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April 1, 2015

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Gold nanoparticles-sensitized wide and narrow band gap TiO₂ for visible light applications: a comparative study†

Sajid Ali Ansari,a Mohammad Mansoob Khan,*a,b Moo Omaish Ansaria and Moo Hwan Cho*a

Gold nanoparticles (AuNPs)-sensitized wide band gap TiO₂ (Au/P-TiO₂) and narrow band gap TiO₂ (Au/M-TiO₂) nanocomposites were prepared using an electrochemically active biofilm. The optical and structural properties of the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites were characterized using standard techniques. The surface plasmon resonance (SPR) absorption characteristics of the AuNPs on the TiO₂ surface extended the absorption edge of P-TiO₂ and M-TiO₂ to the visible light region. The photocatalytic activity of the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites was evaluated by the photodegradation of methylene blue and methyl orange, and 2-chlorophenol under visible light irradiation, where Au/M-TiO₂ nanocomposite exhibited enhanced photocatalytic activity compared to the Au/P-TiO₂ nanocomposite and P-TiO₂ and M-TiO₂ nanoparticles. Furthermore, the higher photoelectrochemical performance of the Au/M-TiO₂ nanocomposite compared to the Au/P-TiO₂ nanocomposite and P-TiO₂ and M-TiO₂ nanoparticles further support its higher visible light active behavior under visible light irradiation. The pronounced photoactivities of the Au/M-TiO₂ nanocomposite in the visible region were attributed to the interfacial synergistic effects of the two phenomena, i.e. the SPR effect of AuNPs and the defect-induced band gap reduction of M-TiO₂ nanoparticles. The present work provides a newer insight into the development of nanocomposites of noble metals and defective metal oxides with high efficiency in the field of visible light-induced photocatalysis.

Introduction

The excessive use of organic chemicals in both industrial manufacturing and normal household uses has led to their leaching into the environment, causing an alarming environmental contamination.1 Organic chemicals are present as pollutants in ground water and surface water, such as wells, ponds and lakes.2 To achieve drinking water quality, pollutants need to be removed to protect the water resources. Several processes, such as adsorption onto supported substrates, ultrasonic irradiation, and electrochemical, biological and chemical oxidation reactions,2–4 have been used widely to destroy or remove these toxins. Among these techniques, the visible light photocatalytic detoxification of organic pollutants has attracted considerable attention because of its many advantageous features, such as the use of very small amounts of catalysts, regeneration of catalysts, utilization of natural sunlight for environmental remediation and clean energy production.5,6 These days, there has been extensive research efforts in the development of novel visible light active photocatalyst materials with high efficiency.5–7 Metal oxide nanostructures, such as TiO₂ and ZnO, have recently shown practical performance as effective photocatalysts utilizing solar light.5,7,8 The metal oxide photocatalyst generally involves the in situ production of strong oxidizing species of superoxide radical anions (*O₂⁻) and hydroxyl radicals (HO·), which triggers a sequence of reactions that ultimately breaks down the dye macromolecules into smaller and less harmful substances, leading to mineralization.5,6,8,9 Among these, TiO₂ has been the prime choice of researchers worldwide owing to its properties, such as low toxicity, low cost, high active surface area etc.5,10 On the other hand, the photocatalytic efficiency of TiO₂ has limited use because of its poor utilization of solar energy (<5% of the solar spectrum), which is due to its wide band gap (~3.2 eV) and the rapid recombination rate of photoexcited charge carriers.10,11

‖ Electronic supplementary information (ESI) available: Schematic diagram of the photolelectrochemical measurements, characterization and photodegradation results of P-TiO₂ and M-TiO₂, results of DRS, SAED, HAADF, EDX, and C1s spectroscopy analyses, photocatalytic degradation plots of MB, MO & 2-CP and stability test spectra of Au/P-TiO₂ and Au/M-TiO₂ nanocomposites. See DOI: 10.1039/c5nj00556f

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Received (in Montpellier, France) 5th March 2015, Accepted 1st April 2015
DOI: 10.1039/c5nj00556f
www.rsc.org/njc

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Many studies have focused on improving the visible light response of TiO$_2$ nanoparticles by doping with metals or non-metals, by fabricating a suitable textural design, and forming a nano-heterojunction by combining them with other metal oxide nanostructures. Recently, defect engineering, which leads to the introduction of defects, such as Ti$^{3+}$ formation and/or oxygen vacancies, has been reported to be an effective way of reducing the band gap of TiO$_2$ nanoparticles. The merits of defects and vacancies are that they preserve the intrinsic crystal structure of TiO$_2$ without introducing impurity elements, leading to enhanced photocatalytic performance under visible light irradiation. Several efforts have been made for defect engineering of TiO$_2$ nanoparticles, which involves a combustion method, high pressure hydrogenation of TiO$_2$, hydrogen thermal treatment, plasma treatment, high energy particle bombardment, etc. On the other hand, most of these processes have their own advantages and disadvantages; they are limited by complicated procedures, high cost and cannot be considered as environmentally benign processes.

The other important aspect of photocatalytic reaction besides extending the light absorption range of TiO$_2$ by defects (Ti$^{3+}$ and/or oxygen vacancy) is to improve the charge separation efficiency. The photosensitization of TiO$_2$ with plasmonic noble metal nanostructures, such as gold nanoparticles (AuNPs), utilizes the unique surface plasmon resonance (SPR) absorbance features of noble metal nanoparticles, which promote charge separation and enhance light absorption. Noble metal nanoparticles/TiO$_2$ nanocomposites can effectively deter the recombination of photoexcited electron–hole pairs, thereby improving the photocatalytic performance of TiO$_2$. Therefore, nanocomposites of AuNPs with TiO$_2$ containing defects (Ti$^{3+}$ and/or oxygen vacancy) are expected to show enhanced photocatalytic properties due to the synergistic effect, i.e., defects induce visible light absorption in TiO$_2$, while the addition of a noble metal helps enhance the visible light absorption because of its SPR effect and the ability to inhibit the recombination of photogenerated electron–hole pairs.

In this study, AuNPs-sensitized wide band gap TiO$_2$ (Au/P-TiO$_2$) and narrow band gap TiO$_2$ (Au/M-TiO$_2$) nanocomposite photocatalysts were synthesized using an electrochemically active biofilm (EAB). The photocatalytic activities of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites were evaluated by the degradation of methylene blue (MB), methyl orange (MO) and 2-chlorophenol (2-CP) under visible light irradiation. The degradation efficiency was also compared with the pure TiO$_2$ (P-TiO$_2$) and defect-induced narrow band gap TiO$_2$ (M-TiO$_2$) nanoparticles. The enhancement of the visible light activity of the Au/M-TiO$_2$ nanocomposite was evaluated further by the photoelectrochemical measurements, such as electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV) in the dark and under visible light irradiation.

**Experimental**

**Materials**

Titanium dioxide nanoparticles (TiO$_2$) were purchased from Degussa, and MB and 2-CP were purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate(m)hydrate (HAuCl$_4$nH$_2$O; n = 3.7) was acquired from Kojima Chemicals, Japan. Sodium sulfate (Na$_2$SO$_4$), sodium acetate (CH$_3$COONa) and MO were obtained from Dusksan Pure Chemicals Co. Ltd, South Korea. Ethyl cellulose and 2-terpineol were supplied by KANTO Chemical Co., Japan and fluorene-doped transparent conducting oxide glass (FTO; F-doped SnO$_2$ glass; 7 Ω sq$^{-1}$) was purchased from Pilkington, USA. Carbon paper (without wet proof, Fuel Cell Earth LLC, USA), and all other chemicals used in this study were of analytical grade and used as received.

**Methods**

Phase characterization was accomplished by X-ray diffraction (XRD, PANalytical, X’pert PRO-MPD, Netherland) analysis, using Cu Kα radiation ($λ = 0.15405$ nm). The optical properties of the samples (Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites) were analyzed by ultraviolet-visible-near infrared (UV-Vis-NIR, Cary 5000, VARIAN, USA) spectrophotometry. The photoluminescence (PL, Kimon, 1 K, Japan) of the samples were recorded over the scanning range, 200–800 nm, with an excitation wavelength of 325 nm. The chemical state and surface composition were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS System, Thermo Fisher Scientific U.K.) using a monochromatized Al Kα X-ray source ($hv = 1486.6$ eV). PL and XPS studies were conducted at the Korea Basic Science Institute (KBSI), South Korea. The size and distribution of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites were observed by field emission transmission electron microscopy (FE-TEM, Tecnai G2 F20, FEI, USA) with an accelerating voltage of 200 kV combined with energy dispersive spectrometry (EDS). The photoelectrochemical and photocatalytic experiments were performed using a 400 W lamp with an intensity of 31 mW cm$^{-2}$ (3 M, $λ > 400$ nm, USA). The photoelectrochemical measurements are presented schematically in Fig. S1 (ESI†). EIS was performed using a three-electrode cell with a 0.2 M Na$_2$SO$_4$ aqueous solution as the electrolyte using a potentiosstat (VersaSTAT 3, Princeton Research, USA). The DPV of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposite photoelectrodes were recorded with a pulse height of 50 mV, a pulse width of 0.005 s and a scan rate of 4 mV s$^{-1}$. The working electrodes were prepared as follows. 100 mg of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites were suspended thoroughly using a mixer after adding ethyl cellulose as a binder and 2-terpineol as a solvent for the paste. The resulting mixture was then coated on a FTO glass electrode using the doctor-blade method. The Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposite-coated (FTO) glass substrates were used as the working electrode. Ag/AgCl (3.0 M KCl) and a Pt gauge were used as the reference and counter electrodes, respectively.

**Natural development of electrochemically active biofilm in an anaerobic environment**

The EAB was developed on a plain carbon paper according to previous reports. In a typical process, a mineral salt medium containing sodium acetate (1 g L$^{-1}$) was prepared in a 250 mL glass bottle into which the carbon paper, which acted as a growing support for EAB, was dipped. Subsequently, 10 mL of...
anaerobic sludge (from a biogas plant in Paju, Korea) was added under strict anaerobic conditions by sparging N₂ gas for 5 min to create an inert atmosphere. All media, including the bacterial inoculum, were changed after two days under strict anaerobic conditions. This process was repeated over a two week period, which resulted in the formation of a uniform layer of a living EAB on the surface of the carbon paper.

**Synthesis of Au/P-TiO₂ and Au/M-TiO₂ nanocomposites**

The EAB developed on a plain carbon paper was used to synthesize the Au/P-TiO₂ or Au/M-TiO₂ nanocomposites, as shown in Fig. 1. The Au/M-TiO₂ nanocomposite involved two synthetic steps, first the modification of TiO₂ followed by the anchoring of AuNPs to the M-TiO₂ surface which is also similar to our previous reports. In short, a 4 mM dispersion of M-TiO₂ was prepared in water. 3 mM Au precursor was added to the above dispersion of M-TiO₂. Subsequently, 0.2 g of sodium acetate was added to the above mixture. The reaction mixture was stirred for 5 min to allow the proper adsorption of AuCl₄⁻ ions onto the M-TiO₂ surface, after which the EAB formed on the carbon paper was hung in the glass bottle. The EAB in this system is associated with the biological oxidation of sodium acetate, leading to the generation of excess of electrons, which assists in the reduction of Au³⁺ ions to Au⁰ on the surface of M-TiO₂. The Au/P-TiO₂ nanocomposite was also synthesized similarly using P-TiO₂ nanoparticles instead of M-TiO₂ nanoparticles (Fig. 1).

Two control experiments were also performed to determine the roles of EAB and acetate.

**Photocatalytic degradation experiments**

The photocatalytic degradation efficiency of the Au/P-TiO₂ and Au/M-TiO₂ photocatalysts under visible light irradiation was examined by the decomposition of MB, MO, and 2-CP. In a simple photocatalysis process, 2 mg of the Au/P-TiO₂ and Au/M-TiO₂ photocatalysts was dispersed in 20 mL of an aqueous solution of MB, MO (10 mg L⁻¹), and 2-CP (30 mg L⁻¹) by stirring for 10 min in the dark to achieve adsorption-desorption equilibrium. The above suspensions were irradiated with visible light to degrade MB, MO and 2-CP. After the start of the reaction, a 2 mL sample of the solution was taken every 1 h, from which the catalyst was separated by centrifugation. The absorbance of the above solution was analyzed by UV-vis spectrophotometry (Optizen 2120UV). The photocatalytic efficiency of the Au/P-TiO₂ and Au/M-TiO₂ photocatalysts was calculated from the obtained absorbance data using the method reported elsewhere.

**Photoelectrochemical studies (EIS and DPV)**

The photoelectrochemical properties of the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites were analyzed using EIS and DPV experiments in the dark and under visible light irradiation. The DPV experiment was carried out under ambient conditions in 50 mL of a 0.2 M phosphate buffer solution (pH = 7), whereas the EIS experiment was performed in 50 mL of an aqueous 0.2 M Na₂SO₄ solution at room temperature.

**Results and discussion**

**Characterization and photodegradation results of P-TiO₂ and M-TiO₂**

The formation of defects in M-TiO₂ (Ti³⁺ formation and/or oxygen vacancies) has already been justified in our previous reports. Some relevant data such as the XRD pattern, UV-visible absorption spectra, electron paramagnetic resonance (EPR) and XPS spectra are provided in the ESI for better understanding. The XRD pattern shows that the (101) peak of M-TiO₂ was shifted to a lower angle compared to that of P-TiO₂ (Fig. S2a, ESI†). The shift of the XRD peak towards a lower angle might be due to lattice expansion by the formation of Ti³⁺ ions (the ionic radius of Ti³⁺ is larger than that of Ti⁴⁺) in M-TiO₂. The band gaps of P-TiO₂ and M-TiO₂ were estimated directly from the UV-visible absorption spectra (Fig. S2b, ESI†), and found to be ~2.85 eV for M-TiO₂, which is red-shifted compared to P-TiO₂ (Eg = 3.10 eV). The observed band gap of M-TiO₂ was substantially smaller than that of P-TiO₂ and was attributed to the presence of defects in M-TiO₂. P-TiO₂ did not show any EPR signals (Fig. S2c, ESI†), whereas M-TiO₂ showed strong EPR signals with a g value of 1.98 which further proves the paramagnetic nature of Ti³⁺ in M-TiO₂. XPS results also revealed the existence of defects in M-TiO₂ (Fig. S2d, ESI†). M-TiO₂ showed significantly higher photocatalytic activity towards MB (Fig. S2e, ESI†) and MO (Fig. S2f, ESI†) degradation under visible light irradiation as compared to P-TiO₂, which was attributed to the presence of defects.

All the above characterization techniques presented here clearly show that defects existed in M-TiO₂. In this study, we used this defective TiO₂ to further synthesize the Au/M-TiO₂ nanocomposite.

**Proposed mechanism for the formation of Au/P-TiO₂ and Au/M-TiO₂ nanocomposites**

The EAB was used for the synthesis of Au/P-TiO₂ and Au/M-TiO₂ nanocomposites, which is a green, cost-effective, surfactant-free, environment-friendly, and mild-condition synthetic method. Fig. 1 presents the synthesis process of Au/P-TiO₂ or Au/M-TiO₂ nanocomposites. The EAB provides an excess of electrons and protons...
by biologically decomposing sodium acetate under anaerobic conditions. The electrons produced by the EAB are responsible for the reduction of $\text{Au}^{3+}$ ions to $\text{Au}^0$ at the surface of the TiO$_2$ nanoparticles, which leads to the formation of Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites (Fig. 1). Furthermore, anchoring of AuNPs to the surface of TiO$_2$ occurred in the absence of surfactants or any other organic ligands. Generally, surfactants or organic ligands are used in the synthesis of metal–metal oxide nanocomposites and it is difficult to completely remove them from the final products and may remain at the interface of metal–metal oxide nanocomposites which generally forms an insulating layer and therefore prevents the formation of an effective Schottky junction. The advantage of this synthesis, to fabricate the Au/M-TiO$_2$ nanocomposite without any surfactant or organic ligand, facilitates the formation of an effective Schottky junction. This is favorable for the effective charge carrier transfer through this Schottky junction during the photocatalytic process. This reaction normally occurs in water at room temperature, which indicates the feasibility of this method for the preparation of a range of nanocomposite materials.

**Structural study**

The phase and structures of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites were examined by XRD analysis (Fig. 2). The unmarked XRD patterns of TiO$_2$ in both the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites showed an identical crystal structure to that of pure TiO$_2$. The (101), (110), (101), (004), (200), (205), (211), (204) and (116) diffraction patterns correspond to the anatase and rutile phases of TiO$_2$. The XRD patterns of anatase and rutile phases of TiO$_2$ were similar to those reported in the JCPDS file No. 73-1764 and 76-318, respectively. The XRD peaks at 38.2° (111), 44.38° (200) and 64.7° 2$\theta$ (220) are characteristic of face centered cubic gold, indicating the successful formation of AuNPs. The peak of AuNPs at 38.2° 2$\theta$ overlapped with the peak of TiO$_2$, resulting in a slight increase in the peak intensity. The XRD pattern also confirmed the formation of AuNPs on the TiO$_2$ surface and the overall formation of Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites. The crystallite sizes were calculated using Scherrer’s equation and the calculated sizes for the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites were $\sim$18.76 and $\sim$19.10 nm, respectively. Further observations suggested that there were no obvious changes in the XRD patterns of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites, suggesting that the anchoring of AuNPs does not affect the crystalline properties of the TiO$_2$. These results further confirmed that the AuNPs were anchored successfully to the TiO$_2$ surface.

**Optical properties**

The light absorption properties of the metal and metal–metal oxide nanocomposites play an important role in the utilization of visible light for a range of applications. The absorption spectra of P-TiO$_2$ and M-TiO$_2$ show the absorption spectra of P-TiO$_2$ and M-TiO$_2$. The absorption spectra reveal M-TiO$_2$ to have significantly higher absorption in the visible light region. The band gap of P-TiO$_2$ and M-TiO$_2$ was estimated directly from the absorption spectra, and found to be $\sim$2.85 eV for M-TiO$_2$, which was red-shifted compared to P-TiO$_2$ ($E_g = 3.10$ eV). The observed band gap of M-TiO$_2$ was substantially smaller than that of P-TiO$_2$ and was attributed to the presence of defects in M-TiO$_2$. The optical properties of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites were examined by UV-visible diffuse absorption/reflectance spectroscopy. Fig. 3a and Fig. S3 (ESI†) show the absorption and reflectance spectra of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites. The absorption spectra of both Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites are dominated mainly by the broad absorption in the range 500–600 nm, which was attributed to the SPR effect of AuNPs deposited on the TiO$_2$ surface. PL spectroscopy has been used widely to investigate the charge separation/recombination of photoinduced charge carriers (electron–hole pairs) in the materials. In addition, the PL emission intensity is related directly to the recombination rate of the photoinduced electron–hole pairs, i.e., the lower the PL emission intensity, the lower the recombination rate of photoinduced electron–hole pairs, hence an increase in the photocatalytic

![Fig. 2](image1.png)  
**Fig. 2** XRD patterns of the Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites. The peaks marked with (*) were assigned to AuNPs.

![Fig. 3](image2.png)  
**Fig. 3** (a) UV-vis diffuse absorption spectra and (b) PL spectra of Au/P-TiO$_2$ and Au/M-TiO$_2$ nanocomposites.
activity of the materials.\textsuperscript{15,23,32} Fig. 3b presents the PL emission spectra of the Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites. The Au/M-TiO\textsubscript{2} nanocomposite showed weaker emission intensity compared to the Au/P-TiO\textsubscript{2} nanocomposite, which is related to the lower recombination rate of the photoinduced charge carriers in the Au/M-TiO\textsubscript{2} nanocomposite. This might be due to the presence of AuNPs and defects in M-TiO\textsubscript{2}, which quenches the PL emission of the Au/M-TiO\textsubscript{2} nanocomposite. This favors its high photocatalytic activity by prolonging the electron–hole pair lifetime.\textsuperscript{32,33}

In addition, the PL emission spectrum of the Au/M-TiO\textsubscript{2} nanocomposite shows a small blue shift compared to the Au/P-TiO\textsubscript{2} nanocomposite, which is similar to a previous report.\textsuperscript{34} This shift was attributed to the anchoring of AuNPs to the M-TiO\textsubscript{2} surface and the interfacial interaction of AuNPs with M-TiO\textsubscript{2}.\textsuperscript{34}

Morphological and compositional studies

Fig. 4a and b presents TEM images of the as-prepared Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites, which clearly shows the well dispersed AuNPs over the surface of the TiO\textsubscript{2} nanoparticle. The HRTEM image of the Au/P-TiO\textsubscript{2} (Fig. 4a’) and Au/M-TiO\textsubscript{2} (Fig. 4b’) nanocomposites revealed AuNP sizes of \textasciitilde6–11 nm. In addition, the lattice fringe spacing of \textasciitilde0.23 and \textasciitilde0.35 nm, corresponds to the (111) plane of AuNPs and the (101) plane of TiO\textsubscript{2}.\textsuperscript{15,23} The SAED pattern shown in Fig. S4 and S5 (ESI\textsuperscript{†}) shows that the nanocomposites (Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2}) are crystalline in nature. Fig. S6 and S7 (ESI\textsuperscript{†}) present the HAADF–STEM images of the Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites. EDS spectra (Fig. S8 and S9, ESI\textsuperscript{†}) show all the elemental compositions of the Au/M-TiO\textsubscript{2} nanocomposites corresponding to Ti, O and Au. TEM analysis further confirms the existence of AuNPs on the TiO\textsubscript{2} surface and the interfacial interaction between the AuNPs and TiO\textsubscript{2}.

The surface composition and chemical state of the Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites were investigated by XPS. Fig. 5a shows the fully scanned spectra (survey) of the Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites, which confirm the presence of Ti, O, C, and Au. The C1s photoelectron peak (Fig. S10, ESI\textsuperscript{†}) in Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites was almost similar which indicates that no additional carbon was added via the EAB support during the synthesis process. This also suggests that the EAB was strongly adhered to the support and the biofilm was highly stable.\textsuperscript{28}

The Au 4f high resolution spectra of the Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites also confirmed the presence of AuNPs (Fig. 5b and c). The binding energies (BE) of the two individual peaks located at 83.32 \textpm 0.02 and 86.82 \textpm 0.02 eV for the Au/P-TiO\textsubscript{2} nanocomposite and at 82.76 \textpm 0.02 and 86.31 \textpm 0.02 eV for the Au/M-TiO\textsubscript{2} nanocomposite were assigned to Au 4f\textsubscript{7/2} and Au 4f\textsubscript{5/2} of the AuNPs, respectively. These doublet peaks suggested the presence of metallic Au in the Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites.\textsuperscript{35} In addition, the BE of Au 4f\textsubscript{7/2} and Au 4f\textsubscript{5/2} in Au/P-TiO\textsubscript{2} and Au/M-TiO\textsubscript{2} nanocomposites shifted to a lower value compared to pure metallic Au (BE of metallic Au is \textasciitilde84.0 eV for Au 4f\textsubscript{7/2} and \textasciitilde87.7 eV for Au 4f\textsubscript{5/2}), which also supports the interfacial interactions between the AuNPs and TiO\textsubscript{2} nanoparticles.\textsuperscript{35,36} Moreover, the BE of Au 4f in the Au/M-TiO\textsubscript{2} nanocomposite shifted to a lower value compared to the Au/P-TiO\textsubscript{2} nanocomposite. This lower shift of the BE in the case of the Au/M-TiO\textsubscript{2} nanocomposite was assigned to the strong interfacial interaction between AuNPs and defective sites on the surface of M-TiO\textsubscript{2}.\textsuperscript{36}

Visible light driven photocatalytic degradation of MB, MO and 2-CP

The effects of the SPR phenomenon of AuNPs on the visible light activity of P-TiO\textsubscript{2} and M-TiO\textsubscript{2} were studied systematically.
by photocatalytic and photoelectrochemical experiments. Generally, a dye degradation experiment is used widely as a model reaction to evaluate the photocatalytic activities of various photocatalysts.\(^1\),\(^7\),\(^9\)–\(^11\) The photocatalytic activities of Au/P-TiO\(_2\) and Au/M-TiO\(_2\) nanocomposites were evaluated by the degradation of colored dyes (MB and MO) and a non-colored organic compound 2-CP under visible light irradiation. Fig 6a and b presents the degradation kinetics plot of MB and MO, and Fig. S11a and b (ESI\(^{†}\)) shows the \(\ln(C/C_0)\) vs. time plot of the MB and MO degradation as a function of the irradiation time.\(^6\),\(^5\) The change in the concentration of MB and MO as a function of the irradiation time.\(^9\),\(^15\) The rate constants of the Au/P-TiO\(_2\) and Au/M-TiO\(_2\) nanocomposites exhibited pseudo-first-order kinetics according to the equation reported elsewhere.\(^25\) The rate constants \((k)\) of the Au/P-TiO\(_2\) and Au/M-TiO\(_2\) nanocomposites for the degradation of MB were 0.2577 h\(^{-1}\) \((R^2 = 0.9884)\) and 0.4669 h\(^{-1}\) \((R^2 = 0.9872)\), respectively. Similarly, the rate constants of the Au@P-TiO\(_2\) and Au@M-TiO\(_2\) nanocomposites for the degradation of MO were 0.06934 h\(^{-1}\) \((R^2 = 0.9964)\) and 0.1631 h\(^{-1}\) \((R^2 = 0.9884)\), respectively. The \(k\) value for the photocatalytic degradation of MB and MO by the Au/M-TiO\(_2\) nanocomposite was \(\sim 2\) and \(2.4\) times higher than that of the Au/P-TiO\(_2\) nanocomposite. As shown in Fig. S11a and b (ESI\(^{†}\)) the Au/M-TiO\(_2\) nanocomposite exhibited much higher photocatalytic activity than the P-TiO\(_2\) and M-TiO\(_2\) nanoparticles and the Au/P-TiO\(_2\) nanocomposite under visible light irradiation.\(^15\) The photocatalytic activity of P-TiO\(_2\) and M-TiO\(_2\) has been reported previously, in which after 6 and 8 h of visible light irradiation, the degradation efficiencies of MB and MO dyes after 6 and 8 h of visible light irradiation, respectively, whereas Au/P-TiO\(_2\) showed only \(\sim 80\)% and \(\sim 44\)% degradation efficiencies for MB and MO after 6 and 8 h of visible light irradiation, respectively.

The photocatalytic degradation of non-colored 2-CP, which did not absorb the light in the visible region, was also performed under visible light irradiation (Fig. S11c, ESI\(^{†}\)). Under visible light irradiation, the Au/M-TiO\(_2\) nanocomposite exhibited excellent photocatalytic degradation ability for the degradation of 2-CP compared to the P-TiO\(_2\) and M-TiO\(_2\) nanoparticles and the Au/P-TiO\(_2\) nanocomposite because of the characteristic SPR absorption of AuNPs and the narrowed band gap of M-TiO\(_2\). Fig. 6c shows the photocatalytic degradation kinetic plot of 2-CP. The \(k\) value of the Au/P-TiO\(_2\) and Au/M-TiO\(_2\) nanocomposites for the degradation of 2-CP was 0.07385 h\(^{-1}\) \((R^2 = 0.9920)\) and 0.1026 h\(^{-1}\) \((R^2 = 0.9870)\), respectively. The \(k\) value of the photocatalytic degradation of 2-CP by the Au/M-TiO\(_2\) nanocomposite was \(\sim 1.4\) times higher than that of the Au/P-TiO\(_2\) nanocomposite. In addition, photodegradation efficiency obtained in this case was also much higher than that previously reported for metal oxides (TiO\(_2\), ZnO and CeO\(_2\)), suggesting the suitability of the Au/M-TiO\(_2\) nanocomposite for environmental remediation processes.\(^5\),\(^9\),\(^10\),\(^12\),\(^13\)

The stability of the Au/P-TiO\(_2\) and Au/M-TiO\(_2\) nanocomposites without the leaching of AuNPs is an important concern, which further determines the usability of the catalyst for a range of reaction conditions. Stability tests were conducted by sonicating the Au/P-TiO\(_2\) and Au/M-TiO\(_2\) photocatalysts in water for one hour. The centrifuged solution was analyzed for any leached AuNPs using an UV-visible spectrophotometer. The absorption spectra of the centrifuged solution of Au/P-TiO\(_2\) and Au/M-TiO\(_2\) (Fig. S12 and S13, ESI\(^{†}\)) showed no absorbance peak in the range 500–600 nm, corresponding to the AuNPs. This confirms that the AuNPs are strongly anchored to the TiO\(_2\) surface and are stable. This analysis confirms the stability of the as-prepared Au/P-TiO\(_2\) and Au/M-TiO\(_2\) nanocomposites.

**Proposed mechanism for the photocatalytic degradation of MB, MO and 2-CP under visible light irradiation**

Fig. 7 presents the possible photoexcitation and electron transfer mechanism of the photocatalytic activities of Au/P-TiO\(_2\) and Au/M-TiO\(_2\) nanocomposites under visible light irradiation. In the case of Au/P-TiO\(_2\) (Fig. 7a), the generation of electrons in the conduction bands and holes in the valence bands under visible light is not a feasible process because of the wide band gap of P-TiO\(_2\) (Fig. 7a).\(^13\) In contrast, Au/P-TiO\(_2\) exhibited little photocatalytic activity due to photon absorption by the SPR effect of AuNPs under visible light irradiation.\(^11\),\(^12\),\(^22\)

On the other hand, in the case of Au/M-TiO\(_2\) (Fig. 7b), M-TiO\(_2\) has a narrower band gap, which results in greater visible light absorption, and photon absorption also occurs due to the SPR phenomenon of AuNPs.\(^22\),\(^24\) The combined effect of these two
processes results in much higher visible light absorption, hence an increase in photocatalytic activity. When Au/M-TiO₂ is irradiated with visible light, the electrons in M-TiO₂ migrate from the valence band to the conduction band, as evident from Fig. 7b,14,15,17,19 and the AuNPs are photoexcited by the SPR phenomenon, leading to the generation of electrons and holes.24,35 The photoexcited electrons are injected into the conduction band of the M-TiO₂ nanoparticles leaving behind holes in the AuNPs.35 The excess of photogenerated electrons on the surface of the Au/M-TiO₂ nanocomposite due to the above-mentioned process is then scavenged by surface adsorbed oxygen to yield highly oxidative species, such as *O₂⁻ and HO²⁺ radicals.6,8,9 The positive holes in the AuNPs and M-TiO₂ are trapped by OH⁻ species to yield reactive HO²⁺ radicals. These reactive radicals are responsible for the degradation and mineralization of MB, MO and 2-CP.5,8,10,36 Therefore, due to the synergistic effect of the narrow band gap of M-TiO₂ and the SPR phenomenon of AuNPs, a large number of photogenerated electrons and holes are produced and separated, which participate in the photodegradation process leading to an increase in photocatalytic activity.

**Photoelectrochemical studies**

The charge transfer resistance and separation efficiency of the photogenerated charge carriers across the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites photoelectrodes were examined by EIS.9,15 Generally, the semicircular arc in the EIS spectra is an expression of the magnitude of the charge transfer resistance at the photoelectrode/electrolyte interface.23,35 In other words, the smaller the arc radius, the smaller the charge transfer resistance and the higher the charge separation efficiency, which leads to higher photocactivity of the photoelectrodes.22,35 Fig. 8a and b presents the EIS spectra of the P-TiO₂ and M-TiO₂ nanoparticles and the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites photoelectrodes in the dark and under visible light irradiation. As shown in the figure, the Au/M-TiO₂ nanocomposite photoelectrode has a much smaller arc radius than the Au/P-TiO₂ nanocomposite, P-TiO₂ and M-TiO₂ nanoparticles. These results suggest that the Au/M-TiO₂ nanocomposite has a lower resistance to interfacial charge transfer. Therefore, the effective separation of photogenerated electron–hole pairs occurs under visible light irradiation.23,37 Overall, the significant enhancement in the photoelectrochemical performance of the Au/M-TiO₂ nanocomposite is due to the synergistic effects of AuNPs and the defect-induced narrow band gap of M-TiO₂. These results are in accordance with the photodegradation results of the Au/M-TiO₂ nanocomposite.

In addition to the photodecomposition process, the charge carriers accumulated on the surface of the photocatalyst are also responsible for inducing charging behavior in the materials.37,38 Therefore, in this case, the charging behavior of the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites was analyzed further by DPV.35 Fig. 8c and d presents the DPV responses of the P-TiO₂ and M-TiO₂ nanoparticles and the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites under visible light irradiation. Au/P-TiO₂ and Au/M-TiO₂ nanocomposites showed well-defined quantized capacitance charging peaks in the dark and under visible light irradiation at ~0.43 V. In addition, the Au/M-TiO₂ nanocomposite under visible light irradiation also exhibited enhanced and excellent charge storage properties compared to P-TiO₂, M-TiO₂ and Au/P-TiO₂. This enhanced performance of Au/M-TiO₂ might be due to the synergistic effects of AuNPs and the defect-induced narrow band gap of M-TiO₂.

**Conclusions**

AuNPs-sensitized wide band gap TiO₂ (Au/P-TiO₂) and narrow band gap TiO₂ (Au/M-TiO₂) were prepared using an electrochemically active biofilm. The photosensitization property of the Au nanoparticles enhanced the absorption of TiO₂ over the broad visible region by acting as light harvesters. As a result, the Au/P-TiO₂ and Au/M-TiO₂ nanocomposites promoted the photocatalytic degradation efficiency of methylene blue, methyl orange and 2-chlorophenol under visible light irradiation. In addition, the Au/M-TiO₂ nanocomposite showed much higher photodegradation ability than the P-TiO₂ and M-TiO₂ nanoparticles and the Au/P-TiO₂ nanocomposite. Furthermore, the electrochemical impedance spectra and differential pulse voltammetry response of the Au/M-TiO₂ nanocomposite under visible light irradiation showed enhanced performance compared to the P-TiO₂ and M-TiO₂ nanoparticles and the Au/P-TiO₂ nanocomposite. These enhanced photocatalytic degradation efficiencies and photoelectrochemical performance were attributed mainly to the surface plasmon resonance effect of the Au nanoparticles excited by visible light irradiation. In addition, the presence of a defect-induced narrowed band gap M-TiO₂ in the Au/M-TiO₂ nanocomposite contributes to higher photocatalytic activities. Owing to the ease of preparation of these materials by a simple, novel and green route as well as high photocatalytic activities, the Au/M-TiO₂ nanocomposite can be applied to a wide range of processes that may lead to its commercialization.
Acknowledgements
This study was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2014R1A6A1031189).

Notes and references