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Surface plasmon resonance-induced visible light photocatalytic TiO_2 modified with AuNPs for the quantification of hydroquinone

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Abstract

The impregnation of size-controlled gold nanoparticles (AuNPs) on an anatase TiO_2 structure (AuNPs@TiO_2) was studied for the photoelectrochemical detection of hydroquinone (HQ) under visible light illumination integrated into a flow injection analysis (FIA) setup. The crystalline form of TiO_2 was preserved during synthesis and the homogeneous distribution of AuNPs over the TiO_2 structure was confirmed. Its photoelectrocatalytic activity was improved due to the presence of AuNPs, preventing charge recombination in TiO_2 and improving its light absorption ability by the surface plasmon resonance effect (SPR). The FIA system was used in order to significantly reduce the electrode fouling during electroanalysis through periodic washing steps of the electrode surface. During the amperometric detection process, reactive oxygen species (ROS), generated by visible light illumination of AuNPs@TiO_2, participate in the oxidation process of HQ. The reduction of the oxidized form of HQ, *i.e.* benzoquinone (BQ) occurs by applying a negative potential and the measurable amperometric response will be proportional to the initial HQ concentration. The influencing parameters on the response of the amperometric photocurrent such as applied potential, flow rate and pH were investigated. The linear correlation between the amperometric response and the concentration of HQ was recorded (range 0.0125 – 1.0 µM) with a limit of detection (LOD) of 33.8 nM and sensitivity of 0.22 A M^{-1} cm^{-2}. In this study, we illustrated for the first time that the impregnation of AuNPs in TiO_2 allows the sensitive detection of phenolic substances under green laser illumination by using a photoelectrochemical flow system.

Keywords: Gold nanoparticles, titanium dioxide, surface plasmon resonance, photoelectrochemical detection, flow injection analysis, reactive oxygen species, hydroquinone.

1. Introduction

Semiconductors-based photocatalysts have been widely used over the years in the fields of environmental applications and energy production [1-3]. Among a diversity of photocatalysts, titanium dioxide (TiO_2) is one of the best known and applied in several studies, such as in water and wastewater treatment, mainly due to its stability and cost effectiveness [1, 4, 5]. Furthermore, the numerous advantages of TiO_2 make it an attractive material for photocatalytic studies. Indeed, the material is biologically and chemically inert, non-toxic and commercially available, and it has excellent optical properties and efficient photocatalytic activity, being able to easily promote the oxidation of organic molecules [1, 6-9]. However, the band gap of TiO_2 is approximately 3.2 eV (anatase, rutile or brookite crystalline form), allowing it to only absorb about 3 to 5% of the solar spectrum radiation on earth [10]. Therefore, in order to promote electrons from the valency band of TiO_2 to its conduction band and, consequently, generating holes in the valence band, it is required to employ a light source with an energy potential superior to TiO_2 band gap (*i.e.* $\lambda \leq 387$ nm) [6].

Photocatalyst-based photoelectrochemical platforms are promising sensing devices, because of their low cost, easy-to-use, portability potential, with low background signal, high sensitivity and stability [9, 11]. One of the most striking advantages of the photoelectrochemical analysis technique is related to the separation of excitation and detection sources, leading to a reduced background signal with a potentially greater sensitivity in comparison to the traditional electrochemical techniques [12-14]. However, the semiconductors-based photocatalysts, such as TiO_2, are affected by the high electrons/holes recombination rate, which may result in a low photocatalytic yield [15, 16]. Concerning about this, in an attempt to build an efficient, stable and powerful photocatalytic material, modifying the semiconductor-based photocatalyst with an appropriate material can be an effective way to overcome the above mentioned disadvantage. Over recent years, numerous studies have been carried out in order to enhance the photocatalytic activity of TiO_2 under the visible light spectrum by using various strategies such as surface modification with adsorbates [17, 18], semiconductor-metal heterojunction [19, 20], non-metal elements doping [21] and metal doping [22, 23]. Among those strategies, incorporation of plasmonic metal nanoparticles into TiO_2 nanostructures is a promising way because a specific light wavelength can excite plasmons in the metal nanoparticles. These plasmons give rise to energetic hot electrons that enhance the photocatalytic process [24]. When nanoparticles of noble metals, such as Au or Ag are incorporated into the TiO_2 matrix, the metal-semiconductor Schottky barrier facilitates the transfer of these hot electrons from the conduction band of metal nanoparticle to conduction band of TiO_2, through the interface [23, 25]. Furthermore, the plasmonic nanoparticles also concentrate light in their vicinity i.e. near-field, working as light harvesters enabling higher visible light absorption by TiO_2 [26]. Therefore, TiO_2 photocatalytic activity and the sensitivity of the method can be significantly improved [15, 27-31].

Among different plasmonic materials, Au nanoparticles (AuNPs) have the advantage of high stability, plasmonic activity and straightforward protocols for synthesis and impregnation into TiO_2 [15, 32]. AuNPs-loaded TiO_2 (AuNPs@TiO_2) has been used in several fields, such as the photooxidation of organic molecules [33, 34], water and wastewater treatment [35, 36], photoelectrochemical cells [37] and dye-sensitized solar cells [38]. Since the plasmonic activity of AuNPs is size-dependent, the loading amount as well as the particle size of AuNPs play a crucial role in the improvement of the photocatalytic activity of TiO_2 [37, 39]. The Au nanoparticles in TiO_2 facilitate absorption of visible light by the plasmonic excitation eventually resulting in hot electron injection and near-field enhancement [26]. According to an alternative hypothesis, the plasmonic Au nanoparticles can also be acting as an electron sink capturing the excited electrons from TiO_2 and reducing the electron-hole recombination [15, 40]. Thus, plasmonic Au nanoparticles can impart visible light activity to TiO_2 for numerous applications, including photoelectrochemical sensing [41].

Photoelectrochemical TiO_2-based sensors have been widely explored for the quantification of organic compounds [11, 42-44]. Various studies have reported the application of photosensors for HQ detection, but most of them use UV as the light source [45-47] and/or have a high limit of detection (LOD) [45, 46, 48]. Hence, in order to utilize visible light for the generation of photoelectrons and enhance the sensitivity of the photoelectrochemical sensing, the TiO_2 modified with AuNPs (AuNPs@TiO_2) was successfully integrated into a flow injection analysis (FIA) system for the nM-range detection of HQ in sewage samples. The AuNPs were impregnated into TiO_2 via a facile photo-assisted synthesis. The quantification mechanism is based on the production of reactive oxygen species (ROS) which can oxidize the target analyte. By applying a negative potential, the oxidized analyte is reduced back to its original form, generating a measurable photocurrent response proportional to its concentration in solution. The sensing platform was also used to detect 4-AP in the same matrix sample. According to the obtained results, the proposed photoelectrochemical sensor integrated into a FIA system represents a new perspective on the use of a portable and accurate setup for monitoring water quality.

2. Experimental

2.1. Materials

4-aminophenol (4-AP), 3-aminophenol (3-AP), 2-aminophenol (2-AP), bisphenol A (BPA), 4-nitrophenol (4-NP), 3-nitrophenol (3-NP), phenol (Ph), Nafion® 117 (5% in a mixture of water and lower aliphatic alcohols), gold (III) chloride trihydrate ($HAuCl_4.3H_2O$), potassium phosphate monobasic (KH_2PO_4) and potassium chloride (KCl) were purchased from Sigma-Aldrich. Mesoporous TiO_2 (Millennium PC500) was obtained from Crystal Global (previously calcined to 450 °C to enlarge its pore size), 2-[4-(2-hydroxyethyl)-piperazinyl] ethane sulfonic acid (HEPES) was purchased from VWR® and hydroquinone (HQ) from Acros. The graphite screen-printed electrode (SPE, DS 110) was purchased from Metrohm DropSens. A phosphate buffer solution (PBS) of 10 mM KH_2PO_4 containing 0.1 M KCl was used as the supporting electrolyte. A NaOH solution was used to set the pH of the buffer solution to pH 7.0. The deionized water was used to prepare all solutions and all reagents were used without purification.

2.2. Apparatus

Photoelectrochemical measurements were performed using a PalmSens4 potentiostat (Utrecht, The Netherlands) with PSTrace software (version 5.8). A photoelectrochemical flow cell made of poly(methyl methacrylate) (PMMA) with an internal volume of 0.15 mL and dimensions of 22.75 x 8 mm (internal) and 36.75 x 25.55 mm (external) was used during the amperometric analysis. A peristaltic pump (Perkin-Elmer, France) equipped with omnifit labware (Diba) and Tygon tubing was used to propel the buffer into the flow line system, at an optimized flow rate (1 mL/min) (Fig. S1). The flow system was equipped with a manual sample injection valve (volume of 50 µL).

A laser source (green laser, $\lambda = 532$ nm, 10 mW), model MGL-III-532 coupled to a power supply model PSU-III-LED, (purchased from Roithner LaserTechnik GmbH, Austria) was used for the initiation of the photocatalytic reaction. A distance of 1.2 cm was set between the surface of the electrode and the green laser.

2.3. Synthesis of AuNPS@TiO_2 and electrode modification

Prior to the preparation of the plasmonic catalyst (AuNPs@TiO_2), the AuNPs were synthesized using a modified Turkevich method [49-52]. Briefly, 1 mL of 0.01 M $HAuCl_4.3H_2O$ precursor solution was added in 98 mL of Milli-Q water (total concentration 0.1 mM) in a two-neck round-bottom flask and further heated up to 100 ºC. Under vigorous stirring, 1 mL of freshly prepared 1 wt.% sodium citrate solution was added and the reaction mixture was left at the boiling temperature for 30 min and cooled down to room temperature then stored in the refrigerator for further use. The colloidal AuNPs solution was stored in the refrigerator in order to avoid their aggregation at ambient conditions and preserve the long-term stability of nanoparticles. This phenomenon affects the photocatalytic properties of AuNPs [53].

For the preparation of plasmonic catalyst, 10 mg of TiO_2 (Degussa P25) was photo-impregnated [54], with 10 mL of colloidal AuNPs solution (2.0 wt.%) under vigorous stirring and UVA irradiation (Philips Cleo UVA, 20 W, 365 nm) for 2 hours. The resulting solution was centrifuged and dried at room temperature. The procedure was repeated for higher amounts of Au loading on TiO_2 (15, 20 and 25 mL, means 3.0, 3.9 and 4.9 wt.%, respectively).

The SPE|AuNPs@TiO_2 sensor was obtained using the same modification procedure of graphite electrode described in our previous work [47]. Briefly, a suspension of 10 g L^{-1} AuNPs@TiO_2 dispersed in a solution of Nafion® containing 25 mM HEPES solution (76:24, v/v) was prepared and a volume of 5 µL from this suspension was used to modify the SPE graphite electrode. Subsequently, the electrode was dried in the dark at room temperature for approximately 2 h. Nafion® acts as an adhesive binder and ion conductor which ensures greater stability to the AuNPs@TiO_2 photocatalyst on the surface of the graphite electrode.

2.4. Characterization

The photometrics analyzes were performed to quantitatively determine the concentration of AuNPs loaded on TiO_2, by using a Spectroquant® photometer (NOVA 60 A) and a gold test kit purchased from MERCK.

The synthesized AuNPs@TiO_2 was characterized by scanning electron microscopy (SEM, model Zeiss EVO LS15) equipped with an energy dispersive X-ray detector (EDX, purchased from Bruker) to determine the elemental composition of nanoparticles. Data collection/processing was carried out using the AZtecEnergy software system, v. 2.1 (Oxford Instruments). The transmission electron microscopy (TEM) images were acquired by JEOL JEM-2100Plus operated at 200 kV.

In order to analyze the crystal structure of the AuNPs@TiO_2, X-ray diffraction (XRD) measurement was performed (Bruker, model D8 Advance). Raman studies were performed to evaluate the phases of AuNPs@TiO_2 sample, using Renishaw InVIA confocal scanning spectrometer, fitted with a 514 nm excitation source. The absorbance of AuNPs@TiO_2 was verified and its band gap energy was calculated from the results obtained by diffuse reflectance analysis, using a UV-DRS spectrophotometer (model V-630, Jasco).

The linear sweep voltammetry (LSV) was performed by a PalmSens4 potentiostat (Utrecht, The Netherlands) and PSTrace software (version 5.8) for the photocurrent transient study, using a step potential of 0.5 mV and scan rate of 0.25 mVs^{-1}, in the potential range between 0.4 V to -0.2 V.

2.5. Analytical procedure

The experimental and operational parameters referring to the proposed setup, such as the working potential, pH and flow rate were optimized in order to improve the photocurrent response. Chronoamperometry was used for all the electrochemical measurements. Deviation studies were performed based on three measurements made per each experiment (n = 3). The LOD was calculated by the equation LOD = $3s_b/a$ (s_b = standard deviation of the blank and a = slope from calibration curve).

The applicability of the proposed sensor was investigated by analyzing effluent water samples collected from the sewage treatment station Aquafin RWZI at Antwerpen-Noord, Belgium. The effluent water sample was filtered using a polyethersulfone membrane (PES) with a pore size of 0.2 μm, obtained from VWR®. The FIA system was equipped with two stream flow tubes and for the sample analysis one of the tubes was used for 20 mM PBS containing 0.2 M KCl and the other one for the carrier solution of the sample (Milli-Q water) (line A, Fig. S1). Thereafter, the buffer solution will be diluted by the carrier solution of the sample (E, Fig. S1), in order to obtain a final concentration of electrolyte of 10 mM PBS containing 0.1 M KCl (pH 7.0).

3. Results and Discussion

3.1. Morphological study

The XRD diffraction pattern of synthesized AuNPs@TiO_2 is shown in Fig. 1a. The results indicate that the AuNPs@TiO_2 sample is composed of an anatase (86%) and a rutile

(14%) phase, which is in accordance with the reference patterns of JCPDS card number 83-2243 and 21-1276, respectively, depicted in Fig. 1a. The diffraction peaks at 2θ values of 25.26°, 37.81°, 47.87°, 53.8°, 54.98°, 62.67° and 75° correspond to the crystallographic planes of (101), (004), (200), (105), (211), (213) and (215), respectively, related to anatase phase. Whereas, the peaks at 2θ values of 27.39°, 41.22°, 54.27°, 56.62° and 68.85° correspond to the rutile phase, and the crystallographic planes are (110), (111), (220), (002) and (301), respectively. The crystallographic peaks of metallic Au (JCPDS 04-0784) are not distinguishable in the diffraction pattern of AuNPs@TiO_2 sample due to its low concentration on the TiO_2 structure and a potential overlap between crystallographic peaks assigned to Au and anatase phase of TiO_2 [38, 55]. The average crystallite size of AuNPs@TiO_2 was estimated from the average of full width at half-maximum (FWHM) at 25.26°, 47.87° and 62.67° corresponding to (101), (200) and (213) diffraction peaks of anatase phase, respectively, by using the Scherrer equation [56]. The calculated average crystallite size is 18.23 nm for AuNPs@TiO_2 sample. Fig. 1b shows the Raman spectrum, in the range of 100-900 cm^{-1}. The Raman bands at 149.7, 195.4, 393.7, 511.1 and 634.4 cm^{-1} are related to the anatase phase. Increased intensity and a small shift of the Raman bands are observed. The red shift of the Raman band observed from 141.6 cm^{-1} to 150.1 cm^{-1} can be related to the surface enhancement by the impregnation of AuNPs, confirming the interaction between AuNPs and TiO_2 which implies an increasing of crystalline defects into TiO_2 [38, 55, 57]. The crystalline defects can act as trapping sites for photogenerated electrons and then deliver them to a collecting electrode for the photocurrent generation [55]. The presence of metallic Au nanoparticles could not be distinguished in the Raman bands of AuNPs@TiO_2 because of the low concentration loaded into TiO_2 structure and the weak Raman sensitivity, as well as reported from XRD results.

The morphology of AuNPs@TiO_2 (3.0 wt.% AuNPs loaded on TiO_2) and synthesized AuNPs is depicted in Fig. 2. During the impregnation process, AuNPs and TiO_2 were assisted by UV irradiation in order to promote their interaction, through the use of photogenerated electrons from the TiO_2 surface reducing the Au source [54]. Fig. 2a shows the SEM image of AuNPs@TiO_2 and Fig. 2b highlights the EDX results, confirming the presence of metallic Au in the sample. The TEM images of AuNPs and AuNPs@TiO_2 are shown in Fig. 2c and 2d, respectively. The average size of synthesized AuNPs is estimated to be around 18.7 ± 3.8 nm (Fig. 2c). The TEM analysis also illustrates that the AuNPs are loaded on TiO_2 and the structural features did not change during the photo-impregnation of AuNPs on TiO_2.

Since the amount of AuNPs loaded on TiO_2 might affect the photo-electrochemical responses, suspensions of AuNPs@TiO_2 with different concentrations of AuNPs were prepared (2.0, 3.0, 3.9 and 4.9 wt.%) and their corresponding photocurrent responses towards benzoquinone (BQ) reduction recorded (Fig. S2). The highest response for the reduction of BQ to HQ (6.0 μM) was obtained for a 3.0 wt.% of AuNPs loaded on TiO_2. Therefore, 3.0 wt.% of AuNPs-loaded TiO_2 was selected as an optimal ratio to be used for the photosensor construction. The optimum amount of AuNPs loaded on TiO_2 (3.0 wt.%) was also quantitatively determined by using a Spectroquant® test kit for Au and the average of all measurements were found to be 2.98 ± 0.13 wt.% (n = 4).

Several parameters and phenomena are taking place, and will contribute to the final response. Firstly, by loading adequate amounts of AuNPs, a Schottky barrier is formed at the interface of Au and TiO_2 [25], which significantly enhances the charge separation of holes and electrons and, thus, resulting in an increase of the photocurrent responses [38, 54]. On the other hand, by loading more AuNPs, they will occupy more active sites and extinguish a larger fraction of incoming light, inducing to a light screening effect. As a consequence, the light cannot reach the photocatalyst surface for efficient photogeneration of holes and electrons [58]. The photooxidation of Au by the photogenerated holes and OH radicals from the TiO_2 surface can also take place [59].

UV-Vis absorbance spectra of AuNPs, TiO_2 and AuNPs@TiO_2 are shown in Fig. 3a. The AuNPs and TiO_2 absorbance spectra exhibit a λ_{max} at 521 nm and 310 nm, respectively. The maximum absorption band for AuNPs@TiO_2 is at λ_{max} 554 nm, revealing the plasmonic resonance effect from AuNPs, indicating that metallic Au is presented in the sample, as already confirmed by the results of EDX and TEM analysis. The broad AuNPs@TiO_2 absorption response is related to the visible light absorption of AuNPs in the sample, which can be associated at least in part to its wide size distribution [60]. The band gap energy of AuNPs@TiO_2 was calculated using the Kubelka-Munk function (Fig. 3b) [61]. The plot $(\alpha h\nu)^{1/2}$ *vs* $h\nu$ is used to determine the E_g by extrapolating the linear region of the curve to the point of intersection with the x axis, where the energy absorption of AuNPs@TiO_2 is observed. The band gap value was determined as 3.17 eV, which is very close to the theoretical band gap of 3.2 eV for anatase phase of TiO_2. This result demonstrates that the photocatalytic ability of TiO_2 can be significantly improved by incorporating gold nanoparticles on its structure [15, 26, 27]. In addition, the SPR properties of AuNPs in the visible range provide a broad spectrum of absorption for TiO_2 [62, 63]. The UV-Vis absorbance spectra of colloidal AuNPs solution, AuNPs@TiO_2 suspension after impregnation and the supernatant of AuNPs@TiO_2 after centrifugation are presented in Figure S3. As expected, the absorbance spectrum of AuNPs@TiO_2 suspension just after impregnation did not show the absorbance peak due to the light scattering by TiO_2 in solution. The results from Figure S3 confirm that there are no traces of AuNPs in the supernatant and corroborate to prove that AuNPs were successfully impregnated on TiO_2.

Linear sweep voltammetry (LSV) was used to study the photocatalytic behavior of the material for HQ quantification. The linear sweep voltammograms of AuNPs@TiO_2 in the presence and absence of 1.0 µM HQ under chopped light illumination are shown in Fig. 4. Reduction photocurrents are distinguishable in the presence of HQ. The recorded responses in the negative potential range are related to the reduction of BQ to its original form, *i.e.* hydroquinone (HQ), which was previously oxidized by ROS generated on AuNPs@TiO_2 surface under green laser illumination.

3.2 Photocatalytic performance of SPE|AuNPs@TiO_2 for HQ sensing

The photoelectrochemical behavior of HQ at the SPE|AuNPs@TiO_2 under green laser source and using a FIA system was evaluated. Typically, the band edges of a n-type semiconductor e.g. TiO_2, are affected by varying the applied potential [64]. At potentials more negative than the flat band potential of TiO_2, there is an excess of the majority charge carrier (electrons) [65]. The cathodic current existent is potential-dependent because it corresponds to the flow of electrons from the conduction band (CB) of TiO_2 to the vacant states of the redox species in the electrolyte [66]. Because of the Schottky barrier on AuNPs/TiO_2 interface, the Au incorporated to TiO_2 acts as a co-catalyst and the photogenerated electrons induced by green light migrate from CB of AuNPs to TiO_2 CB, enabling the sequential oxidation of species on their surface [25, 54, 67]. Then the photoinduced electrons and holes in both TiO_2 and Au react with the molecules available at the surface to generate ROS (e.g. $^{\cdot}O_2^-$ and $^{\cdot}OH$) [68]. Later, the generated ROS oxidize HQ in the electrolyte [47]. Thereby, the reduction of the oxidized form of HQ, *i.e.* benzoquinone (BQ) occurs by applying a negative potential and the measurable photocurrent response is proportional to the initial HQ concentration (Fig. 5).

By analyzing the photocurrent response of the SPE|AuNPs@TiO_2 upon successive addition of different concentrations of HQ (Fig. 6A), a good linear correlation was recorded in the range of 0.0125 – 1.0 µM of HQ by applying a negative potential of -0.14 V versus Ag quasi-reference electrode (Fig. 6B).

In order to confirm the AuNPs@TiO_2 photocatalytic activity under green light illumination for quantification of HQ, several control experiments were performed. The inset of Fig. 6B shows a comparison between the photocatalytic activity of AuNPs@TiO_2 and TiO_2 under green light illumination. The photocurrent response using SPE|TiO_2 compared to SPE|AuNPs@TiO_2 for 1 μM HQ is about 14 times lower because TiO_2 has a very low photocatalytic activity under visible light illumination. Indeed, the impregnation of AuNPs can increase TiO_2 photocatalytic activity under visible light illumination (green laser, λ_{max} 532 nm).

The current responses for HQ detection were recorded using SPE|AuNPs@TiO_2 electrode in the absence of a light source. As it is shown in Fig. S4, the amperometric responses at SPE|AuNPs@TiO_2 without the light illumination are very low. In the dark, the production of ROS is not expected or not sufficient to efficiently oxidize HQ in the electrolyte solution. The same happens when a bare graphite electrode is used under green laser illumination and by applying negative potential (Fig. S5). Switching the light source to UV LED, a low generation of ROS is observed and the photocatalytic activity of AuNPs@TiO_2 achieved is not optimal (Fig. S6).

The linear correlation between the amperometric response of SPE|AuNPs@TiO_2 under green laser illumination and the concentration of HQ was recorded with LOD of 33.8 nM and sensitivity of 0.22 A M^{-1} cm^{-2}. The repeatability study of the electrodes showed a variation of 7.7% RSD in the amperometric response of 1.0 μM HQ (n = 10 per electrode for five different electrodes). Reproducibility was achieved as 18.8% RSD, in the concentration range of 0.0125 – 1.0 μM HQ, confirmed by the sensitivities obtained during inter-days measurements (5 days) using the same electrode (Fig. S7). A decrease of 9.3% in the amperometric response of 1.0 μM HQ was observed, after 50 injections (approximately 100 min of measurement), using a single sensor.

The proposed photosensor presented a good performance and the analytical comparison with various previously reported sensors is shown in the Table S1. The LOD calculated for HQ using SPE|AuNPs@TiO_2 electrode is at least three times better or comparable to that reported in literature. In our previous work [47], we have demonstrated a successful integration of the TiO_2 sensor into a photoelectrochemical flow cell for HQ detection by using a UV (blue light) as illumination source, providing low LOD. In the present work, the improvement of the visible-light photocatalytic activity of commercial TiO_2 by the impregnation of AuNPs into its structure, as well as the integration of the photosensor into a FIA system, even allowed the nM-range detection of HQ. The impregnation of AuNPs into TiO_2 increased its photocatalytic power and in addition increased feasibility to work under visible light illumination (green laser), which composes approximately half of the solar spectrum [26]. In addition, the use of visible light illumination is less dangerous to human health than the UV [69] which makes it a safer system to the user.

3.3 Flow rate optimization

In electroanalysis, mass transport is one of the advantages of FIA systems as it improves the sensitivity of the method, although it can be affected by the flow rate [70]. Therefore, the flow rate was studied in a range from 0.25 to 1.5 mL/min by analyzing the photocurrent of 0.15 µM HQ (Fig. S8). The amperometric responses remained almost constant, with no significant difference between different values of flow rate. Thereby, to prevent wasting a large amount of sample and to secure a fast analysis time, a value of 1.0 mL min^{-1} was selected as the optimum flow rate.

3.4 Working potential and pH optimization

The influence of the working potential on the photocurrent response of a buffer solution containing 0.15 µM HQ was carried out in a potential range from 0.3 to -0.3 V (Fig. 7). Applying positive potentials, the observed photocurrent response is minimal when compared to the responses obtained for negative potentials. Another important observation is that the photocurrent and the baseline (background current), as well as the standard deviation of the responses increase when the working applied potential shifts in the cathodic direction (< -0.2 V) due to the influencing of competing reactions (*e.g.* oxygen reduction) [68, 71]. Therefore, an optimal amperometric response, which combines a greater photocurrent response for HQ detection with low standard deviation, was obtained when a negative potential of -0.14 V vs Ag quasi-reference electrode of the SPE was applied. This potential was chosen as an optimal working potential.

The influence of pH on the amperometric response of 1.0 µM HQ at SPE|AuNPs@TiO_2 was studied in the pH range of 5.0 – 8.0 (Fig. 8). The increase in the photocurrent response is observed by increasing the pH value until it reaches neutral pH and then the photocurrent response decreases, at pH 8.0. This behavior is expected due to the protonation of HQ at a more acid pH range (pH < 7.0) and the gradual deprotonation while the pH is increasing from pH 5.1 until 7.1, where it reaches the maximum value of photocurrent response [72, 73]. At higher pH, there is a partial reduction of protons participation in the electrochemical reaction and then a reduction on amperometric response is observed [72]. Therefore, pH 7.0 was chosen as the optimal pH for further measurements.

3.5 Applicability of SPE|AuNPs@TiO$_2$ modified electrode

The applicability of the SPE|AuNPs@TiO$_2$ sensor under green laser illumination was evaluated for the quantification of 4-AP. The calibration curve from Fig. 9 displays a characteristic behavior of photocurrent response with increasing 4-AP concentrations. The linear correlation between amperometric response and different concentrations of 4-AP in the range from 0.0125 – 0.5 µM is shown (Fig. 9 inset). The LOD calculated was 17 nM, confirming the applicability of the sensor for the detection of 4-AP.

3.6 Interference study for HQ

In order to validate the proposed photosensor with respect to selectivity, an interference study was conducted for 1.0 µM HQ detection at AuNPs@TiO$_2$ photosensor in the presence of phenol (Ph), 4-nitrophenol (4-NP), bisphenol A (BPA), 3-nitrophenol (3-NP), 2-aminophenol (2-AP) and 3-aminophenol (3-AP), considering as possible interfering compounds, as they can coexist in the same environment as the HQ. An increase by 3.7%, 1.5%, 2.6%, 1.4%, 3.3% and 4.8% on the amperometric response of HQ in the presence of Ph, 4-NP, BPA, 3-NP, 2-AP and 3-AP, respectively, was observed (Fig. S9). The position of functional groups and the tendency of some substituents on the aromatic ring to form electron-donor conjugation can explain the predisposition of reactivity from some phenolic structures, such as HQ [47, 74]. Moreover, the presence of multiple hydroxyl groups provides a strong activating effect to the HQ molecule, meaning higher interacting power with the electrode surface [75]. Therefore, the amperometric responses of 10-fold concentrations of the measured phenolic compounds showed no significant influence on the detection of 1.0 µM HQ, confirming the selectivity of the sensor for detecting HQ in the presence of such phenolic molecules.

3.7 Real sample analysis

The optimized photosensor was applied for the detection of HQ and 4-AP in an effluent water sample. The water sample from Aquafin RWZI was analyzed. The accuracy of the proposed method was reported as the percentage of recovery of a given known value of concentration added to the real sample to be analyzed (Table 1). In detail, standard additions to the water sample were performed in three different levels of fortifications (low, mid and high) for HQ (0.01, 0.08 and 0.12 μM) and 4-AP (0.1, 0.2 and 0.35 μM), each replicated 3 times (means n = 9 each organic molecule) and, subsequently, analyzing them by using the AuNPs@TiO_2-based photoelectrochemical sensing platform. The average recovery percentages were obtained in a range of 91.4% to 102.5% for 4-AP and 90.0% to 105.6% for HQ. The recovery acceptance criteria was set as 70 - 110% [76, 77]. Therefore, the results confirm the ability of the proposed sensor for the determination of such phenolic molecules in complex samples.

Conclusions

A novel photoelectrochemical sensing approach was successfully applied for the sensitive detection of HQ and 4-AP under visible light illumination based on the impregnation of size-controlled AuNPs on an anatase TiO_2 structure (AuNPs@TiO_2). The setup is integrated in a flow injection system to avoid the electrode poisoning during electroanalysis by means of periodic washing steps of the electrode surface. The AuNPs@TiO_2 photocatalyst was successfully obtained by a photo-assisted synthesis and later characterized by using XRD, Raman spectroscopy, SEM, EDX, TEM, UV-DR, EIS and LSV analysis. The homogeneous distribution of AuNPs over the TiO_2 structure was confirmed by the morphological characterization. An enhancement in the photocatalytic activity of TiO_2 was verified by using an AuNPs loading of 3.0 wt.%. The improved photocatalytic activity is ascribed to the SPR effect and charge transfer property of AuNPs. The FIA system played an important role on the sensitivity of the method to detect HQ and 4-AP at nM-level within minutes. In addition, the good repeatability and precision of the sensor is ascribed to the stability of the plasmonic catalyst (AuNPs@TiO_2) on the graphite SPE electrode surface. The efficiency and accuracy of the proposed photosensor were demonstrated by sensing HQ and 4-AP in effluent water collected from sewage treatment plant, suggesting a great potential of the photoelectrochemical-based flow injection strategy for monitoring water quality. Moreover, the application of the plasmonic photocatalyst can also be extended for photodegradation studies of organic molecules in several environmental remediation strategies.

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Figure and table captions

Fig. 1 - (a) XRD pattern of AuNPs@TiO_2 sample, anatase, rutile and Au references, (b) Raman spectra of AuNPs@TiO_2 sample and TiO_2 anatase reference. The AuNPs@TiO_2 sample is 3.0 wt.% of AuNPs loaded on TiO_2.

Fig. 2 - (a) SEM image of AuNPs@TiO_2; (b) EDX patterns of AuNPs@TiO_2; TEM images of (c) AuNPs and (d) AuNPs@TiO_2.

Fig. 3 - (a) UV-Vis absorbance spectra of AuNPs, TiO_2 and AuNPs@TiO_2, (b) Tauc plot for the band gap energy determination of AuNPs@TiO_2 sample.

Fig. 4 - Linear sweep voltammogram for AuNPs@TiO_2 electrode under chopped light illumination, in presence (red) and absence (black) of 1.0 µM HQ in 10 mM PBS containing 0.1 M KCl (pH 7.0), using a step potential of 0.5 mV, scan rate of 0.25 mVs^{-1} and potential range of 0.4 V to -0.2 V.

Fig. 5 - Expected photocatalytic reactions on AuNPs@TiO_2 surface under visible light ($\lambda = 532$ nm, green laser) and the photocurrent generation mechanism.

Fig. 6 - (A) Amperometric response for SPE|AuNPs@TiO_2 in the presence of HQ (a) 0.0125, (b) 0.025, (c) 0.05, (d) 0.15, (e) 0.25, (f) 0.5, (g) 1.0, (h) 2.5, (i) 5.0, (j) 10 and (k) 25 µM, in 10 mM PBS containing 0.1 M KCl (pH 7.0) and applied potential of -0.14 V vs Ag quasi-reference electrode (n = 3). (B) Corresponding calibration curve (inset: linear curve in the concentration range from 0.0125 to 1.0 µM at SPE|AuNPs@TiO_2 (black) and at SPE|TiO_2 (red) under green light illumination).

Fig. 7 - Influence of the working potential on the photocurrent response of 0.15 µM HQ at SPE|AuNPs@TiO_2 in 10 mM PBS containing 0.1 M KCl (pH 7.0) (n = 3), using a flow rate of 1 mL/min.

Fig. 8 - Influence of pH on the photocurrent response of 0.15 µM HQ at SPE|AuNPs@TiO_2 in 10 mM PBS containing 0.1 M KCl, using a working potential of -0.14 V vs Ag quasi-reference electrode (n = 3) and flow rate of 1 mL/min.

Fig. 9 - Calibration plot for 4-AP in 10 mM PBS containing 0.1 M KCl (pH 7.0), using SPE|AuNPs@TiO_2 under green light illumination and applied potential of -0.14 V vs Ag quasi-reference electrode (n = 3). Inset: Linear curve in the concentration range from 0.0125 to 0.5 µM.

Table 1 - Recovery results of HQ and 4-AP quantification in effluent sample.