A direct synthesis of platinum/nickel co-catalysts on titanium dioxide nanotube surface from hydrometallurgical-type process streams

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ABSTRACT

Solutions that simulate hydrometallurgical base metal process streams with high nickel (Ni) and minor platinum (Pt) concentrations were used to create Pt/Ni nanoparticles on TiO2 nanotube surfaces. For this, electrochemical deposition – redox replacement (EDRR) was used that also allowed to control the nanoparticle size, density and Pt/Ni content of the deposited nanoparticles. The Pt/Ni nanoparticle decorated titanium dioxide nanotubes (TiO2 nanotubes) become strongly activated for photocatalytic hydrogen (H2) evolution. Moreover, EDRR facilitates nanoparticle formation without the need for any additional chemicals and is more effective than electrodeposition alone. Actually, a 10,000-time enrichment level of Pt took place on the TiO2 surface when compared to Pt content in the solution with the EDRR method. The results show that hydrometallurgical streams offer great potential as an alternative raw material source for industrial catalyst production when coupled with redox replacement electrochemistry.

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1. Introduction

This paper outlines a viable method to grow Pt/Ni nanoparticles on TiO2 nanotube surfaces, directly from solutions that resemble those available in industrial nickel processing. Global nickel resources originate from two different types of ores, sulfides and laterites, which in hydrometallurgical Ni recovery are dissolved to either chloride, sulfate or ammonia media, with or without pyrometallurgical pre-treatment steps. Ni recovery from these solutions is typically achieved by solvent extraction-electrowinning (i.e. a pure electrodeposition) route, although hydrogen reduction and different chemical precipitation methods may also be used. As a result, all Ni processing produces hydrometallurgical solutions that not only contain nickel but also a variety of other metals originally present in the ore - like cobalt, copper and precious metals - and the processes are usually optimised also to recover these other metals (Crundwell et al., 2011). In spite of this, such solutions can still contain trace amounts of precious metals, which are not recovered from solutions due to a high concentration ratio between the base metal (such as Ni) and trace metals (such as Pt).

This is of particular importance in view of the global scarcity of metal resources that has become an imminent concern (Peck et al., 2015) and thus, improved recycling and recovering of metals from impure process solutions, acidic industrial side-streams and other waste streams is becoming a necessity. At the same time, emerging technologies like fuel cells may increase the demand for Pt as a catalyst material even further (Peck et al., 2015) and therefore, identification of alternative (secondary) raw material sources for platinum group metal (PGM) based catalysts is essential.

Ni-Pt combinations have been proved to be extremely effective catalyst materials (Debe, 2012; He et al., 2011, 2013; Kühl and Strasser, 2016; Shao et al., 2016) and thus, process and side-streams associated with Ni metal (McDonald and Whittington, 2008a,b) could be potential raw material sources when trace amounts of Pt is present, especially as annual global nickel production is over 2000 Gg (i.e. 2 million tonnes) and expected to increase up to 140–175% by 2025 (Elshkaki et al., 2017). However, due to the high concentration ratio between Ni and precious metals, the hydrometallurgical solutions in nickel production have not been
considered suitable for recovery of precious metals, and even less, for production of a high-added value Pt catalyst.

On the other hand, the toxic nature of nickel solutions—which are inevitable in hydrometallurgy in order to fulfill the ever increasing global nickel demand—would require new methodologies of how to fully exploit these solutions and also, the minor components present in them. The results presented here show that utilising redox replacement reactions the formation of Pt/Ni catalysts from such solutions is indeed possible, without any additional chemicals.

Usually the redox replacement reaction is used in conjunction with electrochemical deposition and this is the case in our studies (Fig. 1). Firstly, Ni is electrodeposited and then, the redox replacement reaction takes place spontaneously between electrodeposited Ni and Pt$^{2+}$ ions due to the difference in the reduction potentials: the deposited Ni is oxidised by Pt$^{2+}$ and dissolved back to solution as Ni$^{2+}$, whilst Pt$^{2+}$ is reduced to Pt and deposited on the electrode. The half-reaction for the oxidation of Ni is shown in Reaction 1a and the reduction of Pt$^{2+}$ in Reaction 1b, together with their respective standard electrode potentials ($E^\circ$ vs. SHE).

$$\text{Ni}_i \rightarrow \text{Ni}^{2+}_{aq} + 2e^- \quad E^\circ(\text{ox}) = +0.25 \text{ V vs. SHE} \quad (1a)$$

$$\text{Pt}^{2+}_{aq} + 2e^- \rightarrow \text{Pt}_s \quad E^\circ(\text{red}) = +1.20 \text{ V vs. SHE} \quad (1b)$$

The overall redox reaction is displayed in Reaction 2, together with the standard reaction potential, which is the driving force for the spontaneous redox replacement reaction:

$$\text{Ni}_i + \text{Pt}^{2+}_{aq} \rightarrow \text{Ni}^{2+}_{aq} + \text{Pt}_s \quad E^\circ(\text{RR}) = +1.45 \text{ V vs. SHE} \quad (2)$$

In contrast to other electrochemical-redox replacement methods like electrochemical-atomic layer deposition (e-ALD) (Gregory and Stickney, 1991; Vaidyanathan et al., 2006) or surface-limited redox replacement (SLRR) (Brankovic et al., 2001), the goal here is not to deposit smooth monolayers but utilise electrodeposition-redox replacement method (EDRR) to create functional Pt/Ni catalysts directly from solutions resembling hydrometallurgical Ni process solutions.

Moreover, this one step approach differs from those presented in literature about Pt/Ni surfaces prepared by EDRR (Papadimitriou et al., 2008, 2010; Retewe et al., 2009; Tegou et al., 2010; Wang et al., 2011; Zhang et al., 2012) or electroless deposition-redox replacement (Tamašauskaitė-Tamašiūnaitė et al., 2013, 2014). In these previous studies, all the solutions have been optimised for the application, i.e. Pt and Ni concentrations of synthetic solutions are tailored for the most effective catalyst formation and they do not represent industrial solutions. Conversely, this paper demonstrates—for the very first time—that non-optimised solutions and side-streams could be a potential raw material sources for functional Pt/Ni catalyst surfaces. These solutions are indeed challenging as in hydrometallurgical Ni process solutions the Ni content is high and...
Pt content extremely low: for a 10 ppm Pt solution, Ni/Pt concentration ratio is typically \( \approx 20,000 \).

Earlier, the authors have demonstrated that Ag can be recovered from Zn based hydrometallurgical solutions by EDRR (Halli et al., 2017) and Au from copper based solutions (Korolev et al., 2018) whereas this current paper goes beyond that approach: instead of pure recovery of a precious metal, functional Pt/Ni catalytic surfaces are produced and used without any further modifications for photocatalytic \( \text{H}_2 \) generation.

From an industrial perspective, the possibility to utilise under sourced side-streams and process solutions for catalyst production makes EDRR already very attractive method but it has also further advantages: EDRR does not demand any additional chemicals, unlike cementation (precipitation) or solvent extraction traditionally used in hydrometallurgy for metal recovery, no neutralization chemicals are needed either, and when compared to electrowinning (pure electrodeposition), EDRR is more effective with solutions of trace amount of precious metals. This all makes the EDRR method more sustainable than the competing methods.

Overall, this research demonstrates a new route for the exploitation underutilised industrial side-stream solutions, which not only leads to the formation of catalytic surfaces for clean energy production but also has the added benefit of reducing/eliminating the presence of potentially toxic material (Pt) from industrial Ni processing. Furthermore, this method provides a platform for the cost and material competitive large-scale catalyst production based on the principles of circular economy.

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**Fig. 3.** Comparison of deposited nanoparticles on flat \( \text{TiO}_2 \) when using pure galvanostatic pulsing or EDRR method, from solution containing 100 ppm Pt, 60 g/l Ni and 10 g/l \( \text{H}_2\text{SO}_4 \) (Ni + Pt solution) or 60 g/l Ni and 10 g/l \( \text{H}_2\text{SO}_4 \) (Ni solution).

<table>
<thead>
<tr>
<th>Galvanostatic pulsing</th>
<th>EDRR</th>
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<tr>
<td>( i_{(\text{cathodic})} = 100 \text{ mA/cm}^2 )</td>
<td>( i_{(\text{cathodic})} = 100 \text{ mA/cm}^2 )</td>
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<td>( i_{(\text{anodic})} = 10 \text{ mA/cm}^2 )</td>
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<td>Number of pulses: 74</td>
<td>Number of pulses: 74</td>
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<td>Redox replacement time: 0 s</td>
<td>Redox replacement time: 30 s</td>
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<tr>
<td>Number of cycles: 30</td>
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**Fig. 4.** Effect of the first EDRR cycles on Pt/Ni nanoparticle nucleation from 100 ppm Pt, 60 g/l Ni and 10 g/l \( \text{H}_2\text{SO}_4 \) solution: SEM images after the first and the fifth cycle with 10,000 magnification (upper row) and 50,000 magnification (lower row). EDRR parameters: \( i_{(\text{cathodic})} = 100 \text{ mA/cm}^2 \) for 10 ms, \( i_{(\text{anodic})} = 20 \text{ mA/cm}^2 \) for 10 ms, total number of pulses: 74 (37 cathodic-anodic pulse pairs), redox replacement time: 30 s.
2. Materials and methods

Flat TiO$_2$ surfaces were prepared by anodising Ti foil (99.9%) at 20 V for 15 min in 0.5 M H$_2$SO$_4$. In contrast, TiO$_2$ nanotubes were prepared by the immersion of Ti foil in a tri-ethylene glycol electrolyte consisting of 0.3 M NH$_4$F and 3 M H$_2$O, at 60 V at 60°C for 15 min. After anodising, all the samples were annealed in air at 450°C for 1 h.

Ni nanoparticles were prepared on TiO$_2$ surfaces by the electrodeposition – redox replacement (EDRR) method (Ivium CompactStat) from a solution containing 60 g/l nickel (from NiSO$_4$·6H$_2$O, ACS grade, Sigma-Aldrich) and 10 g/l H$_2$SO$_4$ (95–98%, p.a., Carl Roth), while Pt/Ni nanoparticles were deposited from the same base solution (60 g/l nickel + 10 g/l H$_2$SO$_4$) having 10 ppm or 100 ppm Pt (from 1000 mg/l AAS standard, Sigma-Aldrich). Either flat TiO$_2$ or TiO$_2$ nanotube surfaces — with a geometric area 0.5 cm$^2$ — were used as the working electrode, with a Pt sheet (6 cm$^2$) as the counter electrode and Ag/AgCl in 3 M KCl as the reference electrode. The distance between working and counter electrode was 2 cm and the volume of the solution was 20–25 ml.

In EDRR method, the electrodeposition step (ED step) was performed galvanostatically and consisted of a total 74 short cathodic and anodic current pulses. After 37 cathodic-anodic pulse pairs, a redox replacement (RR) step was performed. During this step, no external current or voltage was applied but open circuit potential (OCP) was recorded until a pre-determined time had elapsed. After this, the EDRR cycle was repeated - first with 37 cathodic-anodic pulse pairs followed by a RR step.

In the case of the flat TiO$_2$ surfaces, the cathodic and anodic current pulses had a duration of 10 ms each and the current density was $-100$ mA/cm$^2$ and $+20$ mA/cm$^2$, respectively. The RR step time was either 10, 30 or 60 s and the number of full EDRR cycles was varied (10, 20 or 30 cycles). For TiO$_2$ nanotube surfaces the conditions were modified, such that the cathodic pulse durations were 4 s at $-30$ mA/cm$^2$ and anodic pulses 10 ms at $+30$ mA/cm$^2$, to reflect the higher surface area and lower conductivity of the tubes. The associated RR time was set to be between 60 and 240 s and the number of cycles was either 10 or 20 cycles.

Field-emission scanning electron microscope (FE-SEM Hitachi S4800) was used to characterize the morphology of the samples, whereas X-ray photoelectron spectroscopy (XPS, PHI 5600) provided the chemical composition of the samples. In XPS, the signal intensity was divided by a relative sensitivity factor (RSF) and normalized over all of the elements detected. All data processing was performed using MultiPack v.9.6.0 software.

Photocatalytic H$_2$ generation measurements were conducted by irradiating the TiO$_2$ samples with an AM 1.5 solar simulator (100 mW/cm$^2$) in a quartz tube containing a 20 vol% ethanol-water solution for 5 h. The amount of produced H$_2$ was measured by using a gas chromatograph (GCMS-QO2010SE, Shimadzu) equipped with a thermal conductivity detector and a Restek micropacked Shin Carbon ST column (2 m × 0.53 mm). The quartz reactor was purged with N$_2$ gas for 10 min to remove O$_2$ prior to the initiation of the photocatalytic experiments.

3. Results and discussion

Pt/Ni nanoparticles are formed on TiO$_2$ surface during electrodeposition-redox replacement (EDRR) cycling and a typical EDRR measurement is shown in Fig. 2: short cathodic + anodic current pulses (during the ED step) are followed by redox replacement (RR step) and the EDRR procedure is cycled a number of times. The EDRR profiles for all samples are shown in Supporting Information (Fig. S1).

The ED step (electrodeposition) consists of galvanostatic pulsing between cathodic and anodic currents. Firstly, Ni and possibly some Pt is deposited during the short cathodic current pulse, though simultaneous H$_2$ evolution - that disturbs the deposition - may also take place. This is overcome by applying a short anodic current pulse that not only results in hydrogen desorption, but also makes more surface sites available for deposition in the following cathodic pulse (Kollia et al., 1990; Spanou and Pavlatou, 2010). During the RR step (redox replacement) there is a spontaneous replacement of...
deposited Ni with Pt, due to the difference in electrochemical oxidation/reduction potentials - Pt$^{2+}$ oxidises the electrodeposited Ni to soluble Ni$^{2+}$ while it itself is simultaneously reduced to Pt and deposited to the surface (see Reactions 1–2).

Fig. 3 highlights the need of redox replacement (RR) step in the nanoparticle formation. The galvanostatic pulsing (i.e. ED step) alone is not an effective method for the formation of Pt/Ni nanoparticles as is clearly observed when comparing SEM images of a Pt/

![Fig. 3](image)

**Fig. 6.** (a) The XPS spectrum of Ni2p region (left) and Pt4f region (right), for a sample prepared on flat TiO$_2$ surfaces by EDRR method (redox replacement time: 30 s, number of cycles: 30) from 100 ppm Pt, 60 g/l Ni and 10 g/l H$_2$SO$_4$ solution, (b) the atomic-% and (c) weight-% of Pt and Ni on flat TiO$_2$ surface as a function of number of EDRR cycles and redox replacement time determined by XPS.
Ni nanoparticles prepared with galvanostatic pulsing to those prepared by EDRR method. The used parameters were the same in both of these cases, the only difference being that EDRR has an additional RR step/cycle. For comparison, Fig. 3 also shows the deposition of pure Ni nanoparticles by EDRR method and it is evident that although Pt is not necessary for the nucleation of particles on the surface, it improves it. In addition, the presence of Pt results in a characteristically jagged appearance of the nanoparticles (see Supporting Information, S2). This observation is probably a result of Pt growth on the nanoparticles, both during the redox replacement step and possible co-deposition on previously replaced Pt in the subsequent ED steps.

The positive effect of redox replacement step on nanoparticle formation is partly due to Ostwald ripening, leading to the presence of larger surface features, and partly due to the replenishing of solution nearby the electrode, reducing the possibility of mass-transfer limitation in ED step. Natter and Hempelmann (2003) have found a similar observation with pulse electrodeposition when varying \( t_{\text{off}} \) (i.e. short current-off time between deposition pulses) for Au nanoparticles, i.e. the size of nanoparticles grew with longer \( t_{\text{off}} \) time. It is important to note that - in addition to different materials and solutions (Au in literature (Natter and Hempelmann, 2003) cf. Pt/Ni presented here) - \( t_{\text{off}} \) time has a different purpose than RR time. In pulse electrodeposition, \( t_{\text{off}} \) is applied only for milliseconds between short deposition pulses and pulsing is performed in a single metal electrolyte in order to replenish the surface from adsorbed hydrogen, while RR time is clearly longer and performed after electrodeposition step in multi-metal electrolyte in order to redox replacement reaction to take place. As a result, enrichment of the more noble metal on the surface takes place.

The effect of the initial EDRR cycles on Pt/Ni nanoparticle nucleation is presented in Fig. 4, which comprises of Pt/Ni nanoparticles deposited to flat TiO\(_2\) surface using a single cycle or 5 cycles (the redox replacement time: 30 s). As can be seen, already after a single EDRR cycle particles have nucleated on the surface, although the particle size is relatively small. When the number of cycles is increased, both the particle density and size of the particles increase substantially and start to show the characteristic jagged appearance. Data from XPS shows that the at-% of Pt is 0.29 after a single cycle and it increases to 5.77 at-% after 5 cycles, whereas of Ni at-% remains low (0.77% after 1 cycle cf. 0.87 at-% after 5 cycles), suggesting that even if Pt may co-deposit with Ni during electrodeposition step, it is deposited primarily during the redox replacement step.

The formation of Pt/Ni nanoparticles is further studied as a function of number of cycles and RR time (Fig. 5 - SEM and Fig. 6 - XPS). The associated potential profiles of EDRR (Fig. S1) are shown in Supporting Information.

From Fig. 5 it is seen that the size of nanoparticles increases both as a function of number of cycles and RR time. As previously discussed (Fig. 3), the positive effect of RR time on the size and nanoparticle density can be associated with Ostwald ripening and replenishing the solution nearby the electrode: the dissolution of Ni from the surface during RR step leads to a higher local concentration in the vicinity of the electrode, further diminishing the possible mass-transport limitation in the following ED step.

Fig. 6(a) shows examples of Ni2p and Pt4f spectra for a sample prepared from 100 ppm Pt solution on a TiO\(_2\) surface using the EDRR method (the redox replacement time was 30 s and number of cycles 30). As can be seen, the Pt4f region has well separated spin-orbit components (\( \Delta_{\text{metal}} = 3.35\text{eV} \)). The atomic-% (and weight-%) of Pt was determined by considering the doublet peak of Pt4f region, which can be de-convoluted into four peaks. The presence of two main peaks (69.75 eV and 73.12 eV) is ascribed to the Pt\(^0\) 4f\(_{7/2}\) and Pt\(^0\) 4f\(_{5/2}\), while the other small peaks at 71.0 eV and 75.26 eV correspond to Pt\(^2+\) 4f\(_{7/2}\) and Pt\(^2+\) 4f\(_{5/2}\). Ni2p peak, on the other hand, has split spin-orbit components (\( \Delta_{\text{metal}} = 17.3\text{eV} \)) that comprise of core level and satellite features, which can be resolved into eight peaks. Two peaks are located at 851.25 eV (Ni\(^0\) 2p\(_{3/2}\)) and 868.5 eV (Ni\(^0\) 2p\(_{1/2}\)), indicating the presence of Ni metal. Another

![Redox Replacement time](image.png)
two peaks at 852.40 eV (Ni^{2+}\cdot 2p_3/2) and 869.76 eV (Ni^{2+}\cdot 2p_1/2) are ascribed to the NiO. The other two peaks at 855.14 eV (Ni^{2+}\cdot 2p_3/2) and 872.44 eV (Ni^{2+}\cdot 2p_1/2) are due to the formation of Ni(OH)\textsubscript{2}. The peaks at 860.44 eV and 879.06 eV are the satellite peaks.

As can be observed from Fig. 6(b–c), also the atom-% of Pt (and the respective weight-% of Pt, both determined by XPS) increases with longer RR times. This is due to the mass-transfer limitations related to the low Pt concentration: the mass-transfer quickly limits the redox replacement reaction when Pt content is present only in ppm levels and thus, increasing the replacement time provides longer time for Pt to reach the electrode surface, resulting in higher Pt at-% on the surface. In order to demonstrate more clearly the purity of the end-product, the Pt/Ni ratio is calculated from at-% - Fig. 6(b) – and demonstrates that higher RR time results in higher end-product purity.

The effectiveness of the EDRR, on the other hand, is best discussed in terms of enrichment, which is calculated by comparing the weight-% of Pt on the particles (determined by XPS) to weight-% of Pt in the solution. It is remarkable how effective EDRR is when compared to pure galvanostatic pulsing (Figs. 3 and 6c). For example for a 100 ppm (1 ppm = 0.0001 wt-%) Pt solution, utilising 60 s RR time results in 42 weight-% of Pt on the surface after only 20 EDRR steps. This translates to over 4,200-fold enrichment. In comparison, the reference sample shown in Fig. 3 (30 cycles of galvanostatic pulsing and no RR steps) has a significantly lower Pt content (4.6 wt-%), resulting in a decade lower (460) enrichment, even if the current input in the reference sample is higher (20 cycles in EDRR cf. 30 cycles in galvanostatic pulsing).

To further demonstrate the industrial feasibility of the EDRR method, the formation of nanoparticles was performed from a solution containing only 10 ppm of Pt but with the same Ni concentration (60 g/l of Ni), resulting in concentration ratio Ni/Pt = 20,000. As can be seen in Fig. 7, the formation of Pt/Ni nanoparticles is successful even with such a low concentration of Pt in solution. Moreover, XPS analysis showed that with 60 s replacement time 15 wt-% of Pt was deposited on the surface, a level that is over three times higher than obtained by the pure galvanostatic pulsing (reference sample) from the 100 ppm Pt solution. In the terms of the enrichment, EDRR results in over 10,000-time enrichment of Pt from 10 ppm solution, suggesting that the method is extremely feasible with the solutions with a low level of precious metals.

In order to investigate further the abilities of EDRR in the formation of the high-value added products, experiments were performed using TiO\textsubscript{2} nanotube substrates (Fig. 8 – SEM and Fig. 9 - XPS). TiO\textsubscript{2} nanotube surfaces are promising candidates for the photocatalytic applications as the tubular configuration provides a high light absorption pathway and aids the prevention of the recombination of photo-generated electron/hole pairs (Tong et al., 2012). Moreover, TiO\textsubscript{2} nanotubes have demonstrated drastically enhanced photocatalytic activity in numerous studies when the nanotubes are decorated with “co-catalyst” metal nanoparticles (Christoforidis and Fornasiero, 2017; Liang et al., 2013; Ni et al., 2007; Papadimitriou et al., 2008; Park et al., 2013).

Figs. 8–9 demonstrate that the size and the amount of Pt/Ni nanoparticles on TiO\textsubscript{2} nanotube surface can indeed be controlled by RR time and cycling when using the EDRR method (see also Fig. S2b). The results also show that particles not only nucleate on the top of the nanotubes but also on the outer walls, allowing the exploitation of the 1D nature of the tubes for photocatalysis: the main advantages of 1D materials are the enhanced light absorption combined with short reaction paths of photogenerated carriers (Xiao et al., 2015; Altmare et al., 2016; Nguyen et al., 2015, 2016). The XPS of Pt/Ni ratio (Fig. 9(b), at-% determined by XPS) which has been shown to be a critically important factor in the electrocatalysis of oxygen reduction reaction in numerous studies (Jiang et al., 2017; Toda et al., 1999; Yang et al., 2004).

In order to demonstrate that the EDRR method could be used to produce photocatalytic surfaces from hydrometallurgical base metal streams, proof-of-concept measurements of photocatalytic H\textsubscript{2} generation with the prepared Pt/Ni nanoparticle - TiO\textsubscript{2} nanotube surfaces were performed. Fig. 10 shows that these surfaces indeed possess significant activity for H\textsubscript{2} evolution, the highest being an over 30-fold enhancement (the redox replacement step = 240 s and number of cycles = 20) when compared to a pure TiO\textsubscript{2} nanotube surface. When the photocatalytic activity is compared to TiO\textsubscript{2} nanotube surfaces covered with pure Ni nanoparticles, the H\textsubscript{2} evolution levels are similar for fresh samples (see Supporting Information, S3). However, pure Ni nanoparticles suffers from aging whereas Pt or Pt/Ni are highly stable against oxidation (S3). Moreover, the catalytic activity shown here is comparable with
literature, e.g. our results show a similar \( \text{H}_2 \) evolution rate under 1.5 AM solar illumination as that obtained for atomic layer deposited Pt as co-catalysts on TiO\(_2\) nanotubes (Yoo et al., 2018). The results also indicate that the Pt/Ni ratio is critical for \( \text{H}_2 \) evolution: the sample with highest \( \text{H}_2 \) production has also the clearly highest Pt/Ni ratio \( \approx 8 \), while for all the other surfaces the Pt/Ni ratio \( = 2 \) (Fig. 9(b)). All these samples with a similar Pt/Ni ratio have also similar hydrogen evolution rates (Fig. 10), thus indicating the critical role of Pt/Ni ratio in the particles.

As the presented EDRR method is particularly powerful in tuning the Pt/Ni composition, these results are very promising in the view of preparing photocatalytic surfaces directly from sulfate based process streams or side streams of hydrometallurgical Ni metal plants. EDRR is truly attractive approach for the industrial solutions that contain only a small amount of platinum group metals (PGMs), especially as Pt/Ni nanoparticle formation consumes electricity only during the Ni deposition steps while Pt is “enriched” on the surface via an electroless redox replacement.

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**Fig. 9.** (a) The XPS spectrum of Ni 2p region (left) and Pt 4f region (right), for a sample prepared on TiO\(_2\) nanotube surfaces by EDRR method from 100 ppm Pt, 60 g/l Ni and 10 g/l H\(_2\)SO\(_4\) solution (redox replacement time: 120 s, number of cycles: 20), (b) the atomic-\% and (c) weight-\% of Pt and Ni on TiO\(_2\) nanotube surfaces as a function of number of cycles and redox replacement time, determined by XPS.
reaction, thus enhancing the process economics. It is also worth noting that as EDRR was successful from solutions with Ni/Pt ratio as high as 20,000, the industrial Ni process solutions and side-streams containing trace amounts of PCMs could potentially be “a platinum mine” for clean energy technologies if a future industrial process was developed. For example, in an average size base metal plant 10 m³/h or even 100 m³/h of such solutions are flowing in the processes, and with such amounts the large-scale production of catalysts — which has been identified as one of the main tasks of catalyst development (Debe, 2012) — can truly become possible.

Real hydrometallurgical solutions also contain other metals than Ni and Pt and these will influence both the EDRR process and resultant surface. Previous results of Ag recovery from Zn/Ag solutions [Yliniemi et al., 2018] have shown that although the presence of Fe³⁺ as in impurity may slightly reduce enrichment efficiency, it may improve product purity. This is most likely due to the selective dissolution of Zn by Fe³⁺ as the reduction potential of Fe³⁺/Fe²⁺ (E° = 0.77 V vs. SHE) is higher than that of Zn²⁺/Zn. Thus, both Fe³⁺ and Ag⁺ can oxidise Zn to Zn²⁺ but only Ag is enriched on the surface as Fe³⁺ is reduced to soluble Fe²⁺. Similar behaviour is expected in Ni/Pt solution and when considering performance, this may actually result in increased catalytic activity. Therefore, EDRR performed in hydrometallurgical solutions has huge potential for the recovery of precious metals like Ag (Halli et al., 2017; Yliniemi et al., 2018) and Au (Korolev et al., 2018). Furthermore, this paper shows that EDRR can also directly produce functionalised surfaces with Pt or other trace metals present in hydrometallurgical solutions. Moreover, EDRR method allows control over not only particle size and density, but more importantly, over the precious metal/base metal ratio (here Pt/Ni) in the particles, i.e. EDRR provides also a control over the catalytic activity of these surfaces.

4. Conclusions

The EDRR process outlined here is an effective method for the production of catalytic surfaces and simultaneously, exploiting the hydrometallurgical solutions fully by utilising also the minor components (such as Pt) present in them. Remarkably, the results presented here show a 10,000-time enrichment level of Pt onto the surface when Pt/Ni nanocatalysts are formed from solution simulating hydrometallurgical process streams on TiO₂ surfaces by EDRR. It is also noteworthy, that such an enrichment is possible without any additional use of chemical or further modifications.

By adjusting the different EDRR parameters (number of cycles or redox replacement time), the surface characteristics of the resultant catalytic nanoparticles can be tuned to control the desirable properties like nanoparticle size and distribution. Moreover, preliminary results of the produced Pt/Ni co-catalytic surfaces for photocatalytic H₂ evolution demonstrated the level of performance that is comparable to the standard procedures for co-catalytic Pt/ TiO₂ surfaces found in literature.

Overall, the findings offer a more sustainable circular economy platform, where minor concentrations of valuable metals present in base metal production solutions are used for the preparation of high-value products to be used as photocatalysts in clean energy sector.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2018.08.022.

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