ABSTRACT: In this work, a photocatalytic process was carried out to recover gold (Au) from the simulated non-cyanide plating bath solution. Effects of semiconductor types (TiO₂, WO₃, Nb₂O₅, CeO₂, and Bi₂O₃), initial pH of the solution (3−10), and type of complexing agents (Na₂S₂O₃ and Na₂SO₃) and their concentrations (1−4 mM each) on Au recovery were explored. Among all employed semiconductors, TiO₂ exhibited the highest photocatalytic activity to recover Au from the simulated spent plating bath solution both in the absence and presence of complexing agents, in which Au was completely recovered within 15 min at a pH of 6.5. The presence of complexing agents remarkably affected the size of deposited Au on the TiO₂ surface, the localized surface plasmon effect (LSPR) behavior, and the valence band (VB) edge position of the obtained Au/TiO₂, without a significant change in the textural properties or the band gap energy. The photocatalytic activity of the obtained Au/TiO₂ tested via two photocatalytic processes depended on the common reduction mechanism rather than the textural or optical properties. As a result, the Au/TiO₂ NPs obtained from the proposed recovery process are recommended for use as a photocatalyst for the reactions occurring at the conduction band rather than at the valence band. Notably, they exhibited good stability after the fifth photocatalytic cycle for Au recovery from the actual cyanide plating bath solution.

1. INTRODUCTION

Gold (Au) plating is an essential process used to prepare the surface of some electronic parts in the printed circuit boards (PCBs) owing to its high electrical conductivity, high reliability, excellent planarity, good solderability, and high corrosion resistance.¹,² A high growth rate of the electronics industry is predicted to be observed in our country during 2021−2023 due to a number of various technological developments, such as the rollout of the 5G technology, the increase of smart car markets, and consumer demand for portable computers (PCs), notebooks, tablets, and smartphones, resulting from work from home (WFH) and distance learning of students during the COVID-19 situation.³ Typically, Au plating can be carried out via both cyanide and non-cyanide Au salts by electroplating or electroless plating. The electrolytic Au cyanide plating can be operated in a wide pH range from acidic to alkaline pH, while non-cyanide plating is effective at neutral or alkaline pH.⁴ To achieve a stable plating system, various kinds of complexing agents and additives are employed to obtain a good quality of plated specimens.⁵,⁶ Thus, the spent plating bath solution generated from the process contains various kinds of chemicals and metal ions such as chromium (Cr), copper (Cu), iron (Fe), or nickel (Ni) ions, as well as the residual Au complex. The presence of precious metals such as Au in the effluent is an economic loss. Therefore, various processes have been developed to recover Au from the discharged solution, such as precipitation, electrolysis, adsorptive reduction, ion exchange, solvent extraction, and bioproduction and biorecovery.⁷,⁸ In addition to the mentioned processes, another promising process that can be used to recover Au from the plating bath solution is the photocatalytic process because it possesses the viability to recover Au from aqueous solutions of both chloride species⁹ and cyanide species.⁸ In addition, it is environmentally friendly, involves low operating costs, and can operate at ambient conditions.⁸,¹⁰

The photocatalytic process is a chemical process that occurs under the joint action between light and a photocatalyst.¹¹,¹² The transition-metal oxides or semiconductors such as TiO₂, ZnO, WO₃, etc., are generally used as a photocatalyst because they have no energy levels to promote the recombination of the photogenerated electron (e−) and hole (h⁺) in their
structure. The process efficiency depends upon various parameters, including the redox potential of dissolved metals relative to the utilized semiconductor, the presence of electron and/or hole scavengers, irradiated light intensity, solution pH, and type and loading of utilized semiconductors. Recently, it was reported that TiO₂/SiO₂ exhibited a higher photocatalytic removal of Au(I) from gold–cyanide complexes than bare TiO₂. The presence of hole scavengers such as methanol can promote the deposition of metallic Au on the surface of the utilized photocatalyst. Using an amphiphilic photocatalyst based on a polyoxometallate (W₁₀O₃₂⁶⁻)/surfactant (dimethyl dioctadecyl ammonium) hybrid, the photocatalytic recovery of Au can be carried out under the pH value of 3–6 and depended on the catalyst loading and concentration of sacrificial agents. The photoreduction of Au(III) via TiO₂ increased with the increase of reaction times and photocatalyst loadings. However, excessive loading of TiO₂ increased the solution turbidity, which decreased the exposure of TiO₂ with the light irradiation. The photoreduction decreased with the increase of the initial concentration of Au(III). The presence of Ag(I) and Cu(II) decreased the photoreduction of Au(III) due to the competition in adsorption and reduction, while the presence of Fe(III) can enhance the photoreduction due to the reduction and quick oxidation of Fe(II). The tannin (TA)-presence of Fe(III) can enhance the photoreduction due to the competition in adsorption and reduction, while the increase of the initial concentration of Au(III). The presence of the orthorhombic phase appeared at 2θ values of 22.55, 22.79, 23.07, 23.56, 24.31, 26.54, 28.87, 33.21, 34.12, 35.37, 41.84, 47.21, 48.32, 49.88, and 55.90°, corresponding to the crystal planes of (111), (200), (220), (022), (122), (204), and (206), respectively, (JCPDS file no. 37-1468). The XRD pattern of the parent TiO₂ displayed diffraction peaks at 2θ values of 25.3, 37.8, 48.0, 53.90, 55.10, and 62.70°, corresponding to the crystal planes of (101), (004), (200), (105), (221), and (204), respectively, (JCPDS file no. 21-1272) for the anatase phase and displayed 2θ values of 27.41, 36.06, and 41.21°, corresponding to the crystal planes of (110), (101), and (111), respectively, (JCPDS file no. 21-1276) for the rutile phase. For WO₃, its XRD pattern showed the diffraction peaks of the monoclinic phase at 2θ values of 23.07, 23.56, 24.31, 26.54, 28.87, 33.21, 34.12, 35.37, 41.84, 47.21, 48.32, 49.88, and 55.90°, corresponding to the crystal planes of (002), (020), (120), (112), (022), (202), (122), (222), (004), (040), (140), and (420), respectively, (JCPDS file no. 43-1035). The CeO₂ revealed RXD peaks at 2θ values of 28.54, 33.07, 47.47, 56.31, and 59.08°, corresponding to the crystal planes of (111), (200), (220), (311), and (222), respectively, (JCPDS file no. 340394). For Nb₂O₅, its XRD pattern exhibited the diffraction peak of both orthorhombic and monoclinic phases. The characteristic peaks of the orthorhombic phase appeared at 2θ values of 22.55, 28.30, 28.91, 36.49, 46.09, and 47.47°, corresponding to the crystal planes of (001), (180), (200), (181), (002), and (110), respectively, (JCPDS file no. 71-0336) and the monoclinic structure exhibited a peak at a 2θ of 23.72°, indicating the crystal plane of (405) (JCPDS file no. 37-1468). The XRD pattern of Bi₂O₃ showed the main characteristic peaks of the α-
monoclinic phase at 2θ values of 24.51, 25.71, 26.88, 27.35, 27.96, 33.21, 35.01, 37.58, 46.28, and 52.35°, corresponding to the crystal planes of (1̅02), (002), (111), (120), (012), (121), (022), (112), (3̅11), and (321), respectively, (JCPDS file no. 71-2274). The crystallite sizes of all employed semiconductors estimated using Scherrer’s equation are listed in Table 1 and can be ranked in the order Bi2O3 > WO3 > Nb2O5 > CeO2 > TiO2.

In the heterogeneous photocatalytic process, the adsorption of active species on the surface of semiconductors must occur first, followed by the photocatalytic reaction. The presence of a high specific surface area can induce effective charge adsorption as well as the photocatalytic activity of the utilized photocatalysts. The N2 adsorption/desorption isotherms of all employed commercial semiconductors are shown in Figure 2a. All explored semiconductors exhibited the type IV isotherm according to the IUPAC classification with H4-shaped hysteresis loops, indicating the presence of slitlike pores. The quantitative values of the BET surface area, average pore size, and total pore volume are summarized in Table 1. The TiO2 exhibited the highest BET surface area of 52.38 m²/g and a total pore volume of 0.0629 cm³/g, followed by CeO2 (5.432 m²/g), Nb2O5 (2.487 m²/g), WO3 (0.595 m²/g), and Bi2O3 (0.141 m²/g), respectively.

The optical absorption spectra of all utilized commercial semiconductors were also examined in the wavelength of 300–800 nm at room temperature. As displayed in Figure 3a, both TiO2 and Nb2O5 displayed high absorbance at wavelengths lower than 380 nm and exhibited a very low intensity spectrum at wavelengths higher than 380 nm, indicating their visible light inertness. At an identical wavelength, CeO2 showed a higher absorbance spectrum than TiO2 and Nb2O5; however, it
was still active in the UV region. Either WO$_3$ or Bi$_2$O$_3$ clearly exhibited a larger red shift in the absorbance spectra than other utilized semiconductors up to a wavelength of 480 nm, suggesting their ability to absorb both UV light and the short-wavelength visible light. The optical band gap energy ($E_g$) of all employed semiconductors was quantitatively determined via the Tauc plot according to eq 1:

$$\left(\alpha h\nu\right)^{1/n} = A(h\nu - E_g)$$

(1)

where $\alpha$ is the optical absorption coefficient, $h\nu$ is the photon energy, and $A$ is the proportionality constant. In this equation, $n$ is related to the type of optical transition process in semiconductors ($n = 1/2$ and 2 for the direct and indirect band gap semiconductors, respectively).

The band gap values of all utilized semiconductors were obtained from the x-intercept of the plot of ($\alpha h\nu$)$^{1/n}$ against the photon energy (inset of Figure 3a) and are listed in Table 1. The values of the band gap energy of all utilized semiconductors can be ranked in the order TiO$_2$ > Nb$_2$O$_5$ > CeO$_2$ > Bi$_2$O$_3$ > WO$_3$, indicating the reverse trend of the visible light absorption ability.

2.2. Photocatalytic Recovery of Au from the Simulated Spent Non-Cyanide Plating Bath Solution.

2.2.1. Effect of Semiconductor Types. The photocatalytic recovery of Au from the simulated spent plating bath solution at a pH of 3.2 by commercial semiconductors at a loading of 4 g/L and a light intensity of 4.1 mW/cm$^2$ is shown in Figure 4.

Figure 4. Photocatalytic recovery of Au from the simulated spent plating bath solution at a pH of 3.2 by commercial semiconductors at a loading of 4 g/L and a light intensity of 4.1 mW/cm$^2$.

Under the dark condition, approximately 72 and 33% of Au ions were adsorbed in the presence of TiO$_2$ and CeO$_2$, while only 2–4% of Au ions were adsorbed in the presence of WO$_3$, Nb$_2$O$_5$, and Bi$_2$O$_3$. This indicated the highest adsorption capacity of Au ions via TiO$_2$. Typically, the adsorption of some active substances on the surface of the adsorbent occurs via electrostatic interactions, which usually depend on the available surface area and surface charges of adsorbents. A high adsorption of Au ions in the presence of TiO$_2$, followed by CeO$_2$, might be due to their high BET surface area and total pore volume available to adsorb some AuCl$_4^-$ species compared to other utilized semiconductors. In addition, the value of surface charges or point of zero charges (PZCs) of semiconductors is dependent on the solution pH. That is, when the solution pH is higher than the PZC value, the adsorbent usually exhibits negative surface charges and strongly prefers to adsorb cationic molecules. However, when the solution pH is lower than the PZC value, the adsorbent demonstrates positive surface charges and favors the adsorption of anionic molecules. In this case, the experimental PZC values of TiO$_2$, WO$_3$, CeO$_2$, Nb$_2$O$_5$, and Bi$_2$O$_3$ were ~6.6, ~5.6, ~6.4, ~6.2, and ~10.4, respectively. Thus, all utilized semiconductors displayed positive surface charges, which are able to adsorb the anionic charge of AuCl$_4^-$ in an acidic solution.

Under the light irradiation, the Au ions were completely recovered within 30 min in the presence of either TiO$_2$ or WO$_3$ and within 120, 480, and 480 min in the presence of CeO$_2$, Nb$_2$O$_5$, and Bi$_2$O$_3$, respectively. TiO$_2$ displayed the highest rate of Au recovery even though it has the highest band gap energy (~3.35 eV), probably due to its highest adsorption capacity to the Au ions, which readily proceed to the reaction with the photogenerated $e^{-}$ under the irradiated light. However, this is not the case with WO$_3$. Although it exhibited very low Au ion adsorption capacity, it displayed a very fast rate of Au recovery, probably attributed to its short band gap energy, which can harvest a high quantity of incident light to proceed to the photocatalytic reaction. This suggested that both textural and optical properties of semiconductors played an important role in the photocatalytic recovery of Au from the simulated spent solution.

2.2.2. Effect of Solution pH. Typically, the Au ions can exist in different forms in a chloride solution depending on the solution pH. That is, at a pH below 6.2, the Au ions are dominantly found in the form of tetrachloroaurate (AuCl$_4^-$), while both AuCl$_4^-$ and hydroxylated gold chloride species [AuCl$_4$(OH)$_2$]$^-$ are mainly found at a pH of 6.2–8.4. At a higher pH value (>8.4), the large hydroxylated gold chloride species are still dominant, starting from AuCl$_4$(OH)$_2$ to the others. Figure 5 shows the effect of the initial pH on the photocatalytic recovery of Au from the simulated spent plating bath solution using the TiO$_2$ and WO$_3$ at a loading of 4 g/L.

Figure 5. Effect of initial pH on the photocatalytic recovery of Au from the simulated spent plating bath solution via (a) TiO$_2$ and (b) WO$_3$ at a loading of 4 g/L and a light intensity of 4.1 mW/cm$^2$. 
and a light intensity of 4.1 mW/cm². In the absence of light, approximately 72 and 84% of Au ions were adsorbed by TiO₂ at pH values of 3.2 and 6.5, respectively, but around 27% of Au ions were adsorbed at a pH of 10.0. However, approximately 3-7% of Au ions were adsorbed in the presence of WO₃ for all pH values. This is attributed to the synergistic effect of the PZC value and textural properties of both semiconductors. That is, the TiO₂ exhibited a high adsorption capacity under acidic conditions because it theoretically exhibits the positive surface charges as TiOH₃⁻ species, which can interact well with the negative charge of hydroxylated gold chloride species. However, in a basic solution, TiO₂ exhibited negative surface charges (as TiO⁻), which do not favor electrostatic interactions with the large hydroxylated gold chloride species such as AuCl₂(OH)₃⁻. Therefore, the discrimination of Au ions in the basic environment is possibly caused by the preferential adsorption of Au at the pore surfaces of TiO₂ via the intermolecular cohesion forces. Low adsorption of Au ions in the presence of WO₃ might be due to its low surface area. In the presence of irradiated light, a fast reduction of Au ions was observed in the presence of TiO₂ at all pH values, likely due to the immediately photocatalytic reduction of adsorbed Au ions. In WO₃, although almost similar quantities of Au ions were adsorbed in a dark environment for all pH values, a fast decrease of Au ions was observed via the solution with a pH of 6.5. This might be due to an appropriate aggregation of WO₃ in the solution that has a pH value close to the PZC value, which can induce an effective transfer of e⁻ and h⁺ to the adjacent particles under a thorough stirring condition, resulting in a prolonged e⁻ + h⁺ lifetime as well as an enhanced photocatalytic activity. The sluggish reduction rate of Au ions in a strong basic solution (pH of 10.0) might be due to the steric hindrance of the large hydroxylated gold chloride molecules that competitively combined with the adsorbed WO₃ to proceed with the photocatalytic reaction.

2.2.3. Effect of Complexing Agents. To produce smooth and ductile gold deposits with low stress and hardness as well as a good dimensional tolerance from a typical non-cyanide gold plating bath, two types of complexing agents, including sulfite (SO₃²⁻) and thiosulfate (S₂O₃²⁻), are usually added to promote the bath stability at a near-neutral pH. Thus, the spent solution discharged from the plating unit usually contains a trace quantity of a residual sulfite–thiosulfate mixed agent. To investigate the effect of complexing agents on the photocatalytic recovery of Au from the simulated spent non-cyanide gold plating bath, two types of complexing agents were employed, including Na₂SO₃ and Na₂S₂O₃. Figure 6 shows the photocatalytic recovery of Au from the simulated spent plating bath solution at pH of 6.5 using TiO₂ and WO₃ at a loading of 4 g/L and a light intensity of 4.1 mW/cm².

\[2[Au(S₂O₃)₂]^{3−} \leftrightarrow [Au₂S₂O₆]_{ads} + 3S₂O₃^{2−} \] (R1)

Under irradiated light, the presence of 2 mM Na₂SO₃ did not hinder the photocatalytic recovery of Au using TiO₂, and all Au ions were completely recovered within 5 min. However, it remarkably decreased the photocatalytic recovery of Au using WO₃ in which approximately 80% of Au ions were recovered within 90 min. The presence of 2 mM Na₂S₂O₃ slightly slowed down the photocatalytic recovery of Au using TiO₂ in which all Au ions were completely reduced within 10 min. However, it completely interrupted the photocatalytic recovery of Au using WO₃. This might be due to the synergetic effect of the low surface area of WO₃ and the molecular steric hindrance of Au(S₂O₃)₂⁻.

In the presence of both sulfite and thiosulfate at a pH value of 6.0-7.5, the dominant species of Au ions are reported in the form of sulfite and thiosulfate Au complexes as (Au₂S₄O₆)⁻.−3⁻. As also demonstrated in Figure 6, neither adsorption nor photocatalytic reduction of Au was observed via WO₃ in the presence of mixed complexing agents for all utilized concentrations. Different concentrations of complexing agents exhibited different behaviors of Au ion adsorption in the TiO₂ system. That is, the adsorption of Au ions on the surface
of TiO₂ was extremely low in the presence of low concentrations of mixed complexing agents (1 and 2 mM of each agent). Slightly higher adsorption can be achieved in the presence of high concentrations of mixed complexing agents (3 and 4 mM of each agent). This is probably because a high concentration of (Au₂S₂O₃)(SO₃)₂⁻ in the bulk liquid can initiate a high concentration gradient between the bulk phase and the surface of TiO₂, resulting in an increased mass transfer as well as an increased adsorption capacity.30,31 In the presence of light, increasing the concentration of mixed complexing agents slightly decreased the photocatalytic efficiency for Au recovery compared with that in the absence of complexing agents, probably attributed to the shielding behavior of densely surrounded species in the presence of a high concentration of complexing agents. Based on the obtained results, among all employed commercial semiconductors, TiO₂ exhibited the highest photocatalytic recovery of Au from the simulated spent non-cyanide plating bath both in the absence and presence of complexing agents at all explored concentrations.

2.3. Morphology and Photocatalytic Activity of the Obtained Au/TiO₂. As reported elsewhere, the Au NP-decorated semiconductor exhibited an effective photocatalytic activity for various applications such as wastewater remediation,32–36 hydrogen production from water splitting,37,38 precious metal recovery,19,39 glycerol conversion to value-added compounds,40–42 etc. Thus, the morphology and photocatalytic activity of the Au/TiO₂ obtained from the simulated spent plating bath solution in the absence and presence of mixed complexing agents, denoted Au/TiO₂-NC and Au/TiO₂-C, respectively, were then explored.

As qualitatively shown in Figure 1b, both Au/TiO₂-NC and Au/TiO₂-C exhibited the main characteristic peaks of the TiO₂-based material with comparable anatase content (Table 1), calculated according to the Spurr and Myers equations (eq 2).43 No characteristic peaks of decorated Au were observed, probably because of their presence in good dispersion of small quantities or even in amorphous form. Thus, the SEM-EDX analysis was carried out to identify the presence of decorated Au on the surface of TiO₂. As displayed in Figure 7a-1,b-1, a good dispersion of Au was clearly observed with the entire loading of 1.37 ± 0.02 and 1.02 ± 0.03 wt % in Au/TiO₂-NC and Au/TiO₂-C, respectively (Table 1). On HRTEM analysis, the average particle size of Au in Au/TiO₂-C was significantly smaller than that in the Au/TiO₂-NC (Figure 7a-2,b-2). This is probably due to the effect of different forms of Au complex in the absence and presence of complexing agents during the photocatalytic process. That is, in the presence of sulfite–thiosulfate complexing agents, a large Au complex form such as (Au₂S₂O₃)(SO₃)₂⁻ generally forms.1 This large Au complex might hinder the competitive adsorption and photocatalytic reduction of each other, higher than those in the absence of complexing agents, which in turn reduced the agglomeration of deposited Au NPs on the TiO₂ surface. As regards the textural property, both types of Au/TiO₂ still displayed H₄-shaped hysteresis loops of the type IV isotherm with comparable textural properties (Figure 2b and Table 1), which were slightly better than those of pristine TiO₂. This is due to the good dispersion of Au NPs on the TiO₂ surface.44

\[
x_A = \frac{100}{1 + \left[\frac{I_R}{0.8I_A}\right]}
\]  

(2)

where \(x_A\) is the anatase weight fraction, \(I_A\) is the relative reflection intensities of anatase, and \(I_R\) is the relative reflection intensities of rutile.
The absorption spectra of the Au/TiO₂ obtained from the photocatalytic recovery of Au from the simulated spent plating bath solution in the absence and presence of complexing agents were also explored in the range of 300−800 nm (Figure 3b). It can be observed that the Au/TiO₂ obtained from both conditions exhibited a red shift in absorption toward the wavelength longer than 400 nm, indicating the ability to absorb more incident visible light. The Au/TiO₂-NC revealed an intense broad band centered at a wavelength of 550 nm due to the oscillation and polarization of the excited electrons in the decorated Au structure called LSPR, which can effectively promote visible light absorption. The Au/TiO₂-C exhibited unclear LSPR behavior in comparison with the Au/TiO₂-NC, probably due to the presence of too small particle sizes of Au NPs in its structure, causing a low intensity of light absorption and scattering cross sections as well as the local electromagnetic field enhancement. By applying Tauc’s equation, the band gap energies of both Au/TiO₂ were comparable at 3.19−3.20 eV, which were lower than that of the TiO₂-based material.

The chemical state and bonding of Ti, O, and decorated Au were then examined by XPS analysis. The survey spectra clearly revealed the spectrum of O 1s, Ti 2p, and C 1s peaks of the O, Ti, and C (from carbon tape) (Figure 8). Using high-resolution XPS, the spectra of the pristine TiO₂ showed two symmetric peaks at binding energies of 464.1 and 458.4 eV (Figure 9a-1), corresponding to the Ti 2p1/2 and Ti 2p3/2 components of Ti⁴⁺. The characteristic peaks of both Ti 2p components still appeared at the same binding energy compared with TiO₂. No satellite peaks at the low binding energy of both doublets were observed in both Au/TiO₂ (Figure 9b-1,c-1), indicating the absence of the Ti³⁺ state or the defective structure. The XPS spectra of asymmetric O 1s contained two symmetric peaks of the O₂⁻ and OH⁻ of the crystalline network at binding energies of ~530.2 and ~531.7 eV, respectively (Figure 9a-2,b-2,c-2). The XPS spectra of Au revealed two principal peaks of Au 4f⁷/₂ and Au 4f⁵/₂ at binding energies of 86.7 and 83.1 eV with a spin−orbit splitting of 3.7 eV (Figure 9b-3,c-3), which is in good agreement with the values of the monometallic Au. The presence of shoulder peaks with a higher binding energy for each Au 4f component was not observed, indicating the presence of monometallic Au on the TiO₂ surface. At low binding energy, the XPS spectra of TiO₂, Au/TiO₂-NC, and Au/TiO₂-C, respectively, displayed maximum binding energies of around 2.74, 1.70, and 1.40 eV (Figure 10a), indicating a negative shift of the VB edge of TiO₂ in the presence of decorated Au NPs. According to the obtained VB edges of all samples, the minimum conduction band (CB) of the respective samples would occur at −0.61, −1.50, and −1.79 eV. Therefore, the band positions of all samples are roughly sketched in Figure 10b.

Figure 11 illustrates the photocatalytic activity of the obtained Au/TiO₂ samples through two photocatalytic processes under UV−vis light. It can be seen that both Au/TiO₂-NC and Au/TiO₂-C exhibited comparable photocatalytic activity for MB degradation under UV−vis light. Approximately 80% of MB was degraded within 180 min, which was lower than that of TiO₂, in which around 88% of MB was degraded at the same reaction time (Figure 11a). According to the nature of the photocatalytic process, when the semiconductor or photocatalyst (S) absorbs the irradiated light that has the photon energy higher than its band gap energy, the electron (e⁻) will be excited from the VB to the CB, leaving the hole (h⁺) at the VB, as shown in reaction R2. The photogenerated h⁺ can react with the adsorbed water (H₂O₂) to form hydroxyl radicals (HO⋅) and proton (H⁺) (reaction R3), while the photoexcited e⁻ at the CB can react with the dissolved oxygen (O₂) to form the superoxide radicals (O₂•⁻) (reaction R4). Both HO⋅ and O₂•⁻ generated are the reactive oxidizing species, which can attach and degrade the MB molecules according to reaction R5.

\[ S + h\nu (UV – vis light) \rightarrow S^* (e^- + h^+) \]  
\[ H_2O + h^+ \rightarrow HO^\cdot + H^+ \]  
\[ O_2 + e^- \rightarrow O_2^{•^-} \]  
\[ MB + (HO^\cdot, h^+, O_2^{•^-}) \rightarrow degraded products \]  

where S* is the S in the excited state.

The low photocatalytic activity of MB degradation in the presence of Au/TiO₂ in comparison with the TiO₂ might be attributed to their less-positive VB edge to produce HO* (Figure 10b). Thus, the degradation of MB in the presence of Au/TiO₂ is mainly dominated by the h⁺ or O₂•⁻ and not HO* as usual. The photocatalytic degradation of MB via all employed photocatalysts was then fitted with the Langmuir−Hinshelwood model, as expressed in eq 3.

\[ C/C_0 = \exp(-kt) \]  

where \( C_0 \) is the initial concentration of the substance, \( C \) is the concentration of the substance at a particular time \( t \), and \( k \) is the first-order reaction rate constant.

As tabulated in Table 2, the apparent rate constants for MB degradation in the presence of Au/TiO₂-NC and Au/TiO₂-C were found to be 0.0080 and 0.0085 min⁻¹, which were lower than that of the pristine TiO₂ for 1.38- and 1.30-fold, respectively. The degradation efficiency of Au/TiO₂ prepared from the proposed method gave a rate constant comparable to that of Au/TiO₂ prepared by the sol−gel method (\( k \sim 0.0067 \) min⁻¹) but lower than that of the TiAu1 prepared by the incipient wetness method (\( k \sim 0.0687 \) min⁻¹). Regardless of the photocatalytic reduction of Au from the actual spent cyanide plating bath solution, approximately 3% of...
Au(CN)$_2^-$ was reduced during the reaction time of 2 h using pristine TiO$_2$ as the photocatalyst (Figure 11b). However, approximately 77 and 24% of Au(CN)$_2^-$ were reduced using Au/TiO$_2$-NC and Au/TiO$_2$-C as photocatalysts, respectively. Typically, in the oxygenated system, the reduction reaction of Au(CN)$_2^-$ to Au via the photogenerated e$^-$ occurs at the VB (reaction R6) at a reduction potential of around $-0.57$ V/NHE. Moreover, the dissolved O$_2$ can competitively react with the photogenerated e$^-$ to form H$_2$O$_2$ at a slightly low reaction potential ($-0.146$ V/NHE) according to reaction R7. The generated H$_2$O$_2$ can dissociate in the presence of the incident light or react with the photogenerated e$^-$ to form HO$^*$ radicals (reactions R8). Meanwhile, the formed CN$^-$ ions are readily oxidized by the photogenerated h$^+$ and/or HO$^*$ at VB to form CNO$^-$ according to reactions R9 and R10.61

\[
\begin{align*}
\text{Au(CN)}_2^- + e^- &\rightarrow \text{Au} + 2\text{CN}^- \quad \text{(R6)} \\
\text{O}_2 + 2e^- + 2\text{H}_2\text{O} &\rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \quad \text{(R7)} \\
\text{H}_2\text{O}_2 + \text{H}^+ + e^- &\rightarrow 2\text{HO}^* + \text{HO}^- \quad \text{(R8)} \\
\text{CN}^- + 2\text{h}^+ + 2\text{OH}^- &\rightarrow \text{CNO}^- + \text{H}_2\text{O} \quad \text{(R9)} \\
\text{CN}^- + \text{HO}^* &\rightarrow \text{CNO}^- \quad \text{(R10)} 
\end{align*}
\]

According to the sketched band position (Figure 10b), both TiO$_2$ and Au/TiO$_2$ samples exhibited a more negative CB level than the reduction potential of Au(CN)$_2^-$, indicating their ability to reduce Au(CN)$_2^-$ to Au from the spent cyanide plating bath solution. A lack of photocatalytic reduction of Au(CN)$_2^-$ via TiO$_2$ during the reaction time of 2 h was probably due to a competitive reaction of dissolved O$_2$ with the photoexcited e$^-$, resulting in a low quantity of remaining e$^-$ to react with the Au(CN)$_2^-$ to form H$_2$O$_2$. As the reaction proceeded, a massive amount of dissolved O$_2$ was gradually consumed, and the deposition of Au over the surface of TiO$_2$ could be started. These Au clusters can act as an electron sink to trap the migrated e$^-$, which can prolong the lifetime of e$^-$-h$^+$ pairs as well as increase the photocatalytic efficiency.62–64 The photocatalytic reduction of Au(CN)$_2^-$ via TiO$_2$ was previously observed at around 75% when the reaction time was extended to 8 h (data not shown). This is not for the case of Au/TiO$_2$ samples in which a faster photocatalytic reduction of Au(CN)$_2^-$ was observed. This might be due to a combined effect between the presence of Au NPs that acted as the electron sink during the reaction, which can improve the charge transfer rate and decrease the band gap energy of both Au/TiO$_2$ samples compared with TiO$_2$, effectively harvesting the incident light to drive the excitation of e$^-$ from the VB to the CB to perform the photocatalytic reduction. The Au/TiO$_2$-C exhibited slightly lower activity to reduce Au(CN)$_2^-$ than the Au/TiO$_2$-NC, due to its lower LSPR behavior. Using the Langmuir–Hinshelwood model, the Au/TiO$_2$-NC exhibited...
apparent rate constants for Au(CN)\textsubscript{2}\textsuperscript{−} recovery of 0.0234 min\textsuperscript{-1}, which was higher than those for TiO\textsubscript{2} and Au/TiO\textsubscript{2}-C of around 46.8- and 7.0-fold, respectively (Table 2).

Based on the obtained results, although the Au/TiO\textsubscript{2}-C exhibited a photocatalytic recovery of Au from the actual spent cyanide plating bath solution lower than that of Au/TiO\textsubscript{2}-NC, it displayed the photocatalytic activity higher than that of pristine TiO\textsubscript{2} of around 25% at 2 h. The repetitive photocatalytic recovery of Au from the actual spent cyanide plating bath solution was then studied using the obtained Au/TiO\textsubscript{2} as the original photocatalyst. Briefly, after the first experiment, the solid NPs were separated from the plating bath solution by centrifugation at 11 000 rpm, washed thoroughly with deionized water, dried at 80 °C for 3 h, and then subjected to the second experiment, and this was repeated. As displayed in Figure 12a, the quantity of decorated Au on the TiO\textsubscript{2}-based material increased with increasing photocatalytic cycles. Moreover, the Au/TiO\textsubscript{2} obtained at a particular cycle can enhance the fast dwindling of Au(CN)\textsubscript{2}\textsuperscript{−} from the cyanide plating bath solution in the next cycle, probably due to a high

**Table 2. Apparent Reaction Rate Constants for the Photocatalytic Activity of TiO\textsubscript{2} and Au/TiO\textsubscript{2}**

| photocatalyst     | MB degradation \( k \) (min\textsuperscript{-1}) | \( R^2 \)  | Au recovery \( k \) (min\textsuperscript{-1}) | \( R^2 \)  |
|------------------|-------------------|-----------|-------------------|-----------|
| TiO\textsubscript{2} | 0.0110             | 0.9274    | 0.0005            | 0.9516    |
| Au/TiO\textsubscript{2}-NC | 0.0080           | 0.9760    | 0.0234            | 0.9982    |
| Au/TiO\textsubscript{2}-C | 0.0085           | 0.9865    | 0.0035            | 0.9988    |
LSPR behavior in the presence of high Au content in the Au/TiO2 NPs. After the fifth cycle, the size of decorated Au NPs was distributed in the range of 6–19 nm with an average value of 10.39 ± 3.28 nm (Figure 12b). The deposited Au NPs can simply separate from the TiO2-based material using selective dissolution via a commercial chemical such as Aqua regia.

According to the nature of the proposed application of the obtained Au/TiO2-C for the Au recovery from the actual cyanide plating bath solution, the properties of the obtained Au/TiO2 at each photocatalytic cycle changed accordingly due to the accumulation of decorated Au. Thus, the stability of the employed photocatalyst was examined from the phase change of the TiO2-based material. As shown in Figure 13, the XRD pattern of the Au/TiO2 obtained at the fifth cycle (Au/TiO2-C(5)) still maintained the main characteristic peaks of the TiO2-based material. The Au/TiO2-C(5) NPs were found to exhibit almost similar anatase contents (∼84.86%) compared to the Au/TiO2-C NPs (∼84.28%), suggesting their stability after the fifth use.

3. CONCLUSIONS

Among all employed semiconductors, the photocatalytic recovery of Au from the simulated non-cyanide plating bath solution was accomplished well using the commercial TiO2 as the photocatalyst at a loading of 4 g/L and pH of 6.5 because of its high surface area. The presence of either Na2S2O3 or Na2SO3 at the concentrations of 1–4 mM insignificantly affected the photocatalytic recovery of Au. The Au was completely recovered within 5 and 15 min in the absence and presence of mixed complexing agents for all investigated concentrations. However, the presence of complexing agents remarkably affected the morphology of obtained Au/TiO2 samples as well as the LSPR behavior. That is, the Au/TiO2-C exhibited LSPR behavior lower than the Au/TiO2-NC with a negative shift of the VB edge position. Regardless of the photocatalytic activity, both Au/TiO2 samples exhibited poor photocatalytic activity for MB degradation in comparison with TiO2 due to their less-positive VB position to produce the HO* radicals. However, both Au/TiO2 samples exhibited a higher photocatalytic activity to recover Au from the spent cyanide plating bath solution than TiO2. This is because the deposited Au clusters promote the red shift of light absorption of TiO2 as well as LSPR behavior. The Au/TiO2-C exhibited an anatase content comparable to that of the TiO2-based material after the fifth photocatalytic cycle of Au recovery from the actual cyanide plating bath solution.
4. MATERIALS AND METHODS

4.1. Chemicals. All chemicals employed in this work were analytical grade, including chloroauroic acid (99.9% HAuCl₄·3H₂O; Sigma-Aldrich), sodium hydroxide (NaOH; Sigma-Aldrich), sodium thiosulfate (99.5% Na₂S₂O₃·5H₂O; Kemaus), and sodium sulfate (98% Na₂SO₄; Kemaus). Five commercial semiconductors were utilized as photocatalysts, including titanium dioxide (TiO₂; 99.5%, Sigma-Aldrich), tungsten(VI) oxide (WO₃; 99.9%, Sigma-Aldrich), niobium(V) oxide (Nb₂O₅; 99.99%, Sigma-Aldrich), cerium(IV) oxide (CeO₂; 99.995%, Sigma-Aldrich), and bismuth(III) oxide (Bi₂O₃; 99.999%, Sigma-Aldrich).

4.2. Photocatalytic Recovery of Au from the Simulated Spent Non-Cyanide Plating Bath Solution. The photocatalytic recovery of Au from the simulated spent non-cyanide plating bath solution was tested via several types of commercial semiconductors at an identical loading under UV−vis light irradiation. In each experiment, approximately 1.2 g of the respective semiconductors was dispersed in 300 mL of the simulated spent plating bath solution and filled in a 400 mL double-wall cylindrical glass reactor, which was then placed in the middle of the UV-protected box at the right position to receive the irradiated light. Afterward, the solution was agitated continuously with a magnetic stirrer at a constant rate of 400 rpm in the absence of light for 30 min to provide a good dispersion and equilibrium adsorption of Au ions on the surface of the semiconductor. After the equilibration period, the system was irradiated with the UV−vis light (100−600 nm) generated by a high-pressure mercury lamp (120 W; RUV 533 BC, Holland) at a light intensity of 4.1 mW/cm². The temperature of the photoreactor was precisely controlled at around 32 °C using the water circulation system as the reactor jacket. As the time proceeded, approximately 5 mL of the solution was sampled and centrifuged at 11 000 rpm (5804R, Eppendorf) to separate the solid portion from the aqueous mixture, and then the remaining Au ions were analyzed by flame atomic absorption spectrometry (Flame-AAS, AAnalyst 200+ flas 400; PerkinElmer). The amount of recovered Au from the simulated spent plating bath solution could be obtained by subtracting the initial concentration of Au ions with the unrecovered one. The results reported here are the average value of three repetitive experiments, and the acceptable error in this work was not greater than 3%.

4.3. Characterizations. The light absorption capacity and the diffuse reflectance spectra over the wavelength range of 300−800 nm were measured by ultraviolet−visible−near-infrared spectrophotometry (UV−vis; Lambda 950, PerkinElmer). The crystallite structure of all semiconductors was analyzed by X-ray diffractionmetry (XRD; D2 Phaser, Bruker). The surface morphology and chemical composition of the fresh semiconductors and Au-decorated semiconductors were primarily observed via scanning electron microscopy (SEM; JSM-IT-500HR, JEOL) with energy-dispersive X-ray spectroscopy (EDX; JED-2300, JEOL) and high-resolution transmission electron microscopy (HRTEM; JEM-3100F, JEOL) with an accelerating voltage of 300 kV. The surface area, average pore size, and total pore volume were examined using a Multipoint Surface Area Analyzer (Tristar II3020, Micromeritics) via the Brunauer−Emmett−Teller (BET) method. The bonding and chemical state of the elements were determined with an X-ray photoelectron spectrometer (XPS; Axis Supra, Kratos, U.K.) with a Delay Line detector (DLD) and a monochromatic Al Kα (hv = 1486.6 eV) source. Accurate binding energies (±0.1 eV) were established with respect to the position of the adventitious carbon C 1s peak at 284.8 eV.

4.4. Photocatalytic Activity of the Obtained Au NP-Decorated Semiconductors. The photocatalytic activity of the Au NP-decorated semiconductors was examined with two photocatalytic processes, including the MB degradation and the Au recovery from the actual spent cyanide plating bath solution. The experimental setup of the MB degradation was similar to that in Section 2.2. In each experiment, approximately 200 mL of MB solution (50 mg/L, pH 7.58) with a photocatalyst loading of 0.25 g/L was first stirred at 300 rpm in the dark condition for 30 min and then irradiated by UV−vis light (100−600 nm) at a light intensity of 4.1 mW/cm². As the reaction proceeded, approximately 2.5 mL of MB solution was collected at a particular time and centrifuged at 11 000 rpm (5804R, Eppendorf) to separate the solid particles from the solution. Finally, the remaining MB concentration was quantitatively determined by measuring the absorbance at 664 nm using a UV−vis spectrophotometer (UV-1800, Shimadzu).

The Au recovery from the actual spent cyanide plating bath solution was determined using a similar experimental setup with the KAu(CN)₂ as the Au precursor at a photocatalyst loading of 4 g/L. The spent solution had a pH of 8.8−9.0 and contained Au ions of around 6.55 ± 0.12 mg/L and a trace quantity of iron (Fe), nickel (Ni), zinc (Zn), and copper (Cu) at concentrations less than 0.14, 0.99, 0.40, and 0.18 mg/L, respectively. The remaining concentration of Au ions in the spent solution was measured along the reaction times by flame atomic absorption spectrometry (Flame-AAS, AAnalyst 200+ flas 400; PerkinElmer).

AUTHOR INFORMATION

Corresponding Author
Mali Hunsom − Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Nakhon Pathom 73170, Thailand; Associate Fellow of Royal Society of Thailand (AFRST), Bangkok 10300, Thailand; orcid.org/0000-0002-4434-5276; Email: mali.hun@mahidol.edu

Authors
Naphaphan Kunthakudee − Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Nakhon Pathom 73170, Thailand
Tarawipa Puangpetch − Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
Prakorn Ramakul − Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06362

Notes
The authors declare no competing financial interest.

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