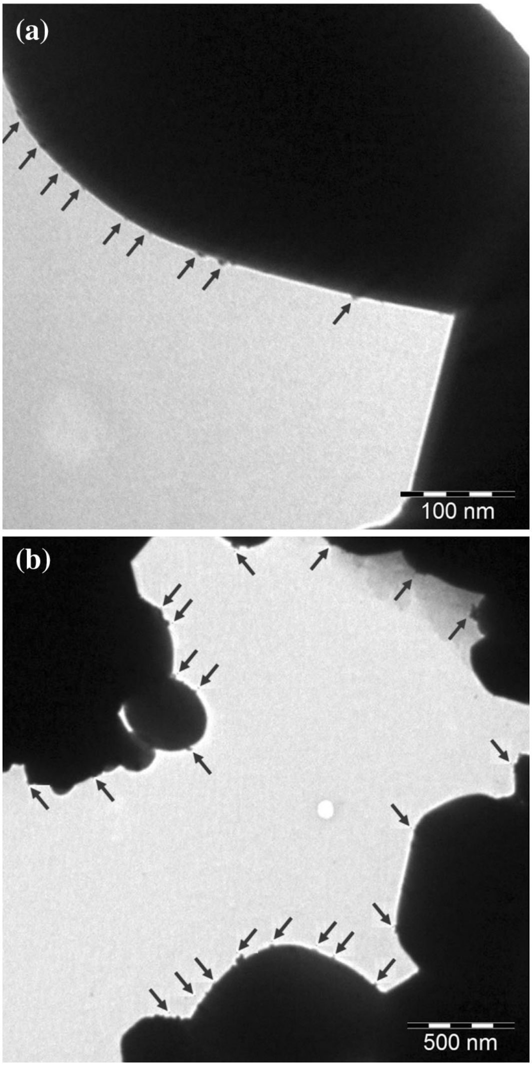

Fig. 3 TEM images of **a** Pt–TiO_2–AR and **b** Rh–TiO_2–AR photocatalysts. *Arrows* indicate possible noble metal islands on the TiO_2 surface

resulting noble metal nanoparticles (determined using TEM) were 5.7, 5.4, 8.1 and 9.2 nm, i.e. almost two orders of magnitudes smaller than the average TiO_2–AR particles (Fig. 3). This means that several noble metal islands are situated on each rutile particle, and this can greatly enhance the charge separation during the photoreactions. The dispersion of the noble metal nanoparticles on the TiO_2 surface was nearly consistent.

All of the photocatalytic measurements in this series were carried out in the presence of 50 mM oxalic acid. Our results demonstrated that all of the above-mentioned noble metals on TiO_2–AR are suitable for the promotion of H_2 evolution from oxalic acid during visible light excitation (Fig. 4). The photon absorption properties were almost the same for each catalyst (Fig. 5), although the best-performing 1 wt% Pt–TiO_2–AR resulted in nearly three times more evolved H_2 than in the case of Au–TiO_2–AR. The reduction of the hydrogen ions is strongly dependent on the material quality of the deposited noble metal. Using different noble metals results in different overvoltage for hydrogen generation. Platinum group metals such as Pt, Rh, and Ru reduce this overvoltage to near 0 V. This phenomenon can explain why using Au deposited samples resulted in three times less evolved H_2 [33].

Photocatalytic H_2 production in the presence of various organics

Pt–TiO_2–AR exhibited pronounced photocatalytic activity in the presence of oxalic acid. We examined the possibility of finding an even more suitable organic sacrificial reagent with which to enhance the rate of H_2 evolution. Seven common, readily oxidizable organic compounds (Table 2) were compared under identical

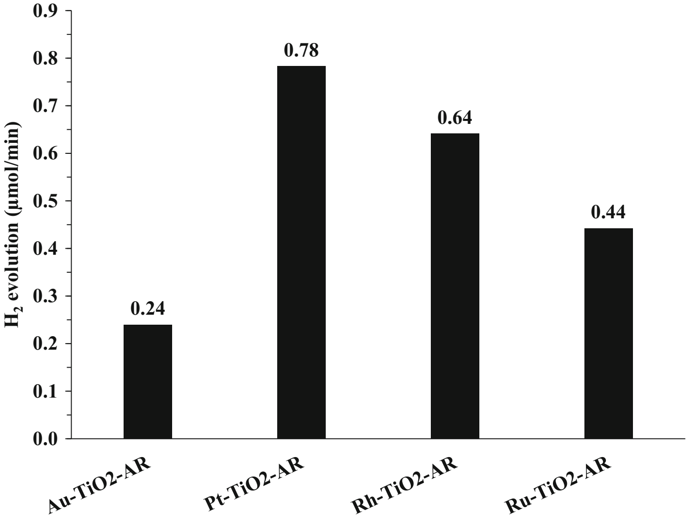

Fig. 4 Average H_2 evolution rates in the 120–240 min period of irradiation on different noble metal-modified TiO_2–AR photocatalysts (1 g/L). Sacrificial reagent: oxalic acid ($c_{initial} = 50$ mM)—VIS irradiation (400–480 nm, $\lambda_{max} = 425$ nm)

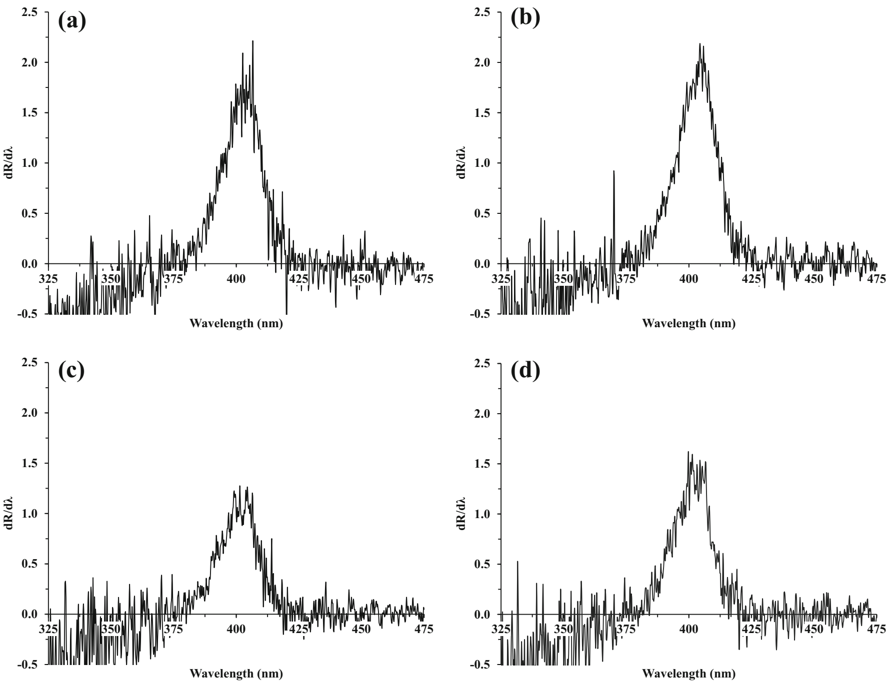

Fig. 5 Excitation wavelengths of different noble metal-modified TiO_2–AR catalysts according to DRS measurements: **a** Au–TiO_2–AR, **b** Pt–TiO_2–AR, **c** Rh–TiO_2–AR, **d** Ru–TiO_2–AR

Table 2 Properties of the organic compounds that were used as sacrificial reagents during photocatalytic H_2 generation

Name	Molecular formula	Acidity (pK_a)	pH of 50 mM solution
Oxalic acid	$C_2H_2O_4$	1.25; 4.14	2.01
Formic acid	CH_2O_2	3.77	2.50
D,L-Lactic acid	$C_3H_6O_3$	3.86	2.45
D-Glucose	$C_6H_{12}O_6$	–	5.90
Acetaldehyde	C_2H_4O	13.57	3.39
Methanol	CH_4O	15.5	4.33
Ethanol	C_2H_6O	15.9	5.01

reaction conditions. The steady-state H_2 evolution rates are presented in Fig. 6. The use of lactic acid as a sacrificial electron donor in the reaction mixture instead of oxalic acid resulted in an outstanding H_2 production, nearly four times higher. The presence of formic acid also led to a marked enhancement of the photocatalytic formation of H_2. It appears that the application of substances with an acidic character as sacrificial agents instead of the alcohols mostly studied in the literature may be favorable. Our concept was to increase the amount of H^+ in water by decreasing the pH. However, the oxidational step also means a speed limiting factor

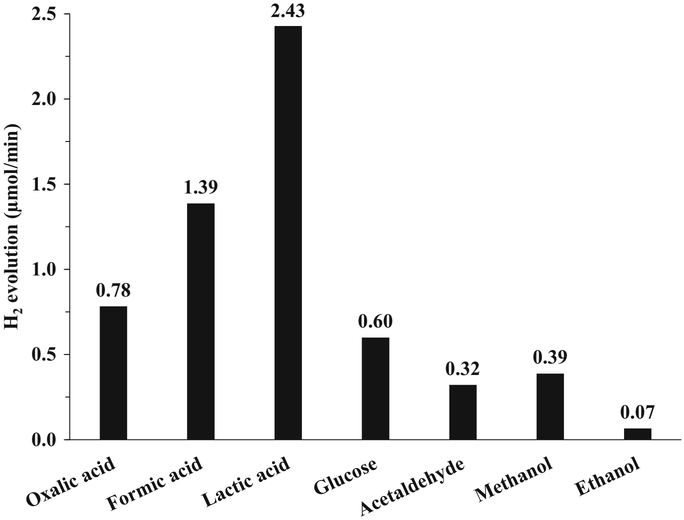

Fig. 6 H_2 evolution rates on Pt–TiO_2–AR photocatalysts (1 g/L) in the presence of various sacrificial reagents ($c_{initial} = 50$ mM)—VIS irradiation (400–480 nm, $\lambda_{max} = 425$ nm)

for H_2 generation. By using organic acids as a model component, we ensured the higher amount of H^+ in water and the presence of an easily oxidizable reaction partner.

Conclusions

Commercially available TiO_2 photocatalysts deposited with noble metal nanoparticles were examined for their applicability in photocatalytic H_2 production during visible light irradiation. An effective set of reaction conditions were identified: considerable H_2 generation was observed when catalysts were used with rutile content. Pt-modified Aldrich rutile demonstrated outstanding efficiency due to its ability to be excited with photons in the range of 400–425 nm. Of the noble metals used, Pt proved most appropriate in enhancing the H_2 evolution rates. However, Rh on TiO_2 also appears to be a good choice for harvesting the energy of photons >400 nm, especially in view of the recent fall in price and its ability to produce high amount of gaseous hydrogen relative to Pt–TiO_2. As concerns the effect of various organic compounds, carboxylic acids seem to have huge potential in this field of photocatalysis, especially lactic acid which can be easily produced through biotechnological processes. With Pt–TiO_2–AR in the presence of lactic acid, we observed a 6-fold higher level of H_2 production than in the case of using methanol.

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