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Influence of Photo-Deposited Pt and Pd onto Chromium Doped TiO₂ Nanotubes in Photo-Electrochemical Water Splitting for Hydrogen Generation

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Abstract: Hydrogen (H₂) is considered as an ideal fuel for the future. The photo-electrochemical (PEC) water splitting employing semiconducting materials and induced irradiation, preferably of solar spectrum, presents a viable route for H₂ production. In this work, self-ordered chromium-doped TiO₂ nanotube (CT) was fabricated using in-situ electro-anodization. CT surface modification was then performed by photo-deposition of Pt and Pd particles, producing Pt-CT and Pd-CT catalysts, respectively. Their morphological features, crystallinity, surface composition, and optical absorption have been inspected by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), Raman, and UV-vis absorption spectroscopy. Linear sweep voltammetry, chronoamperometry, and open circuit potential methods have been applied to study PEC activities of Pt-CT and Pd-CT catalysts in a form of electrodes. It was found that Pt-CT and Pd-CT electrodes possess excellent photo-generated electron/hole (e^-/h^+) separation and transport properties. The enhanced photocurrent responses of 4 and 3 times more than that of CT are revealed for Pt-CT and Pd-CT, respectively. The activity of as-prepared Pt-CT and Pd-CT catalysts was then tested for H₂ generation. The maximum amount of the evolved H₂ followed decreasing order: 1.08 > 0.65 > 0.26 mL cm⁻² h⁻¹ for Pt-CT, Pd-CT, and CT electrodes, respectively, clearly showing the positive contribution of photo-deposited (nano)particles onto CT surface.

Keywords: electro-anodization; TiO₂ nanotubes; photo-deposition; platinum; palladium; photo-electrochemical water splitting

1. Introduction

Hydrogen (H₂) is alternative to fossil fuels, superior to renewable energy sources such as wind and solar; H₂ is storable and transportable fuel, and could be easily accessible whenever required [1,2]. There are different methods for H₂ production; such as the petroleum cracking, hydrocarbon reforming, the electrolysis of water, photocatalytic and photoelectrochemical (PEC) water splitting [3,4]. Ever since the discovery of water splitting on TiO₂ by Fujishima and Honda [5] semiconductor-based photocatalysts have triggered broad scientific interest. PEC water splitting is considered as the most environmentally friendly and cost-effective technology to produce H₂ [6]. A wide range of materials, such as TiO₂, ZnO, WO₃, ZrO, etc. have been introduced and explored for PEC water splitting process, however, TiO₂ still remains the basic material in the most of applications [7–9]. The plausible explanation can be found in its low price, high chemical stability, suitable band-edge positions for required reactions, and relatively long electron lifetime. However, TiO₂ has several limitations, such as fast recombination of photogenerated e^-/h^+ pairs and

relatively wide bandgap (3.2 eV) requiring its excitation under wavelengths < 390 nm (i.e., by UV irradiation) [10,11]. Therefore, several strategies have been developed and applied to overcome these limitations, including metal or non-metal doping, composites with other semiconductors and/or carbon-based materials, dye sensitization, and noble-metal deposition [8,10]. For example, doping with transitional metal ions, like chromium used in this work for TiO_2 doping, enhances the visible light absorption by introducing an intermediate band. Besides, such approach can also contribute through the creation of trapping sites for photogenerated e^-/h^+ , thus subsequently decreasing the recombination of photogenerated charges [12–14]. Among other mentioned strategies, loading of noble-metals as co-catalysts onto the surface of the main photocatalytic material, has been shown as one of the most effective approaches to enhance H_2 production rates [15]. Such co-catalyst effectively reduces the recombination process by capturing the photo-generated e^- , enabling their participation as active reaction sites for effective water splitting reactions [16,17]. Besides, co-catalyst acts as a protective layer minimizing photo-corrosion of the light absorbing semiconductors, positively contributing to the overall system effectiveness [18,19]. The optimization of the co-catalyst amount is highly required; otherwise, it may cause the opposite effect lowering overall effectiveness. Namely, deposition of co-catalyst on the surface would lead toward decreasing the charge recombination, however if too large amount of surface is deposited, it may block the light penetration or act as the surface trap states. Noble metals such as Au, Ag, Pt, and Pd are widely used as co-catalysts in such purposes, particularly in the case of efficient H_2 production [20,21].

Recently, our research groups have been involved in the synthesis of new nanocomposites based on highly ordered one dimensional structure of TiO_2 by one-step in-situ electroanodization process using various transition metal ions as dopants [12,14,22,23]. Accordingly, chromium-doped TiO_2 nanotube (CT), which showed better photo-electrochemical activity than that of pristine TiO_2 NTs, is reported in our previous work [12]. In the current study the water splitting efficiency of new photocatalysts consisting of chromium-doped TiO_2 nanotubes decorated with photo-deposited Pt and Pd (nano)particles was investigated. The series of obtained Pt-CTs and Pd-CTs (–1, –2, –3, –4, –5 and –6; numbering stands for photo-deposition time varied as 10, 20, 40, 60, 100 and 120 min, respectively), along with pristine CT, were submitted to thorough inspection to establish their morphology, crystallinity, surface composition, optical absorption, electrochemical and semiconducting properties as well as the activity in PEC water splitting for H_2 evolution.

2. Results and Discussion

2.1. Characterization

Our previous results revealed that highly ordered TiO_2 nanotube arrays can be synthesized with the electro-anodization method. However, in the case of CT, amount of K_2CrO_4 in in-situ electro-anodization can change the morphology of the obtained material. For example, when K_2CrO_4 concentration > 15 mM was used, a porous film instead of nanotube arrays was observed (SEM images of pristine CT can be found in the ref [12]). Hence, in this work, CT electrode was synthesized according to the optimal conditions established in our previous study [12]. As can be seen from both Figures 1 and 2, highly ordered and uniform crystalline CT nanotubes with the small layer of photodeposited platinum and palladium were successfully fabricated with the average 130 nm in diameter (marked with dashed lines in Figures 1B and 2B), 30 nm in wall thickness, and ~ 8 – 10 μm in length. It should be mentioned that the deposited Pt and Pd did not change the morphology of CT (Figures 1 and 2). As can be seen from Figure 1C,D, showing Pt-CT-2, Pt particles are fairly homogeneously distributed over the surface of the CT and are of spherical shape. Accordingly, it can be concluded that shorter period of time used for photo-deposition (e.g., 20 min as in the case of Pt-CT-2) yielded isolated Pt particles onto CTs (Figure 1D). On the other hand, the increase in photo-deposition-time > 60 min led to a partial agglomeration of Pt particles onto the CT, as can be seen for images corresponding to Pt-CT-4 (Figure 1E,F), as well as those for Pt-CT-5, and Pt-CT-6 (Figure S1, Supplementary Materials). In the

case of as-prepared Pd-CT materials (Figure 2 and Figure S2, Supplementary Materials), interesting effects regarding the time employed for photo-deposition can be observed, particularly when comparing to Pt photo-deposition in the same time intervals. Namely, as can be approximated comparing the same photo-deposition time intervals for Pt and Pd, it seems that more Pd particles were present onto CTs. The example of such effect can be observed when comparing Figures 1A and 2A, presenting Pt-CT-1 and Pd-CT-1, respectively, at the same magnification.

Figure 1. SEM images of decorated CT with Pt photo-deposition: Pt-CT-1 (A,B), Pt-CT-2 (C,D), Pt-CT-4 (E,F) at different magnitude, the red lines show the selected part of SEM images at higher magnitude, cross section (G), and side view (H) of Pt-CT-6.

Figure 2. SEM images of decorated CT with Pd photo-deposition: Pd-CT-1 (A,B), Pd-CT-2 (C,D), Pd-CT-3 (E,F) at different magnitude, the red lines show the selected part of SEM images at higher magnitude, large agglomerates marked with yellow circles in (C), cross section (G), and side view (H) of Pd-CT-6.

In the case of latter material, a distribution of small light dots (Pd particles) can be clearly seen all-over CT surface, which is not so obvious in the case of photo-deposited Pt particles. However, such higher amount deposited onto CT surface presumably resulted with increased agglomeration rate (Figure 2E, marked with yellow circles). The agglomeration effect is particularly obvious in the case of Pd-CT-6 (Figure S2, Supplementary Materials; images with the lower magnification, i.e., 5 μm) where presence of larger agglomerates (in size of $3 \times 4 \mu\text{m}$) are clearly noticeable. Differences in amount and size of deposited Pt and Pd can be plausibly explained by their different interactions due to differences in atomic mass and density of both metals. Similar effect was observed by Pisarek et al. [24] using magnetron sputtering technique to decorate titania nanotubes surface by Pt and Pd nanoparticles. Additional confirmation for effects observed can be also found in other studies on the decoration of TiO_2 -based materials with Pt and Pd [25,26]. It should be emphasized that the agglomeration occurred at both Pt-CT and Pd-CT materials prepared in this study is much lower than that obtained in our previous study at comparable conditions using CT substrate for photo-deposition of Au and Ag as surface-decorative co-catalysts [13]. Such findings are in good agreement with the literature [27–30]. Hence,

depending on the type of metals, metals cluster size as well as the agglomeration rate are different due to parameters such as binding energy between nanoparticles and between nanoparticles and a substrate (CT in our case), photo-reduction speed, and nanoparticle nucleation and growth rate. For example, the interaction of Au-Au is much stronger than that of Au-substrate made of metal oxides [27].

Accordingly, larger Au particles and sintering were observed on different substrates [30]. However, comparing to Au, Pt binds more strongly to metal oxides and small (nano)particles could be deposited at the surface of substrate. Since the photo-reduction process of Pd (II) in aqueous solution is quite fast [28], more agglomeration was observed comparing to Pt decorated surface in our study. It should be noted that larger or agglomerated particles on the top of CT surface demonstrated that deposited noble metals are not able to penetrate the interlayer and/or concentrate on the outer walls. In such case, agglomerated structures can still act as centers of charge recombination, however, simultaneously can cover the top of the nanotubes, consequently decreasing the efficiency of PEC for H₂ production.

The crystal structures of as-prepared electrodes were investigated by XRD. Figure 3A shows the XRD patterns of CT, Pt-CT-6, and Pd-CT-6. As can be seen, in all cases anatase phase is dominant, exhibiting major peaks at 25.3°, 38.0°, 48.1°, 53.9° and 70.3° (2 θ) which were well indexed to the lattice planes of (101), (004), (200), (105) and (220), respectively (ICDD-JCPD:01-086-1156) [13], indicating that TiO₂ pertains mainly to anatase. The plausible explanation why characteristic peaks corresponding to Cr are not detected in none of tested materials might be due to incorporating into the TiO₂ crystal lattice or rather small size of dopant introduced by used electro-anodization method. Our previous work it was demonstrated that higher concentration of Cr did not change the XRD patterns of Ti nanotubes, i.e., TiO₂ phase [12]. However, the presence of Cr has recently been confirmed in our previous research by XPS analysis [31]. The representative diffraction peaks for the face-centered cubic crystal structure of Pd, namely (111), (220) and (222) [32], were observed at 40°, 69° and 87° (2 θ) in the XRD patterns of Pd-CT-6 sample. Similarly, in the case of Pt decorated CTs (Pt-CT-6) diffraction peaks at 40° and 69° (2 θ), corresponding to the face-centered cubic phase of Pt (220) and Pt (222) [33], respectively, can be observed. Such findings indicate that Pt and Pd at CT surface are present in metallic form.

Figure 3. XRD patterns of CT, Pt-CT-6 and Pd-CT-6 (A); comparison of Raman spectrum of CT, Pt-CT-1 and Pt-CT-6 (B1), and CT, Pd-CT-1 and Pd-CT-6 (B2), EDX spectrum of Pt-CT-6 (C1) and Pd-CT-6 (C2), and UV-Vis spectrum of Pt-CT-6 (D1) and Pd-CT-6 (D2) electrodes.

The interactions between co-catalysts (Pt or Pd) and substrate (CT) can have an influence on the size and amount of deposited co-catalysts as well as electron charge transfer between Pt and Pd and CT which may lead to the substantial changes in PEC activity. To understand the interactions between Pt, Pd, and substrate material, the Raman spectra of Pt-CT, Pd-CT, and pristine CT were compared (Figure 3(B1,B2)). The peaks observed for pristine CT at 153, 401, 526 and 643 cm^{-1} , although latter three are of weaker intensity, are the characteristic Raman bands of anatase which can be assigned to E_g , B_{1g} , doublet of $A_{1g} + B_{1g}$ and E_g modes of the anatase phase, respectively [34]. The strongest E_g mode at 153 cm^{-1} , arising from the extension vibration of the anatase structure, is well resolved, clearly indicating anatase phase in pristine CT [34,35]. Comparing the Raman spectra of selected Pt-CT and Pd-CT samples at shortest and longest period of time used for the photo-deposition (Pt-CT-1 and Pt-CT-6, and Pd-CT-1 and Pd-CT-6) with the pristine CT showed shifting of peaks in the case of surface decorated materials. Namely, the Raman peaks at 153 and 520 cm^{-1} of pristine CT shifted towards higher wavenumbers (159 and 526 cm^{-1} , respectively) in all Pt-CT and Pd-CT recorded samples. In addition, the magnitude of the titanium peaks increased after surface-decoration by Pt and Pd particles. However, it should be emphasized that peaks magnitude decreased with increasing of photo-deposition time in both cases, which is particularly evident in the case of CTs surface decorated with Pd (Figure 3(B1,B2)). Since Raman spectra demonstrate the existence of chemical and/or physical interactions between Pt and Pd particles with pristine CT, such effect can be assigned to changes of vibrational modes of anatase structure at the CT surface by deposited co-catalysts. The EDX spectra in Figure 3(C1,C2) provide insight in the surface composition of surface-decorated CT with Pt and Pd particles. Hence, the obtained results; high Ti and O content, clearly exhibit the existence of TiO_2 lattice in synthesized nanotubes, while lower Cr content indicates its presence in CTs, although XRD (Figure 3A) did not reveal its presence in a known crystal polymorph. The detected Pt and Pd clearly show their presence in the surface-decorated electrodes. Furthermore, the presence of carbon, nitrogen, potassium, fluorine, and chlorine in the spectrum of EDX can be assigned to leftovers of precursors used in synthesis and photo-deposition. EDX mapping of the Pt-CT-6 and Pd-CT-6 electrodes, showed in Figures S3 and S4 (Supplementary Materials), demonstrates that noble metals used for CT surface-decoration (Pt and Pd) are uniformly dispersed on the top of CT substrate, in spite of several agglomerates observed through SEM analysis (Figures 1 and 2 and Figures S1 and S2, Supplementary Materials). Generally, particle size and distribution of particles on the surface of substrate (in our case CT) could have a strong influence on the PEC performance [36,37].

The optical properties of all as-prepared Pt-CT and Pd-CT materials were analyzed by recording their UV-Vis spectra in the range of 250–600 nm (Figure 3D), Figures S5 and S6 (Supplementary Information)). A noticeable shift in the absorption edge of CT with photo-deposited Pt and Pd co-catalysts comparing to the pristine CT towards the visible-light region can be observed in the normalized UV-vis spectra (Figure 3(D1,D2)). It was found that both Pt-CT and Pd-CT, regardless the time used for the photo-deposition, increased absorb light in the whole UV-vis range, presumably as a consequence of local surface plasmon resonance (LSPR) effect caused by deposited Pd and Pt particles. The optical bandgap values were estimated by employing the Tauc's model [38]. The same calculation procedure was already used for TiO_2 nanotubes and pristine CT [12], yielding bandgap energy values of ~3.2 eV and ~2.82 eV, respectively [12]. As can be seen, the surface decoration with Pt and Pd resulted with more red-shifting and consequently further decrease of bandgap energy of as-prepared electrodes; to values of 1.8–2.2 eV for Pt-CT and 2.1–2.8 eV for Pd-CT electrodes (Figure 3(D1,D2)) and Figures S5 and S6 (Supplementary Materials)). Such results indicate on their ability to effectively utilize visible part of solar spectrum.

2.2. Photo-Electrochemical Characterization

PEC water splitting aiming at the production of H_2 with large positive change in the Gibbs free energy ($\Delta G^\circ = + 237.2 \text{ kJ mol}^{-1}$) is a thermodynamically uphill reaction. In

addition, H_2 production is a low efficiency process due to the high recombination rates of photogenerated e^-/h^+ pairs in the most cases of applied photocatalytic materials. In order to increase the process efficiency, a sacrificial agent (usually various alcohols) is usually required, enabling the reactions with holes while the photogenerated electrons would remain yielding H_2 production. Since our previous research revealed that EG (with ~ 5 vol%) showed enhancement in H_2 production rates [13], the same sacrificial agent was also used in this work.

The photo-sensitivity of all samples was investigated by measuring LSV (Figure 4 and Figures S7–S10, Supplementary Material), scanning responses of as-prepared electrodes during dark, under illumination, and by switching on and off the light simulator. Generally, the photocurrent was enhanced significantly under light and returned to the background value as the light was turned off. The anodic peak observed in Pt-CT electrodes with photo-deposition time > 40 min (Pt-CT-5 and Pt-CT-6) can be assigned to EG oxidation (Figures S7 and S8 (Supplementary Material)). However, such effect was not observed in Pt-CTs electrodes prepared by lower photo-deposition time (Pt-CT-1, Pt-CT-2 and Pt-CT-3 with photo-deposition time of 10, 20 and 30 min, respectively) (Figure 4, Figures S7 and S8, Supplementary Materials). On the other hand, all Pd-CT electrodes exhibited the appearance of anodic peak regardless the time used for photo-deposition of Pd particles onto CT surface, even at the lowest applied time period (i.e., 10 min) (Figure 4, Figures S7 and S9, Supplementary Materials).

Figure 4. LSV of Pt-CT-1 (A) and Pd-CT-1(B) electrodes under illumination of Xe lamp, in the dark and chopped light in solution of KOH (1 M) with 5 vol% EG.

Accordingly, it seems that Pd-CT electrodes have more potential for EG oxidation which can be of large interest for studying the EG electro-oxidation in fuel cells application [39]. However, that was not the subject of this study, thus it was not studied in details here. Thus, we investigated their behavior using LSV measurement in the same system, but without EG presence (Figure S10 (Supplementary Information)), and results revealed the absence of anodic peak in all cases. It should be mentioned that obtained results are in good agreement with literature where Pd-based materials showed superior photo-electrocatalytic activity for EG oxidation at alkaline conditions comparing to their analogues using Pt nanoparticles [9,40]. On the other hand, it is well known that Pt-based electrocatalysts exhibit an excellent performance for EG oxidation in acidic media [41].

Figure 5 shows the CA curves for Pt-CT and Pd-CT electrodes at 1.5 versus RHE in a solution of KOH (1 M) with 5%V EG. During dark period (0–100 s), tested electrodes mostly did not show current density response, indicating that as-prepared electrodes would act as photocatalysts primarily. After switching visible light illumination on, an initial rapid increase in current density can be observed, followed by decreasing within short period of time (50 s) reaching afterwards relatively steady-state conditions, indicating that all as-prepared electrodes possess superior long-term stability. Such effect proved the

photo-activity of as-prepared electrodes. Figure 5A,C show that the current density of undoped TiO₂ nanotubes increased when Cr was introduced in the TiO₂ nanotube structure, forming CT; from 0.035 mA cm⁻² to 0.23 mA cm⁻², respectively. Such results speak in favor to the increased activity under visible light, as well as decreased charge recombination [12]. Generally, the photocurrent density of Pt-CT electrodes (0.49–0.92 mA cm⁻²) is higher than that of Pd-CT electrodes (0.39–0.72 mA cm⁻²). It should be noted that the highest obtained photocurrent density was 0.92 mA cm⁻² which was recorded for Pt-CT-3 among all tested electrodes, while Pd-CT-5 showed maximum among Pd-decorated CTs (0.72 mA cm⁻²) (Figure 5A,C), which is actually 4 and 3 times more than that of pristine CT (0.23 mA cm⁻²) [13]. Moreover, the photocurrent response was also repeatable during on-off cycles upon light illumination (Figure 5B,D).

Figure 5. Photocurrent responses of Pt-CT (A,B), and Pd-CT electrodes (C,D) for long time (1200 s) and under chopping light (Xe lamp), at a potential of 0.6 V vs. Ag/AgCl, OCP curves of Pt-CT (E) and Pd-CT (F) samples in solution of KOH (1 M) with 5 vol% EG.

The OCP transients were also measured for all as-prepared Pt-CT and Pd-CT electrodes in order to reproduce the catalytic conditions without an externally applied bias. As can be seen in Figure 5E,F, during dark conditions in the beginning of OCP experiments, lasting for 15 min, electrodes reached stable potentials. Upon switching the light on, the potentials rapidly shifted toward more negative values, reaching after certain period stable value. Such behavior, typical for n-type semiconductors, may be assigned to the injection of photogenerated e^- by Pt-CT and Pd-CT electrodes into the counter electrode. During the last period within OCP experiments (~9 min) the light was switched off, and the potentials positively shifted and reached near initial values in several minutes (in most cases < 3 min). Such effect indicates on the electron storage properties of as-prepared electrodes. After the light was turned off, OCP decay kinetics reflects the charge recombination kinetics. Therefore, the fitting of a bi-exponential function to OCP decay profiles was employed with two time constants (Equation (1)) to estimate the average recombination lifetime [42]:

$$V(t) = A_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

$$\tau_m = \tau_1 \tau_2 / (\tau_1 + \tau_2) \quad (2)$$

where V , t , A_1 and A_2 , τ_1 , τ_2 , and τ_m are potential decay, time, fitting constants, exponential lifetime component for band-to-band and band-to-surface state band recombination processes, and the harmonic mean of decay lifetime, respectively. The total half-lives are equal to $\log(2\tau_m)$, which are calculated for all as-prepared Pt-CT and Pd-CT electrodes and summarized in Table S1 (Supplementary Material). Apparently, OCP decay of Pt-CT electrodes is much slower comparing to that of Pd-CTs, indicating that charge recombination at the surface of CT is more efficiently suppressed with the deposition of Pt than with Pd particles.

The EIS measurement conducted at the potential of 0.2 V vs. Ag/AgCl has also been employed to study electrochemical reaction process induced by Pt-CT and Pd-CT electrodes. As can be observed (Figure 6), the impedance arc diameter of studied electrodes under light illumination was smaller than that obtained under dark. Furthermore, Pt-CT-3 displayed the smallest impedance arc diameter. Presence of Pt as co-catalyst yielded decrease of electron transfer resistance more than in the case of Pd particles. Accordingly, it can be concluded that Pt-CT electrodes have better electrical conductivity under light illumination, which can be assigned to the surface plasmon resonance effect and the better charge transfer.

Figure 6. EIS plot of Pt-CT-3 and Pd-CT-3 under illumination and dark, in solution of KOH (1 M) with 5 vol% EG.

2.3. PEC Water Splitting for H₂ Evolution

The utilization of noble metals has been broadly employed for the surface decoration of semiconducting materials to efficiently perform water splitting aiming at H₂ generation due to the following reasons: (i) the LSPR effect, which facilitates harvesting of solar irradiation to generate and transfer plasmonic carriers; and (ii) enabling the trapping of conduction band electrons, thus boosting the charge separation. PEC water splitting with Pt-CT and Pd-CT electrodes in this study was conducted using an inverted burette setup (Figure 7C) and the evolved H₂ (Figure 7) was quantitatively measured by electrolyte displacement in an inverted burette. As can be seen (Figure 7), Pt-CT electrodes produced much more H₂ than Pd-CT electrodes at comparable conditions; i.e., photo-deposition time used for surface decoration with chosen noble metals.

Figure 7. PEC water splitting and H₂ generation of Pt-CT (A) and Pd-CT (B) samples during 1 h at 1.5 V vs. RHE in solution of KOH (1 M) with 5 vol% EG, reusability investigation of the Pt-CT-3 (C) and Pd-CT-5 (D) electrodes.

The maximum amount of the evolved H₂, 1.08 mL cm⁻¹ h⁻¹ was obtained with Pt-CT-3, the electrode which showed the highest photocurrent density among all studied (Figure 7A). On the other hand, the maximum evolved H₂ amount by Pd-CTs, was 0.65 mL cm⁻¹ h⁻¹ (1.66 times lower than that obtained by Pt-CT-3), achieved by Pd-CT-5. It is worth to note that Pt-CT and Pd-CT electrodes synthesized in this work provide higher amount of the evolved H₂ than some of materials used in other studies (Table 1).

Table 1. Comparison of H₂ evolution using noble-metals surface decorated TiO₂-based nanocomposites.

Name	Electrolyte	Light Source	Rate of H ₂ Evolution	Reference
1Pt-3WO ₃ -TiO ₂ NTs	Water with 20 vol% ethanol	UV	5 μ L h ⁻¹	[43]
Pt-TiO ₂ NT	Water with 20 vol% ethanol	UV	0.31 mL h ⁻¹	[44]
Pt-TiO ₂ NTs	Na ₂ SO ₄ (2 M)	Vis	27.4 μ mol h ⁻¹	[37]
Pt-TiO ₂ NTs	Water-ethanol	UV	$\approx$ 0.11 mL h ⁻¹	[45]
Pd-TiO ₂ NTs	Water with 50 vol% methanol	UV	70 μ L h ⁻¹	[46]
Pd-TiO ₂	Methanol-water (1:1)	UV	$\approx$ 0.35 mL h ⁻¹	[47]
Pd-TiO ₂ NTs	Na ₂ SO ₄ (2 M)	Vis	28.9 μ mol h ⁻¹	[37]
Pt1Pd1Ag6-TiO ₂ NTs	Water with 50 vol% methanol	UV	70 μ L h ⁻¹	[46]
Pt-CT-3	KOH (1 M) with 5 vol% EG	Vis	1.08 mL h ⁻¹	This work
Pd-CT-5	KOH (1 M) with 5 vol% EG	Vis	0.65 mL h ⁻¹	This work

Generally, when two materials with different work functions (ϕ_m) are in contact, a Schottky barrier is created at the junction, acting as an energy barrier for electron transfer. The electron transfer is facilitated from a material of lower work function, e.g., in our case TiO_2 (4.2 eV), to one that has a higher work function, e.g., both Pt and Pd in our case. Since Pt exhibits higher work function ($5.12 \text{ eV} < \phi_m < 5.93 \text{ eV}$) than Pd ($5.12 \text{ eV} < \phi_m < 5.35 \text{ eV}$) [48,49], it provides low overpotential for water splitting and consequently H_2 evolution, thus Pt has been showed as more effective co-catalyst than Pd when used for surface decoration of CTs. The stability of Pt-CT-3 and Pd-CT-5 electrodes, which showed the highest effectiveness in H_2 generation among Pt-CT and Pd-CTs, respectively, was examined for PEC water splitting during three cycles of 60 min. As can be seen in Figure 7C,D, there are no significant decreases in activity during consecutive cycles, which proves the good stability of the as-prepared electrodes in the PEC water splitting.

3. Materials and Methods

3.1. Chemicals

The following chemicals, purchased from Sigma Aldrich (Taufkirchen, Germany), were used without any purification: Ti plates (99.6%) of 1 mm thickness, hydrofluoric acid (HF, 48%), nitric acid (HNO_3 , 70%), hydrochloric acid (HCl, 37%), potassium hydroxide (KOH, $\geq 85\%$), ethylene glycol (EG, $\text{C}_2\text{H}_6\text{O}_2$, $\geq 99\%$), potassium chromate (K_2CrO_4 , $\geq 99.95\%$), ammonium fluoride (NH_4F , $\geq 99.99\%$), potassium hexachloroplatinate (K_2PtCl_6 , 98%), palladium chloride (PdCl_2 , 99.9%). Deionized water was used in all experiments within this work.

3.2. Fabrication of Nanocomposites (CT) Using In-Situ Electro Anodization

Titanium plates of 1 mm thickness ($1 \text{ cm} \times 3 \text{ cm}$) were used to grow titania nanotubes. The addition of an appropriate amount of K_2CrO_4 as chromium source in the electrolyte, resulted with the fabrication of CT electrode using in-situ electro anodization, which enable the penetration of Cr into the Ti structures [12]. Prior to anodization, Ti plates were mechanically polished by different grit size of silicon carbide papers (SiC, Tehran, Iran), and thereafter cleaned by rinsing with deionized water. Afterward, the plates were chemically etched with a mixture of $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$ in a volume ratio of 1:4:5 for 30 s, and thereafter washed with deionized water. In-situ electro-anodization was performed at room temperature in a solution of EG containing 0.005 M K_2CrO_4 , 0.1 M NH_4F , and 1 mL deionized water at 60 V for 6 h. Ti and a graphite electrode were used as the anode and cathode electrodes, respectively. After anodization, Ti electrodes were washed with deionized water and dried at room temperature. Ti electrodes were annealed at 400°C for 2 h with a ramp of 2°C min^{-1} using a F3L-1720 furnace (AZAR Furnaces, Tehran, Iran) to achieve the materials of high crystallinity.

3.3. Photo-Deposition Process

Surface decoration of CT with Pt and Pd was accomplished using the photo-deposition method. Solutions were consisted of the appropriate concentrations of metal chloride precursors (K_2PtCl_6 and PdCl_2). Since these components are slightly soluble in water, an appropriate amount of HCl was used to dissolve them. In a typical experiment, 2 mL ethanol as a sacrificial donor was added to 18 mL of the metal chloride solutions. Photo-deposition was performed by illuminating the solution of metal chlorides in which electrodes were immersed in with a high-pressure mercury lamp (400 W, Zhejiang, China). The electrodes were exposed to such process for 10, 20, 40, 60, 100 and 120 min irradiation, and thereafter washed with deionized water. Accordingly, obtained electrodes are denoted onward throughout the manuscript as Pt-CT-1, Pt-CT-2, Pt-CT-3, Pt-CT-4, Pt-CT-5, and Pt-CT-6 corresponding to illumination time of 10, 20, 30, 40, 60, and 120 min, respectively. The same analogy is made in the case of Pd-decorated CT electrodes.

3.4. Characterization of Materials

The surface morphology and microstructure of as-prepared materials, as well as the surface elemental analysis were studied using a field emission scanning electron microscope equipped with an energy dispersive X-ray (EDX) mapping port Philips XL30 (Eindhoven, The Netherlands). In order to determine phase composition, X-ray diffraction (XRD) patterns were obtained using Philips X'Pert system (Enschede, The Netherlands). The data were recorded in the 2θ range of 20° – 90° . UV-Vis spectra were recorded on a JASCO V-570 UV-visible spectrophotometer (Portland, OR, USA) to study of light absorption properties of the samples. In addition, the Raman spectra of the samples were obtained using TakRam N1-541 (Tehran, Iran) at a laser power of 50–200 mW.

3.5. Photo-Electrochemical Measurement

All electrochemical and PEC measurements were carried out in a quartz three electrodes cell in 1 M KOH solution containing 5% vol. EG with a potentiostat/galvanostat OGF 500 (Origaflex, Clichy, France), where the saturated Ag/AgCl electrode and the platinum foil electrode worked as the reference electrode and the counter electrode, respectively. The working electrode was made of as-prepared catalysts (Pt-CT and Pd-CT) of which an area of 1 cm^2 was immersed into the electrolyte. A 35-W Xe lamp (200 mW cm^{-2} , and $420 < \lambda < 700\text{ nm}$) (Briteye, Isfahan, Iran), is used for all PEC experiments. Linear sweep voltammetry technique (LSV) with a scan rate of 10 mV s^{-1} , photocurrent measurement, chronoamperometry (CA) at 1.5 V vs. RHE electrode, and open circuit potential (OCP) have been used to study PEC performance of as-prepared electrodes. All of these techniques were studied in the presence and absence of illumination as well as by light switching on and off. Electrochemical impedance spectroscopy (EIS) measurements for studying the semiconductor/electrolyte interface were performed using an IM6ex system (Zahner-Elektrik, Kronach, Germany). The frequency range was from 100 kHz to 100 mHz, while the amplitude of the imposed sinusoidal voltage was 10 mV. The impedance was recorded at a potential of 0.2 V (vs. Ag/AgCl).

3.6. Photo-Electrochemical Water Splitting

A three electrode configuration was used for PEC water splitting and H_2 production. Different Pt-CT and Pd-CT (depending on the time-exposure to noble-metal deposition) electrodes were immersed in a KOH (1 M) solution containing 5 vol % EG and under illumination (200 mW cm^{-2} , Xe lamp). The cathode (Pt Mesh) was inserted into an inverted burette, where H_2 was collected via electrolyte displacement. The variation of the electrolyte level in the burette, which is proportional to the volume of H_2 production (Figure 1C), was recorded in predefined time-intervals ($t = 0, 7.5, 15, 22.5, 30, 37.5, 45, 52.5$ and 60 min).

4. Conclusions

Self-ordered chromium-doped TiO_2 nanotubes (CT), ~ 8 – $10\text{ }\mu\text{m}$ in length, were fabricated using in-situ electro-anodization, which were afterwards successfully decorated with Pt and Pd metal particles using photo-deposition technique. The thorough inspection of morphological, surface and optical properties, as well as crystallinity of as-prepared materials exhibited following characteristics. CT structures are quite uniform in size and shape, and possess rather uniform distribution of deposited Pt and Pd over CT surface, while the agglomeration of noble metals was found to be photo-deposition time dependent. XRD revealed that TiO_2 pertain to anatase phase, while EDX clearly proved existence of chromium as dopant in CT. In addition, the presence of Pt and Pd as co-catalyst at CT's surface was confirmed by XRD, EDX and Raman. It was found that as-prepared Pt-CT and Pd-CT materials have lower bandgaps (1.8–2.2 eV and 2.1–2.8 for Pt-CT and Pd-CT electrodes, respectively) comparing to the CT ($\sim 2.82\text{ eV}$). The electrochemical characterization indicated good photocatalytic properties of as-prepared materials, as well as their stability during exposure to visible irradiation. Pt-CT-3 (0.92 mA cm^{-2}) and Pd-CT-5

(0.72 mA cm^{-2}) showed the highest photocurrent density among Pt and Pd-decorated CTs, which is 4 and 3 times more than that of CT. Besides, Pt-CT electrodes showed (i) much lower charge recombination and (ii) better electrical conductivity under visible light illumination, than observed in the case of Pd-CTs. As a consequence of determined electrochemical and semiconducting properties, Pt-CT showed higher H_2 generation in PEC water splitting than Pd-CTs at comparable conditions; even 1.66 times H_2 was produced during 60 min course. It should be noted that both materials showed excellent stability during consecutive cycles; < 2% decrease was observed in the PEC water splitting efficiency during repetitive cycles.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/2/212/s1>, Figure S1: SEM images of Pt-CTs electrodes at different magnitude, Figure S2: SEM images of Pd-CTs samples at different magnitude, Figure S3: EDX-mapping of Pt-CT-6 electrode, Figure S4: EDX-mapping of Pd-CT-6 electrode, Figure S5: UV-Vis spectra of Pt-CT electrodes (A-F: Pt-CT-1 to Pt-CT-6), inset figs are Tauc plot of UV-Vis absorption data for calculation of band gap, Figure S6: UV-Vis spectra of Pd-CT electrodes (A-F: Pd-CT-1 to Pd-CT-6), inset figs are Tauc plot of UV-Vis absorption data for calculation of band gap, Figure S7: LSV of Pt-CT (A) and Pd-CT (B) electrodes in under illumination of Xe lamp in a solution of KOH (1M) with 5 vol% EG, Figure S8: LSV of Pt-CT electrodes (A-F: Pt-CT-1 to Pt-CT-6), in the dark, under illumination, and chopped light of Xe lamp in a solution of KOH (1M) with 5 vol% EG, Figure S9: LSV of Pd-CT electrodes (A-F: Pd-CT-1 to Pd-CT-6), in the dark, under illumination, and chopped light of Xe lamp in a solution of KOH (1M) with 5 vol% EG, Figure S10: LSV of Pd-CT electrodes under illumination of Xe lamp in a solution of KOH (1M) without EG, Table S1: The total half-lives of photogenerated charge carriers calculated using bi-exponential function fitting of OCP decay profiles of Pt-CTs and Pd-CTs electrodes.

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References

- Hisatomi, T.; Domen, K. Reaction systems for solar hydrogen production via water splitting with particulate semiconductor photocatalysts. *Nat. Catal.* **2019**, *2*, 387–399. [CrossRef]
- Vinoth Kanna, I.; Paturu, P. A study of hydrogen as an alternative fuel. *Int. J. Ambient. Energy* **2020**, *41*, 1433–1436. [CrossRef]
- Hisatomi, T.; Kubota, J.; Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem. Soc. Rev.* **2014**, *43*, 7520–7535. [CrossRef] [PubMed]
- Reddy, I.N.; Reddy, C.V.; Ravindranadh, K.; Cho, M.; Kim, D.; Shim, J. A study of coral reef-like tetragonal Mn_3O_4 nanostructure photoelectrode for photoelectrochemical water splitting under visible irradiation. *J. Electroanal. Chem.* **2020**, *874*, 114488. [CrossRef]
- Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nat. Cell Biol.* **1972**, *238*, 37–38. [CrossRef] [PubMed]
- Roger, I.; Shipman, M.A.; Symes, M.D. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nat. Rev. Chem.* **2017**, *1*, 1–13. [CrossRef]

7. Zhang, J.; Li, L.; Xiao, Z.; Liu, D.; Wang, S.; Zhang, J.; Hao, Y.; Zhang, W. Hollow sphere $\text{TiO}_2\text{-ZrO}_2$ prepared by self-assembly with polystyrene colloidal template for both photocatalytic degradation and H_2 evolution from water splitting. *ACS Sustain. Chem. Eng.* **2016**, *4*, 2037–2046. [\[CrossRef\]](#)
8. Ni, M.; Leung, M.K.; Leung, D.Y.; Sumathy, K. A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. *Renew. Sustain. Energy Rev.* **2007**, *11*, 401–425. [\[CrossRef\]](#)
9. Wang, L.; Meng, H.; Shen, P.K.; Bianchini, C.; Vizza, F.; Wei, Z. In situ FTIR spectroelectrochemical study on the mechanism of ethylene glycol electrocatalytic oxidation at a Pd electrode. *Phys. Chem. Chem. Phys.* **2010**, *13*, 2667–2673. [\[CrossRef\]](#)
10. Zhao, C.; Luo, H.; Chen, F.; Zhang, P.; Yi, L.; You, K. A novel composite of TiO_2 nanotubes with remarkably high efficiency for hydrogen production in solar-driven water splitting. *Energy Environ. Sci.* **2014**, *7*, 1700–1707. [\[CrossRef\]](#)
11. Ding, L.; Ma, C.; Li, L.; Zhang, L.; Yu, J. A photoelectrochemical sensor for hydrogen sulfide in cancer cells based on the covalently and in situ grafting of CdS nanoparticles onto TiO_2 nanotubes. *J. Electroanal. Chem.* **2016**, *783*, 176–181. [\[CrossRef\]](#)
12. Momeni, M.M.; Ghayeb, Y. Photoelectrochemical water splitting on chromium-doped titanium dioxide nanotube photoanodes prepared by single-step anodizing. *J. Alloy. Compd.* **2015**, *637*, 393–400. [\[CrossRef\]](#)
13. Sharifi, T.; Ghayeb, Y.; Mohammadi, T.; Momeni, M.M. Enhanced photoelectrochemical water splitting of CrTiO_2 nanotube photoanodes by the decoration of their surface via the photodeposition of Ag and Au. *Dalton Trans.* **2018**, *47*, 11593–11604. [\[CrossRef\]](#)
14. Mohammadi, T.; Ghayeb, Y.; Sharifi, T.; Momeni, M.M. RuO_2 photodeposited on W-doped and Cr-doped TiO_2 nanotubes with enhanced photoelectrochemical water splitting and capacitor properties. *New J. Chem.* **2020**, *44*, 2339–2349. [\[CrossRef\]](#)
15. Al-Azri, Z.H.; Chen, W.-T.; Chan, A.; Jovic, V.; Ina, T.; Idriss, H.; Waterhouse, G.I. The roles of metal co-catalysts and reaction media in photocatalytic hydrogen production: Performance evaluation of M/ TiO_2 photocatalysts (M= Pd, Pt, Au) in different alcohol–water mixtures. *J. Catal.* **2015**, *329*, 355–367. [\[CrossRef\]](#)
16. Chen, D.; Liu, Z.; Guo, Z.; Yan, W.; Xin, Y. Enhancing light harvesting and charge separation of Cu_2O photocathodes with spatially separated noble-metal cocatalysts towards highly efficient water splitting. *J. Mater. Chem. A* **2018**, *6*, 20393–20401. [\[CrossRef\]](#)
17. Reddy, I.N.; Reddy, C.V.; Sreedhar, A.; Cho, M.; Kim, D.; Shim, J. Effect of plasmonic Ag nanowires on the photocatalytic activity of Cu doped Fe_2O_3 nanostructures photoanodes for superior photoelectrochemical water splitting applications. *J. Electroanal. Chem.* **2019**, *842*, 146–160. [\[CrossRef\]](#)
18. Gaikwad, A.; Tyagi, D.; Betty, C.; Sasikala, R. Photocatalytic and photo electrochemical properties of cadmium zinc sulfide solid solution in the presence of Pt and RuS_2 dual co-catalysts. *Appl. Catal. A Gen.* **2016**, *517*, 91–99. [\[CrossRef\]](#)
19. Momeni, M.M.; Mahvari, M.; Ghayeb, Y. Photoelectrochemical properties of iron-cobalt WTiO_2 nanotube photoanodes for water splitting and photocathodic protection of stainless steel. *J. Electron. Chem.* **2019**, *832*, 7–23. [\[CrossRef\]](#)
20. Cai, Q.; Liu, Z.; Han, C.; Tong, Z.; Ma, C. $\text{CuInS}_2/\text{Sb}_2\text{S}_3$ heterostructure modified with noble metal co-catalyst for efficient photoelectrochemical water splitting. *J. Alloy. Compd.* **2019**, *795*, 319–326. [\[CrossRef\]](#)
21. Bowker, M.; Morton, C.; Kennedy, J.; Bahruji, H.; Greves, J.; Jones, W.; Davies, P.R.; Brookes, C.; Wells, P.; Dimitratos, N. Hydrogen production by photoreforming of biofuels using Au, Pd and Au–Pd/ TiO_2 photocatalysts. *J. Catal.* **2014**, *310*, 10–15. [\[CrossRef\]](#)
22. Momeni, M.M.; Ghayeb, Y.; Ghonchehi, Z. Fabrication and characterization of copper doped TiO_2 nanotube arrays by in situ electrochemical method as efficient visible-light photocatalyst. *Ceram. Int.* **2015**, *41*, 8735–8741. [\[CrossRef\]](#)
23. Momeni, M.M.; Akbarnia, M.; Ghayeb, Y. Preparation of S–W-codoped TiO_2 nanotubes and effect of various hole scavengers on their photoelectrochemical activity: Alcohol series. *Int. J. Hydrogen Energy* **2020**, *45*, 33552–33562. [\[CrossRef\]](#)
24. Pisarek, M.; Kędzierzawski, P.; Andrzejczuk, M.; Hołdyński, M.; Mikołajczuk-Zychora, A.; Borodziński, A.; Janik-Czachor, M. TiO_2 Nanotubes with Pt and Pd Nanoparticles as Catalysts for Electro-Oxidation of Formic Acid. *Materials* **2020**, *13*, 1195. [\[CrossRef\]](#)
25. Schierbaum, K.; Fischer, S.; Torquemada, M.; De Segovia, J.; Roman, E.; Martin-Gago, J. The interaction of Pt with TiO_2 (110) surfaces: A comparative XPS, UPS, ISS, and ESD study. *Sur. Sci.* **1996**, *345*, 261–273. [\[CrossRef\]](#)
26. Su, R.; Dimitratos, N.; Liu, J.; Carter, E.; Althahban, S.; Wang, X.; Shen, Y.; Wendt, S.; Wen, X.; Niemantsverdriet, J. Mechanistic insight into the interaction between a titanium dioxide photocatalyst and Pd cocatalyst for improved photocatalytic performance. *ACS Catal.* **2016**, *6*, 4239–4247. [\[CrossRef\]](#)
27. Grabowska, E.; Marchelek, M.; Klimczuk, T.; Trykowski, G.; Zaleska-Medynska, A. Noble metal modified TiO_2 microspheres: Surface properties and photocatalytic activity under UV–vis and visible light. *J. Mol. Catal. A Chem.* **2016**, *423*, 191–206. [\[CrossRef\]](#)
28. Harada, M.; Inada, Y. In situ time-resolved XAFS studies of metal particle formation by photoreduction in polymer solutions. *Langmuir* **2009**, *25*, 6049–6061. [\[CrossRef\]](#)
29. Gomes, J.F.; Lopes, A.; Bednarczyk, K.; Gmurek, M.; Stelmachowski, M.; Zaleska-Medynska, A.; Quinta-Ferreira, M.E.; Costa, R.; Quinta-Ferreira, R.M.; Martins, R.C. Effect of noble metals (Ag, Pd, Pt) loading over the efficiency of TiO_2 during photocatalytic ozonation on the toxicity of parabens. *ChemEngineering* **2018**, *2*, 4. [\[CrossRef\]](#)
30. Chen, M.; Goodman, D.W. Catalytically active gold on ordered titania supports. *Chemic. Soc. Rev.* **2008**, *37*, 1860–1870. [\[CrossRef\]](#)
31. Sharifi, T.; Ghayeb, Y.; Mohammadi, T.; Momeni, M.M.; Bagheri, R.; Song, Z. Surface treatment of titanium by in-situ anodization and NiO photodeposition: Enhancement of photoelectrochemical properties for water splitting and photocathodic protection of stainless steel. *Appl. Phys. A* **2021**, *127*, 1–12. [\[CrossRef\]](#)
32. Fu, Y.; Wei, Z.; Chen, S.; Li, L.; Feng, Y.; Wang, Y.; Ma, X.; Liao, M.; Shen, P.; Jiang, S. Synthesis of Pd/ TiO_2 nanotubes/Ti for oxygen reduction reaction in acidic solution. *J. Power Sources* **2009**, *189*, 982–987. [\[CrossRef\]](#)

33. Abida, B.; Chirchi, L.; Baranton, S.; Napporn, T.W.; Kochkar, H.; Léger, J.-M.; Ghorbel, A. Preparation and characterization of Pt/TiO₂ nanotubes catalyst for methanol electro-oxidation. *Appl. Catal. B Environ.* **2011**, *106*, 609–615. [\[CrossRef\]](#)
34. Zhang, W.; He, Y.; Zhang, M.; Yin, Z.; Chen, Q. Raman scattering study on anatase TiO₂ nanocrystals. *J. Phys. D Appl. Phys.* **2000**, *33*, 912–916. [\[CrossRef\]](#)
35. Wang, J.; Lin, Z. Anodic formation of ordered TiO₂ nanotube arrays: Effects of electrolyte temperature and anodization potential. *J. Phys. Chem. C* **2009**, *113*, 4026–4030. [\[CrossRef\]](#)
36. López-Tenllado, F.; Hidalgo-Carrillo, J.; Montes, V.; Marinas, A.; Urbano, F.; Marinas, J.; Ilieva, L.; Tabakova, T.; Reid, F. A comparative study of hydrogen photocatalytic production from glycerol and propan-2-ol on M/TiO₂ systems (M= Au, Pt, Pd). *Catal. Today* **2017**, *280*, 58–64. [\[CrossRef\]](#)
37. Li, F.; Huang, H.; Li, G.; Leung, D.Y. TiO₂ nanotube arrays modified with nanoparticles of platinum group metals (Pt, Pd, Ru): Enhancement on photoelectrochemical performance. *J. Nanoparticle Res.* **2019**, *21*, 29. [\[CrossRef\]](#)
38. Tauc, J. Absorption edge and internal electric fields in amorphous semiconductors. *Mater. Res. Bull.* **1970**, *5*, 721–729. [\[CrossRef\]](#)
39. Livshits, V.; Philosoph, M.; Peled, E. Direct ethylene glycol fuel-cell stack—study of oxidation intermediate products. *J. Power Sources* **2008**, *178*, 687–691. [\[CrossRef\]](#)
40. Nguyen, S.T.; Lee, J.-M.; Yang, Y.; Wang, X. Excellent durability of substoichiometric titanium oxide as a catalyst support for Pd in alkaline direct ethanol fuel cells. *Ind. Eng. Chem. Res.* **2012**, *51*, 9966–9972. [\[CrossRef\]](#)
41. Yue, H.; Zhao, Y.; Ma, X.; Gong, J. Ethylene glycol: Properties, synthesis, and applications. *Chem. Soc. Rev.* **2012**, *41*, 4218–4244. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Melvin, A.A.; Illath, K.; Das, T.; Raja, T.; Bhattacharyya, S.; Gopinath, C.S. M–Au/TiO₂ (M= Ag, Pd, and Pt) nanophotocatalyst for overall solar water splitting: Role of interfaces. *Nanoscale* **2015**, *7*, 13477–13488. [\[CrossRef\]](#)
43. Spanu, D.; Recchia, S.; Mohajernia, S.; Schmuki, P.; Altomare, M. Site-selective Pt dewetting on WO₃-coated TiO₂ nanotube arrays: An electron transfer cascade-based H₂ evolution photocatalyst. *Appl. Catal. B Environ.* **2018**, *237*, 198–205. [\[CrossRef\]](#)
44. Nguyen, N.T.; Altomare, M.; Yoo, J.E.; Taccardi, N.; Schmuki, P. Noble metals on anodic TiO₂ nanotube mouths: Thermal dewetting of minimal Pt Co-Catalyst loading leads to significantly enhanced photocatalytic H₂ generation. *Adv. Energy Mater.* **2015**, *6*, 1501926. [\[CrossRef\]](#)
45. Nguyen, N.T.; Yoo, J.; Altomare, M.; Schmuki, P. “Suspended” Pt nanoparticles over TiO₂ nanotubes for enhanced photocatalytic H₂ evolution. *Chem. Commun.* **2014**, *50*, 9653–9656. [\[CrossRef\]](#)
46. Nguyen, N.T.; Ozkan, S.; Hejazi, S.; Denisov, N.; Tomanec, O.; Zboril, R.; Schmuki, P. Providing significantly enhanced photocatalytic H₂ generation using porous PtPdAg alloy nanoparticles on spaced TiO₂ nanotubes. *Int. J. Hydrogen Energy* **2019**, *44*, 22962–22971. [\[CrossRef\]](#)
47. Kwak, B.-S.; Chae, J.-H.; Kim, J.-Y.; Kang, M.-S. Enhanced hydrogen production from methanol/water photo-splitting in TiO₂ including Pd component. *Bull. Korean Chem. Soc.* **2009**, *30*, 1047–1053.
48. Beasley, C.; Kumaran Gnanamani, M.; Santillan-Jimenez, E.; Martinelli, M.; Shafer, W.D.; Hopps, S.D.; Wanninayake, N.; Kim, D.Y. Effect of metal work function on hydrogen production from photocatalytic water splitting with MTiO₂ catalysts. *ChemistrySelect* **2020**, *5*, 1013–1019. [\[CrossRef\]](#)
49. Van Langeveld, A.; Hendrickx, H.; Nieuwenhuys, B. The surface composition of Pd-Cu alloys: A comparative investigation of photoelectric work function measurements, Auger electron spectroscopy and calculations based on a broken bond approximation. *Thin Solid Films* **1983**, *109*, 179–192. [\[CrossRef\]](#)