Original Article

Plasmonic hybrid platinum-titania nanocomposites as highly active photocatalysts: self-cleaning of cotton fiber under solar light

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ABSTRACT

In the present paper, a one-step, simple, efficient and low-cost strategy was demonstrated for preparing of highly stable hybrid platinum-titania (Pt@TiO2) photocatalyst by solvothermal wet chemical process. Platinum (Pt) in the metallic form combined with titania (TiO2) in the crystallographic anatase form has been manufactured using Dimethyl Suloxide (DMSO) as a solvent and surfactant using titanium (IV) butoxide and hydrogen hexachloroplatinate(IV) precursors. Full characterization of the hybrid nanomaterials including their morphology, crystalline structure and optical properties was determinate using different experimental techniques such as XRD, TEM and UV-vis spectroscopy. TEM images showed spherically shaped Pt nanoparticles (NPs) of the diameter 5–10 nm with good particle size distribution. The EDXRF data revealed that Pt NPs are in metallic form. Optical investigation show that Pt@TiO2 NPs exhibits a good optical response under UV-vis light excitation compared to bare-TiO2. Furthermore, photocatalytic investigation of Pt@TiO2 colloids photocatalyst towards the photodegradation of diuron, as a model organic pesticide was reported. The hybrid Pt@TiO2 photocatalyst prove high-performance on the photodecomposition of the pesticide under solar light within only 60 min. In the other hand, the plasmonic hybrid Pt@TiO2 was incorporated into the cotton fabric to attain a modified fiber with high self-cleaning activity.

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1. Introduction

As a vital semiconductor material, titanium dioxide or titania (TiO$_2$) nanomaterials have been extensively studied. Good physical and chemical properties combined with high stability in acidic and alkaline solutions make it the most popular semiconductors [1–13]. It has been classified as one of the most considered nano-compounds in materials science for its photocatalytic efficiency. Photocatalysts area has been potentially useful in various settings due to its new technology for environmental contamination. Most testified photocatalysts such as ZnO, ZnS, GaAs and CdS have many limitations such as toxicity and the weak stability in aqueous solution. However, TiO$_2$ are more stable in aqueous media compared to the most frequent photocatalysts and do not produce pollution, which make it close to be the ideal photocatalyst. Nerveless, many recent researches prove that the photocatalytic activity of TiO$_2$ can be improved by combining the plasmonic resonance (SPR) properties of noble metal nanoparticles (NPs) such as gold (Au), silver (Ag) and platinum (Pt) and the intrinsic optical properties of TiO$_2$ [14–22]. Due to this SPR property, noble metals can act as electron sinks that promote multi-electron transfer reactions that are crucial to improve the photocatalytic efficiency of the nanomaterials. Among those, Pt NPs are very commonly used as catalysts in numerous important engineering applications, in the chemical, petrochemical, refining processes, fuel cells, automotive, fine chemical production and energy sectors [23–27]. These NPs have been produced via a variety of methods such as colloidal systems, reduction, micro-emulsion, the sol-gel and sono-chemical methods, gamma irradiation and electrodeposition giving rise to a diverse range of sizes and shapes. To optimize the catalyst performance, its activity, selectivity and stability while keeping the amount of Pt (which is scarce and expensive) at a minimum, a combination of Pt with TiO$_2$ is a very promising solution [28]. Generally, the improvement of activity of Pt@TiO$_2$ photocatalysts compared to pure TiO$_2$ or Pt is attributed to the enhancement of electron life time [29]. In another area, specially with growing require for hygienic, the demand of self-cleaning protective equipments and surfaces has developed speedily in recent years. However, the self-cleaning process was discovered by Wilhelm Barthlott team in 1973 [30]. The primary marketable materials made in cooperation with industrial society were silicone resin house paint and ceramic roof tiles. In the same context, we present in this research work a novel approach to prepare an efficient and stable self-cleaning Pt@TiO$_2$ photocatalyst adopting a simple solvothermal method without the use of any template or substrate. We will demonstrate that the combination of Pt and TiO$_2$ highly improves the photocatalytic activity of the final hybrid nanomaterials. We also present also a comparative study on self-cleaning efficiency of bare TiO$_2$ and Pt@TiO$_2$ NPs toward cotton fiber. However, the hybrid Pt@TiO$_2$ nanocomposites exhibit high performance to completely remove the stained dyes within 9 h.

2. Experimental

2.1. Synthesis of hybrid Pt@TiO$_2$ nanocomposites

To obtain hybrid Pt@TiO$_2$ nanomaterials, Titanium(IV) butoxide (reagent grade, 97% Sigma) and Hydrogen hexachloroplatinate(IV) hydrate (99.9%, ACROS Organics) with molar ratio Pt:Ti = wt 3% were dissolved in 50 ml of DMSO. The resulting solution was subsequently heated slowly to 190°C and maintained at this temperature for 1 h. The resulting hybrid Pt@TiO$_2$ nanocomposite was recovered by centrifugation rinsed with ethanol and deionized water several times and finally dried at 70°C in the dark. The obtained powder was then calcined at 400°C for 1 h to induce more crystallinity to the final product and to provoke the complete removal of the solvent molecules entrapped inside the surface particles. This step is very important to maintain the nanomaterials very stable under strong synthesis conditions and also make their surface suitably clean for photocatalytic activity. However, pre-adsorbed organic molecules may weaken the photocatalytic properties of the hybrid nanomaterial.

2.2. Structural, morphological and optical characterizations

The microstructure, of the obtained hybrid nanomaterial was characterized by D8 Advance Bruker, USA X-Ray diffractometer. The morphology was observed by Philips Tecnai F-20 SACTEM operating at 200 kV. Scherrer’s formula used to calculate the typical crystallite size. UV–vis absorption spectra were recorded on a UV–vis Perkin–Elmer Lambda 11 spectrophotometer. Quantitative elemental analysis has been carried out using Energy dispersive X-ray fluorescence spectrometer (Quant’X EDXRF, Thermo Fisher Scientific Inc., USA). Thermo analytical DTA (differential thermal analysis) coupled with TGA (thermo gravimetric analysis) measurements were performed on a SETSYS Evolution 1750/SETARAM instrument. The IR data were collected in the 4000–450 cm$^{-1}$ range with a Perkin-Elmer FT-IR Spectrum BX spectrophotometer.

2.3. Photocatalytic activity and self-cleaning experiments

The photodecomposition reaction of the hybrid Pt@TiO$_2$ NPs was investigated through the degradation of an organic pesticide in aqueous solution under simulated solar light irradiation (halogen lamp) as the model reaction. The photodecomposition percentage (P-D%) of the organic pesticide was determined using the following relation:

$$P-D(\%) = \frac{(C_0 - C_t)/C_0} {\times 100}$$

Where $C_0$ and $C_t$ are the initial and instantaneous organic pesticide concentrations. The self-cleaning test was performed as described in our previous work [35].
3. Results and discussion

3.1. Structural, morphological and optical characterizations

Phase identification was done for the obtained XRD patterns to identify the phases comprising each powder sample. The crystalline phases were recognized by matching all characteristic peaks with the JCPDS files [31]. Anatase TiO\textsubscript{2} phases can be easily detected (JCPDS # 01-084-1286) with three supplementary diffraction peaks are detected at 2\theta = 38.33, 44.21 and 64.79° and can be attributed to the (111), (200), (220) and (311) planes of FCC platinum (JCPDS # 01-087-0646), see Fig. 1. No other peaks for by product phases were observed. Average Pt crystallite size (~4 nm) is calculated from XRD peak broadening using the Debye-Scherrer equation [32]. A powerful procedure for refining the experimental XRD data was performed using the Rietveld method [33]. The TiO\textsubscript{2} and Pt in the Pt@TiO\textsubscript{2} hybrid sample were refined as tetragonal and cubic phase with I\textsubscript{4}1/amd and Fm\textsubscript{3}m and space group respectively. The wt % values of the two phases were refined as well. The average R-values results obtained from the Rietveld refinements were about R\textsubscript{wp} (%) = 3–8, which indicates reliable qualities of fits. In accordance with Vigard’s law [34], both the cell parameters a and c of the anatase cell are decreasing upon the combination of Pt with TiO\textsubscript{2}, which is attributed to the constraint of the Ti-atoms with the smaller Pt-atoms at the anatase surface. The total weight percent for TiO\textsubscript{2} in the

![Fig. 1](image1.png) - The calculated (red line) and observed (black dots) diffraction patterns for the pure (lower) and hybrid Pt@TiO\textsubscript{2} (upper) samples as obtained from the Rietveld adjustments using the MAUD program, the positions of the diffraction lines of Pt are marked with (*) and the other peaks belong to the Anatase phase of TiO\textsubscript{2}.

![Fig. 2](image2.png) - TEM images of hybrid Pt@TiO\textsubscript{2} NPs taken at different scales with their particle size distribution histogram.
Fig. 3 – HRTEM image of hybrid Pt@TiO$_2$ NPs. The inset in the right and in the left show the HRTEN image of single Pt@TiO$_2$ particle with their typical selected-area electron diffraction pattern, respectively.

Table 1 – The structural and microstructural parameters of the hybrid Pt@TiO$_2$ NPs as obtained by the Rietveld refinements of the XRD patterns.

<table>
<thead>
<tr>
<th></th>
<th>Pure titania</th>
<th>Pt@titania</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>100%</td>
<td>98.5 (6)%</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.792 (4)</td>
<td>3.7900 (8)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.508 (12)</td>
<td>9.4878 (5)</td>
</tr>
<tr>
<td>D (Å)</td>
<td>18 (2)</td>
<td>10 (2)</td>
</tr>
<tr>
<td>ε</td>
<td>0.005 (1)</td>
<td>0.0006 (2)</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
<td>1.5 (6)%</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.927 (2)</td>
<td></td>
</tr>
<tr>
<td>D (Å)</td>
<td>21 (3)</td>
<td></td>
</tr>
<tr>
<td>ε</td>
<td>0.0038 (4)</td>
<td></td>
</tr>
</tbody>
</table>

Hybrid material phase is about 98.5% and the Pt phase was estimated to be 1.5%, as seen in Table 1.

The size and shape of the hybrid Pt@TiO$_2$ NPs are crucial and highly influence the photocatalytic performance of the nanomaterials. The overview TEM images presented in Fig. 2 show that the hybrid NPs consisted of quasi-spherical particles with Pt nanocrystals in the cores (around 7 nm, histogram–Fig. 2) surrounded by TiO$_2$ NPs forming the decoration. The inter-planar spacing between atoms (d-spacing) of the anatase TiO$_2$ (101) plane is observed (d-spacing = 0.352 nm) in the high-resolution TEM (HRTEM) images (Fig. 3). On the other hand, the inter-planar spacing of the Pt metal phase is also observed (d-spacing = 0.22 and 0.196 nm) and can be attributed to the (111) and (200) lattice planes. Selected-area electron diffraction (SAED) showed a typical multiple-ring pattern (inset of Fig. 3). The fringe spacing observed is characteristic of the (101) lattice plane of the tetragonal TiO$_2$ anatase phase and the lattice planes (111) and (200) of the FCC Pt metal phase.

The EDXRF measurements confirm the presence of Ti and Pt elements in the sample and prove the high purity of the prepared Pt@TiO$_2$ hybrid. However, as can be seen in the EDXRF spectrum illustrated in Fig. 4, the K-lines and L-lines of Ti and Pt, respectively, can easily be excited and detected at a low photon energy (Ti-K$_α$ = 4.509 keV, Ti-K$_β$ = 4.932 keV, Pt-L$_{1,3}$ = 8.353 keV, Pt-L$_{1,2}$ = 9.453 keV, Pt-L$_{6γ}$ = 10.043 keV, Pt-L$_{6γ1,2,3}$ = 11.185 keV, Pt-L$_{6γ1}$ = 12.982 keV and Pt-L$_{6γ6}$ = 13.336 keV).

To study the optical properties and response of the prepared hybrid Pt@TiO$_2$ nanomaterials, a UV-vis absorption analysis covering a range from approximately 200–800 nm was performed. The obtained spectrum is illustrated in Fig. 5. As can be seen, besides the broad absorption peak at 337 nm characteristic of TiO$_2$ NPs ($E_g$ = 3.35 eV determined by Tauc-method), we found that Pt NPs exhibit two steady absorption
maxima in UV regions at 207 and 270 nm respectively. Based on previous work [33], these two absorption peaks can be attributed to the plasmonic excitation of conduction electrons. The absorption peaks are the result of the absorption of the photon by electrons, which are excited to a higher energy level within the conduction band.

4. Degradation of diuron by photoassisted heterogeneous catalysis

The photocatalytic activity of the as-prepared hybrid Pt@TiO$_2$ was studied via the photodegradation of a diuron solution as a model reaction to evaluate the photocatalytic efficiency of the photocatalyst. Fig. 6 shows the photocatalytic decomposition of the diuron solution under solar light. The hybrid photocatalyst exhibits a higher percentage of degradation. As can be seen, after only 60 min, the diuron molecules have been completely degraded. The relative concentration variations of the diuron solution versus illumination time are shown in Fig. 7. TiO$_2$ and Au–TiO$_2$ NPs are also shown to give further insight into the photocatalytic activity. It can be clearly observed that the adsorption capacity of TiO$_2$ has been improved greatly when coupled with Pt NPs. Indeed, after 60 min of the photocatalysis experiment, the photodegradation of diuron was of only 51% and 75% of pure TiO$_2$ and Au–TiO$_2$ NPs respectively, while it reached 100% for the hybrid Pt@TiO$_2$ photocatalyst. In the other hand we found that even after 5 cycles of photocatalytic reaction, the hybrid nanomaterials exhibit good photocatalytic activity. A possible proposed photo-reaction and photocatalytic mechanisms can be observed in Scheme 1(a and b).

5. Self-cleaning Tests of Pt@TiO$_2$/CF

Before testing the self-cleaning activity of the obtained Pt@TiO$_2$/cotton fiber, it is necessary to confirm the incorporation of the hybrid Pt@TiO$_2$ into the cotton fiber (CF). For that, XRD and FTIR were performed simultaneously. Fig. 8(a) shows the XRD patterns of bare TiO$_2$, CF, Pt@TiO$_2$, and Pt@TiO$_2$/CF for comparison. It is clear that the Pt@TiO$_2$ NPs was incorporated into the CF. However, the XRD pattern of Pt@TiO$_2$/CF exhibits both CF and Pt@TiO$_2$ characteristics peaks. This result is in agreement with the FTIR measurements presented in Fig. 8(b).
Fig. 7 – (a, b) Plot of ln(C0/C) versus irradiation time with the kinetics of the degradation of diuron obtained under simulated solar light using the hybrid Pt@TiO2 photocatalyst and (c) cycles of photocatalytic reaction.

Scheme 1 – (a) Schematic illustration of the possible photo-catalytic degradation mechanism of hybrid Pt@TiO2 photocatalyst in DMSO and (b) Schematic illustration of the photocatalytic degradation mechanism of diuron by hybrid Pt@TiO2 photocatalyst under sunlight irradiation.

Upon addition of the Pt@TiO2 NPs into the CF, all characteristics chemical groups of the CF were detected at the Pt@TiO2 surface, which approves the successful coating of the CF by the hybrid Pt@TiO2. Fig. 8(c) shows the TGA behavior of the Pt@TiO2 before and after incorporation into the CF. Apparently, after the analysis of the TGA curve, no weight loss can be detected in the examined region (25–800 °C). Consequently, the hybrid Pt@TiO2 nanomaterial exhibits high thermal stability even up to 1000 °C. On the other hand, as can be seen, the CF is very fragile again temperature, the first decomposition occurs from 290 to 310 °C and can be attribute to the depolymerization of the fabric cellulose [35,36]. No change can be detected in the mass loss of the Pt@TiO2/cotton fiber compared to the bare CF. To study the photocatalytic self-cleaning performance of the prepared Pt@TiO2/CF, the CF was immersed in Pt@TiO2. Fig. 9 displays the SEM images of pure CF and modified CF with Pt@TiO2 NPs. As can be seen (Fig. 9a) the CF exhibits smooth microstructure surface while, upon coating the CF with Pt@TiO2 NPs, the surface turn roughness with clearly deposited Pt@TiO2 particles (Figure 11b). EDX mapping images (Fig. 9c and d) confirm the homogeneous distribution of the hybrid Pt@TiO2 on the CF surface. The self-cleaning photocatalytic activity of the hybrid Pt@TiO2 was examined using MB and orange II dyes. Fig. 10 shows the
Fig. 8 – (a) XRD Patterns of Pt@TiO₂, CF and Pt@TiO₂/CF, (b) FTIR Spectra of CF, Pt@TiO₂ and Pt@TiO₂/CF and (c) TGA curves of CF, Pt@TiO₂ and Pt@TiO₂/CF.

Fig. 9 – SEM images and EDX mapping of CF and Pt@TiO₂ coated CF.
Fig. 10 – Simulated sunlight induce decolorization of MB and orange II dyes using bare TiO$_2$ (a,c,e) and hybrid Pt@TiO$_2$/CF (b,d,f).
qualitative photodegradation of the samples under simulated sunlight. Compared to bare TiO₂, the hybrid Pt@TiO₂ exhibits high capability to degrade the MB and orange II and consequently discolored the CF (Fig. 10a). This can be attributed to the plasmonic properties of Pt, which enhance more the intrinsic photocatalytic properties of the TiO₂.

6. Conclusion

In summary, we have successfully developed an efficient one-pot experimental procedure to prepare hybrid Pt@TiO₂ nano-photocatalyst with controllable size and morphology. Full characterizations of the obtained hybrid nanomaterials confirm the preparation of core-shell Pt@TiO₂ nanocomposites with high thermal stability (up to 1000 °C) and good optical response due to the plasmonic properties induced by metallic Pt NPs. The hybrid nanomaterials exhibit high photocatalytic activity again diuron pesticide and perfect self-cleaning response when incorporated into the cotton fiber. This method can be exploited to prepare many other metal-metal oxides nanomaterials with high yield and low cost price. On the other hand, this hybrid material can be useful for other applications such as water splitting and electronic devices.

Conflicts of interest

The authors declare no conflict of interest

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