Preparation of nitrogen-doped TiO$_2$ nanotube deposited with gold nanoparticles for photocatalytic phenol degradation under visible light

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Abstract. One of the many functions of TiO$_2$ photocatalysts is degrading organic compounds. TiO$_2$ photocatalysts have a band gap of 3.2 eV, which is equivalent to the energy of ultraviolet (UV) photons with a wavelength of 388 nm and allows them to be effectively activated only by UV light. However, they are less effective under visible (Vis) light. Researchers have developed many ways to use the photocatalytic properties of TiO$_2$ under visible light via nitrogen doping. Further, the photocatalytic activity of N-doped TiO$_2$ can be improved via surface plasmon resonance. In this study, N-doped TiO$_2$ nanotubes (N-TiO$_2$ NTs) are prepared and deposited with Au nanoparticles (Au/N–TiO$_2$ NTs) via electrodeposition. The TiO$_2$ NTs and Au/N-TiO$_2$ NTs are characterized using UV-VIS spectrometry, Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry (XRD), field emission scanning electron microscopy, energy dispersive spectroscopy (EDS), and linear sweep voltammetry (LSV). The photocatalytic test under tungsten lamp illumination of a 20-ppm phenol solution in a batch reactor shows a phenol degradation of 60 %, whereas a 20-ppm bisphenol A (BPA) solution is degraded by 40 %.

1. Introduction
The increasing human needs for energy, in particular for fossil fuels, have led the industry to rapidly evolve in this field. However, this must be balanced with the development of exploration technologies that are environmentally friendly because the untreated waste produced by such fuels exploration will pollute the environment. Phenol and its derivatives (phenolics) are among such hazardous waste products [1]. An alternative way proposed to deal with pollutants such as phenols and phenolics is using photocatalysts. Photocatalytic reactions can be applied for environmental repair using sunlight as energy source.

TiO$_2$ has environmentally friendly properties and is nontoxic, inexpensive, and stable. Because of these advantages, TiO$_2$ is developed for several environmentally friendly applications [2]. For example, it is used for coating the vessel bottoms to make them water resistant by its hydrophobic properties. TiO$_2$ can be used to degrade organic pollutants, such as phenols and derivatives, via photocatalysis. TiO$_2$ anatase phase has a quite wide energy gap (band gap) of ~3.2 eV, which is equivalent to the energy of ultraviolet (UV) photons with a wavelength of 388 nm. Hence, TiO$_2$ is photocatalytically active only under UV light and cannot be effectively used under visible light, although this is very abundant and easily available owing to sunlight. Therefore, activating the photocatalytic activity of TiO$_2$ using visible light would be beneficial.

In this study, TiO$_2$ nanotubes were modified via nitrogen doping (N-TiO$_2$ NTs) and decorated with Au nanoparticles (Au/N-TiO$_2$ NTs) via electrodeposition. Then, their ability to degrade phenols under visible light was tested.

2. Materials and methods
2.1. Materials
The materials used to prepare the modified nanotubes and test their photocatalytic activity included a titanium plate (imported from China), deionized water, ammonium fluoride (Merck), sodium nitrate (Merck), ethylene glycol (Merck), a 4.5 × 1-cm Pt electrode, absolute ethanol, and a 5-mM chloroauric (III) acid solution.

2.2. Synthesis
The Ti plate was cut into smaller plates with a size of 4.5 × 1 cm², which were sanded with abrasive paper of 1500 mL. To obtain polished and clean surfaces, the plates were sonicated for 30 min with acetone and for another 30 min with ethanol, rinsed with distilled water, and dried. Then, the plates were anodized by placing them in an electrolytic solution with the Pt electrode as the cathode for 1 h with a potential of 40 V. The electrolytic solution comprised urea and NH₄F in ethylene glycol concentration of 0.3% and 2% distilled water [3]. The amorphous TiO₂ obtained was calcined at 450 °C for 2 h. Then, the N-doped TiO₂ was deposited with metallic Au nanoparticles via electrodeposition by placing it as the cathode in an electrolytic solution (HAuCl₄; 2.5 × 10⁻⁴ M), whereas the anode was a woven Pt wire. Electrodeposition performed at a potential of −1.5 V for 60 s. Then, the cathode was removed and dried in a desiccator for 24 h.

2.3. Characterization
The TiO₂ plate obtained were analyzed via UV-Vis diffuse reflectance spectroscopy (UV-DRS) to determine the band gap, by Fourier transform infrared spectroscopy (FTIR) to identify the functional groups, by X-ray diffractometry (XRD) to determine the crystal structures, by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) to study the morphology, and by linear sweep voltammetry (LSV) to evaluate the photocatalytic activity.

2.4. Testing phenol and BPA degradation ability
Phenol standard solutions were prepared by taking aliquots from the stock solution and obtaining concentrations of 5, 10, 15, 20, and 25 ppm; standard bisphenol A (BPA) solutions were made with the same concentrations. After analyzing the standard solutions using the UV-Vis spectrophotometer, the degradation of phenol and BPA was measured by analyzing 20 ppm of their standard solutions without potential bias for 1 h and in three different modes: 1) without photocatalyst, 2) with photocatalyst under UV light, and 3) with photocatalyst under visible light.

3. Results and discussion

3.1. Characterization
The addition of modified Au nanoparticles on the surface of the N–TiO₂ plates did not shift their energy gap but a new peak characteristic of Au nanoparticles appeared around 560 nm. This peak indicates that the Au/N–TiO₂ photocatalyst is active in the visible light region. This absorbance peak
### Table 1. XRD data.

| 2θ   | Crystal  | % Intensity |
|------|----------|-------------|
| 25.29 | TiO, Anatase | 100         |
| 35.08 | TiO, Anatase | 7.26        |
| 38.38 | Ti plate | 60.77       |
| 40.15 | Ti plate | 69.71       |
| 47.61 | Au NP | 3.20        |
| 47.94 | TiO, Anatase | 16.64      |
| 52.96 | TiO, Anatase | 37.11      |
| 62.91 | Ti plate | 20.38       |

**Figure 2.** XRD spectrum of Au/N-TiO nanotubes.

**Figure 3.** SEM images of (a) N-TiO2 NTs, (b) Au/N-TiO2 NTs, (c) cross section Au/N-TiO2 NTs, and (d) EDS spectrum of Au/N-TiO2 NTs.

is the result of the plasmon resonance phenomenon on the surface of the Au nanoparticles, which initiates the photocatalytic activity of the Au/N–TiO2 NTs. The presence of two peaks in the UV and visible light ranges indicates that the Au/N–TiO2 photocatalyst can be activated in both cases. From the curve in figure 1, the value of the energy gap required to activate the Au/N–TiO2 photocatalyst for \( F(R) = 0 \) was calculated to be 2.16 eV.

Figure 2 shows an XRD spectrum of Au/N–TiO2 NTs and crystal structure related to 2θ value listed in table 1. Based JCPDS2-1095, the characteristic peaks of Au are those at 38°, 44°, 82°, 98°, 111°, and 116°. Yazid et al. [4] reported a peak of Au at 47.6°, and in our XRD spectrum there is a peak at 47.61°; this suggests that Au was deposited on the surface of the TiO2 NTs, with a crystallite size of 26.64 nm.

The elemental analysis shown in figure 3 and table 2 proves the Au nanoparticles had been successfully deposited on the surface of the N–TiO2 plate via electrodeposition and no impurity element is present.
Table 2. EDS results

| Element | wt. % | at. % |
|---------|-------|-------|
| NK      | 1.52  | 3.02  |
| OK      | 27.50 | 53.06 |
| TiK     | 68.17 | 43.71 |
| AuM     | 1.34  | 0.21  |
| Matrix  |       |       |

Table 3a. The absorbance values of the phenolic compounds for 60 min. at 216 nm

| Time (min) | Adsorption | Photolysis | Photocatalysis |
|------------|------------|------------|---------------|
|            | TiO | N-TiO | Au/N-TiO | UV | VIS | TiO | N-TiO | Au/N-TiO | TiO | N-TiO | Au/N-TiO |
| 0          | 1.880 | 1.883 | 1.882 | 1.883 | 1.881 | 1.882 | 1.884 | 1.880 | 1.885 | 1.886 | 1.882 |
| 10         | 1.878 | 1.880 | 1.887 | 1.707 | 1.820 | 1.220 | 1.193 | 1.197 | 1.830 | 1.588 | 1.374 |
| 20         | 1.872 | 1.876 | 1.874 | 1.556 | 1.795 | 0.790 | 0.809 | 0.765 | 1.789 | 1.436 | 1.085 |
| 30         | 1.870 | 1.877 | 1.869 | 1.450 | 1.735 | 0.574 | 0.576 | 0.548 | 1.746 | 1.338 | 0.934 |
| 40         | 1.875 | 1.872 | 1.862 | 1.407 | 1.694 | 0.467 | 0.479 | 0.465 | 1.702 | 1.257 | 0.833 |
| 50         | 1.873 | 1.868 | 1.859 | 1.368 | 1.545 | 0.403 | 0.398 | 0.388 | 1.696 | 1.163 | 0.774 |
| 60         | 1.869 | 1.861 | 1.853 | 1.326 | 1.620 | 0.376 | 0.370 | 0.367 | 1.680 | 1.128 | 0.752 |

Table 3b. The absorbance values of the phenolic compounds for 60 min. at 276 nm

| Time (min) | Adsorption | Photolysis | Photocatalysis |
|------------|------------|------------|---------------|
|            | TiO | N-TiO | Au/N-TiO | UV | VIS | TiO | N-TiO | Au/N-TiO | TiO | N-TiO | Au/N-TiO |
| 0          | 0.603 | 0.602 | 0.604 | 0.602 | 0.604 | 0.603 | 0.603 | 0.603 | 0.601 | 0.604 | 0.602 |
| 10         | 0.600 | 0.599 | 0.598 | 0.504 | 0.589 | 0.450 | 0.467 | 0.448 | 0.588 | 0.554 | 0.501 |
| 20         | 0.598 | 0.596 | 0.596 | 0.455 | 0.567 | 0.360 | 0.371 | 0.357 | 0.568 | 0.510 | 0.426 |
| 30         | 0.598 | 0.598 | 0.595 | 0.409 | 0.544 | 0.285 | 0.291 | 0.295 | 0.545 | 0.472 | 0.362 |
| 40         | 0.595 | 0.594 | 0.596 | 0.380 | 0.525 | 0.224 | 0.229 | 0.223 | 0.523 | 0.430 | 0.311 |
| 50         | 0.593 | 0.593 | 0.593 | 0.369 | 0.509 | 0.144 | 0.175 | 0.169 | 0.507 | 0.402 | 0.283 |
| 60         | 0.590 | 0.590 | 0.589 | 0.365 | 0.496 | 0.120 | 0.123 | 0.114 | 0.490 | 0.395 | 0.250 |

Figure 4. LSV characteriztion of Au/N-TiO NTs under UV (left) and Vis (right) illumination

Figure 4 shows that the current response of Au/N-TiO NTs illuminated by UV and tungsten lamps was higher than without illumination. When illuminated by the tungsten lamp (visible light), the current response was smaller than when exposed to UV light; however, the response was higher.
3.2. Testing phenol and BPA degradation ability

Table 3 reports the absorbance values of the phenolic compounds from the beginning till the end of a 60-min degradation reaction. The absorbance peak at 216 nm reached a value of 0.752 after 60 min (table 3a), while that at 276 nm was still there with a value of 0.250 (table 3b). This is indicative of the bonding orbitals or $n\rightarrow\sigma^*$ or $n\rightarrow\pi^*$ allegedly owned by the intermediate compounds of short-chain acids.

Table 4 reports the absorbance values of PBA from the beginning till the end of a 60-min degradation reaction. The absorbance peak at 224 nm reached a value of 0.748 after 60 min (table 4a), whereas that at 275 nm was still there with a value of 0.169 (table 4b). This is indicative of the bonding orbitals or $n\rightarrow\sigma^*$ or $n\rightarrow\pi^*$ allegedly owned by the intermediate compounds of short-chain acids.

4. Conclusions

Gold nanoparticles were successfully deposited on the surface of N-doped TiO$_2$ nanotubes via electrodeposition. The synthesized Au/N-TiO$_2$ NTs had a band gap of 2.16 eV. The Au/N-TiO$_2$ NTs exhibited better photocatalytic activity under visible light compared to TiO$_2$ NTs and N-TiO$_2$ NTs, according to the results of phenol and BPA degradation; however, TiO$_2$ NT still showed better photocatalytic activity under UV light.

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