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Short communication

Comparative study of metal nanoparticles anchored TiO₂ using polyoxometalate intermediate in photodegradation of azo dye pollutant in aquatic environments

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ABSTRACT

Herein, metal nanoparticles (Au, Ag, and Pt) are locally deposited on TiO₂ with an UV-switchable polyoxometalate intermediate to achieve highly active photocatalyst nanohybrids. The successful preparation of these nanohybrids was confirmed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), Zeta potential (ZP), and UV–visible spectroscopy. TEM images showed the anchoring of metal nanoparticles of an average size of 20 nm on the TiO₂ surface. A comparative study revealed that the bandgap energy was reduced in the order of Pt@PW-TiO₂ (2.90 eV) > Ag@PW-TiO₂ (2.95 eV) > Au@PW-TiO₂ (3.05 eV). Likewise, the photocatalytic efficiency of fabricated nanohybrids was investigated in the degradation of reactive blue 19 (RB19), an azo dye model, under UV–visible light illumination and different experimental conditions. Optimal photodegradation occurred at pH = 3.8 with 0.33 gL⁻¹ of photocatalyst exposed to light for 60 min. Under optimal conditions, the maximum and minimum photodegradation abilities were observed using Pt and Au deposited hybrids. A kinetic study of RB19 photodegradation was also conducted, resulting in pseudo-first order reaction rate constants of 0.0203, 0.025, and 0.0808 min⁻¹, respectively, for the Au@PW-TiO₂, Ag@PW-TiO₂, and Pt@PW-TiO₂ nanohybrids. Finally, the most probable mechanism for RB19 degradation using prepared photocatalysts is presented.

1. Introduction

In these years, TiO_2 and its composites have gained significant attention in wide range of applications due to their economical price, easy access, nontoxic characteristics, small crystal size, and highly porous structure [1–3]. TiO_2 is known for its photo-generated charge carriers, which make it a highly promising candidate for photocatalytic applications. However, the most prominent drawback associated with Titania is its inherent large bandgap (Eg: ~3.0–3.2 eV) which results in a low quantum yield and hence the majority of studies are performed on its reduction [4]. One of the effective ways to overcome the large bandgap restriction of TiO_2 is deposition of noble metal nanoparticles (NPs) on its surface. Deposition of metal NPs can effectively capture electrons that are necessary for the interfacial charge transfer processes. Numerous valuable attempts have been made to optimise the photocatalytic efficacy of TiO_2 -based materials by adding different transition metals [5–7]. For example, Khaki and colleagues fabricated copper NPs doped TiO_2/ZnO nanocomposite using the sol-gel method [8], which showed high efficiency in photodegradation of methyl orange and methylene blue dye models.

The surface of TiO_2 has been decorated with metal nanoparticles using various deposition techniques, such as self-assembling monolayers and liquid phases [5,9–11]. Most of these methods required severe reaction conditions, such as high temperatures and pressures. These techniques also often result in free metal nanoparticles forming in the solution as undesired products. Recently, polyoxometallates (POMs)

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Table 1

Physicochemical properties of RB19.



were effectively utilized as green reducing agents and stabilizers in the local deposition of metal NPs on TiO₂ [12,13] and metal-organic frameworks [14]. POMs are inorganic metal-oxide clusters with outstanding inherent properties, such as high thermal/chemical stability and high catalytic activity properties [15,16]. They can participate in multielectron redox reactions without evident structural changes [17]. They have been used in the green synthesis of different metal NPs as mild reductants and stabilisers [13]. Hence, they were used for the locally-formation and interlinking of gold NPs on the surface of TiO₂. It was shown that different types of POM can efficiently reduce metal ions to corresponding NPs on TiO₂ surfaces. In addition to enhancing the electron charge transfer between TiO₂ and gold NPs, the synergic photocatalytic performance of TiO₂ and POM also resulted in greatly improved Titania's photocatalytic behavior [13]. For example, the results revealed the photocatalytic performance of Au/POM/TiO2 nanotubes was enhanced 4.1-fold in nitrobenzene degradation, compared to pristine TiO₂ nanotubes [18].

Despite these studies, a clear understanding of the role and privilege of different metal nanoparticles in POM supported TiO_2 remains unclear. This study aims to compare the photocatalytic performance of TiO_2 deposited with different noble metal nanoparticles (Au, Ag, and Pt) with a POM intermediate. In this regard, phosphotungstic acid (PW), as a kind of POM, acts as a locally reducing agent and a bridge between TiO_2 and metal nanoparticles (MNPs). As a result of the locally reduced metal, nanohybrid solutions are formed without free metal nanoparticles. The photocatalytic efficiency of fabricated nanohybrids was investigated and compared in the photodegradation of Reactive Blue 19 (RB19), as a dye model, under UV–visible light irradiation. The effect of different parameters, including pH, dosage, and photodegradation time was also studied. Kinetic studies were conducted to explore the dynamic photodegradation rate of RB19 dye.

2. Experimental

2.1. Materials

Anatase titanium dioxide (TiO₂, 99.8 %) and gold (III) chloride trihydrate (HAuCl₄H₂O, 99.9 %) were purchased from Sigma-Aldrich. All the other substances including phosphotungstic acid hydrate (H₃[P (W₃O10)₄]. xH₂O, 99.995 %), 2-propanol (C₃H₈O, 99.8 %), silver nitrate (AgNO₃, extra pure), hexachloroplatinic (IV) acid hexahydrate (H₂(PtCl₆)6H₂O, 40 %), hydrochloric acid (HCl, 37 %) and sodium hydroxide (NaOH, 97.0 %) were obtained from Merck Company. As received, the chemical materials were consumed without further treatment. Moreover, Remazol Brilliant Blue R (C₂₂H₁₆N₂Na₂O₁₁S₃, Reactive blue 19, RB19) was bought from Sigma-Aldrich (Dye content 50 %). The molecular structure and physicochemical properties of RB19 are presented in Table 1. All the solutions was prepared using deionized water.

2.2. Synthesis of M NPs anchored PW modified TiO_2 (M/PW-TiO₂) nanohybrid

Metal nanoparticles deposited on PW modified TiO₂ was synthesized in accordance with the earlier study [13]. In the first step, 500 mg of TiO₂ was dispersed in PW aqueous solution (250 mL, 1 mM) and stirred overnight to modify TiO₂ with PW. After washing with deionized water, the solid material (called PW-TiO₂) was separated and dried at 60 °C. Then, 100 mg of PW-TiO₂ was dispersed in 25 mL distilled water using



Scheme 1. Schematic of the synthesis of M@PW-TiO2 nanohybrids.



Fig. 1. XRD patterns of (a) Au@PW-TiO₂, (b) Pt@PW-TiO₂, and (c) Ag@PW-TiO₂.

an ultrasonic bath (SW 3H, Swiss) for 20 min at room temperature. Afterward, 10 mL of 2-propanol was added to the solution, as a sacrificial agent, followed by the addition of 50 mL of H(AuCl₄).3H₂O, AgNO₃, or H₂(PtCl₆).6H₂O (1 mM). The mixture was irradiated with UV light (15 W, $\lambda = 253$) for 60 min, while the distance between the quartz reactor cell and the irradiation source was around 10 cm [19]. Our observations indicated that the UV-vis peaks of metal ions faded after 45-60 min, indicating that the reaction had been completed and colorchanging was evident in the solutions from milky to light-purple, lightgray, and dark-gray for Au@PW-TiO₂, Pt@PW-TiO₂, and Ag@PW-TiO₂, respectively. The color changes are associated with the surface plasmon resonance, which is the resonant oscillation of conduction electrons in metal nanoparticles in response to incident light. The frequency of the oscillation depends on the size, shape, and composition of the nanoparticles. The resulting nanohybrids were separated, washed with mili-Q water, and dried at 70 °C for 6 h (see Scheme 1).

2.3. Instruments

All three types of nanocomposites were characterized via X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and UV-visible spectroscopy (UV-vis). For the TEM analysis, nanocomposite samples were made by drop coating the solutions onto a carbon-coated copper grid, using a LEO 912 AB (Zeiss, Germany) instrument. The X-ray diffraction patterns were obtained by a D8-Advance (Bruker, UK) diffractometer at room temperature using Cu K α radiation ($\lambda = 0.15406$ nm) in a wide range of scanning angle ($2\theta =$ 5-80°). Moreover, the FTIR spectra of the nanocomposite powders were measured by KBr pellet method using Thermo Nicolet Avatar-370 spectrometer (Nexus, USA) in the range of 400-3900 cm-1. EDX analysis was performed using a LEO 1450 VP (Zeiss, Germany) instrument. The concentration of RB19 dye was measured by the UV-vis diffusive reflectance spectra (Analyticjena-SPEKOL 1300, Germany) using a V-670 (JASCO, Japan) spectrophotometer.

2.4. Evaluation of photocatalytic activity

Photoactivity of as-prepared nanomaterials was studied in RB19 degradation under simulated sunlight. In order to control the solution temperature, a double-wall beaker jacket was used. In a typical procedure, a certain amount of M@PW-TiO₂ nanohybrid (2, 5, and 10 mg) was added to RB19 aqueous solution (30 mL, 20 mgL⁻¹, pH = 6.7±0.5) and stirred for 15 min in a dark place to equilibrate. The solution was then irradiated under a Xe arc lamp (100 W), as a solar light source. The samples were collected every 10–15 min, immediately filtered and the dye concentration was measured using UV–vis spectrophotometry at λ = 600 nm. According to the following equation, photodegradation efficiency was measured:

$$\text{Efficiency}\left(\%\right) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 is RhB initial concentration (mg/L) and C_t is RhB concentration at t time (mg/L).

In order to study pH effects, experiments were also conducted at acidic pH of 3.8 ± 0.5 , neutral, and basic pH of 9 ± 0.5 , which was adjusted using HCI and NaOH solutions (0.1 M). All experiments were conducted twice and the average values are reported.

3. Results and discussions

3.1. Characterization of M@PW-TiO₂ nanohybrids

The one-pot synthesis of M@PW-TiO₂ was carried out under UV light irradiation. In this process, 2-propanol acts as a sacrificial agent and reduces doped $PW_{12}O_{40}^{-0}$ on the surface of titania reduced to $PW_{12}O_{40}^{+0}$ under UV-light illumination, as shown in Eq. (2). Simultaneously, it acts as a reducing agent for metal ions (AuCl⁴⁻, PtCl₆²⁻, and Ag⁺) on the surface of TiO₂, resulting in locally formed MNPs on the surface (see Eqs. (3) to (5). Unlike some studies [19–21], these steps were conducted in a one-pot process, saving time and energy.

$$PW_{12}O_{40}^{3-} + (CH_3)_2CH_2OH \xrightarrow{hv} PW_{12}O_{40}^{4-} + (CH_3)_2CHO$$
(2)

$$3PW_{12}O_{40}^{4-} + AuCl_4^{-} \rightarrow 3PW_{12}O_{40}^{3-} + Au^0 + 4Cl^{-}$$
(3)

$$4PW_{12}O_{40}^{4-} + PtCl_6^{2-} \rightarrow 4PW_{12}O_{40}^{3-} + Pt^0 + 6Cl^-$$
(4)

$$PW_{12}O_{40}^{4-} + Ag^+ \to PW_{12}O_{40}^{3-} + Ag^0$$
(5)

Fig. 1 shows the XRD patterns of the M@PW-TiO₂ nanohybrids, demonstrating their successful formation. They show that there is a large



Fig. 2. TEM micrographs of three different metal decorated nanocomposites including (a) Au@PW-TiO₂, (b) Pt@PW-TiO₂, and (c) Ag@PW-TiO₂.



Fig. 3. EDX spectra of (a) Au@PW-TiO₂, (b) Pt@PW-TiO₂, and (c) Ag@PW-TiO₂.

proportion of anatase TiO₂ in these compounds, as well as a smaller fraction in rutile. As a result of careful observation, two peaks are clearly evident at $2\theta = 44.3^{\circ}$ and 64.5° in (pattern a), which can be attributed to the (200) and (220) planes of polycrystalline gold, respectively (JCPDS 03-065-2870). In pattern b, peaks are observed at 44.3° , 64.4° , and 77.5°, corresponding to the (111), (200), and (220) crystallographic planes of Ag nanoaprticles, respectively. In the case of Pt@PW-TiO₂ nanoparticles, the peaks at 46° , 67.8° , and 81.2° are corresponding to the (200), (220), and (311) crystallographic planes, respectively. Due to the identical lattice of metallic silver and gold, the XRD pattern of Ag@PW-TiO₂ (pattern c) is almost the same as that of Au@PW-TiO₂. However, the most significant diffraction peaks assigned to the (111) planes of Ag, Pt, and Au are expected to be observed in the range of $38 < 2\theta < 39$ [19,22], but, due to the significant characteristic peaks of Titania at these angles, they cannot be distinguished.

Fig. 2 clearly displays TEM images of MNPs anchored to TiO_2 . It shows quasi-spherical and hexagonal TiO_2 nanoparticles, decorated with Au, Pt, and Ag nanoparticles (dark spots) in a relative size of 20 nm. There is a higher contrast in TEM images of MNPs than in TiO_2 because

gold, platinum, and silver are heavier than TiO₂. A higher contrast of metal nanoparticles may be attributed to differences in the electron scattering behavior of these materials in comparison to TiO₂. Furthermore, TEM images showed that free metal nanoparticles were not formed on titania, which suggests that PW acts as a localized reducing agent.

The elemental analysis was carried out using EDX spectra, as shown in Fig. 3. It has been observed that the metal loadings of the nanohybrids are 4.10 %w/w, 6.16 %w/w, and 5.17 %w/w for Au, Pt, and Ag NPs, respectively. However, the FTIR analysis clearly confirmed the presence of PW on TiO₂ surface, no sharp characteristic energy peaks appeared for PW, which is probably due to the small amount of PW on the TiO₂ surface, or interference from diverse peaks with almost the same energy values after deposition of metal nanoparticles.

The bandgap energy is a key parameter indicating the photocatalytic activity of a nanocompound. It can be measured using the Tauc equation, as expressed in Eq. (6) [23]:

$$(\alpha hv) = B(hv - E_g)^{\frac{1}{2}}$$
(6)



Fig. 4. Calculation of bandgap energy for the fabricated samples.

where α , h, ν , B, and E_g are the adsorption coefficient, Planck constant, frequency of light, a constant, and bandgap energy, respectively. The value of n is determined by the characteristics of the optical transition of the nanocomposite and its value is 1 and 4 for direct and indirect transitions, respectively [24,25]. For TiO₂, n = 4 for indirect transitions.

The indirect bandgap energy for the three M@PW-TiO₂ nanohybrids can be calculated by plotting $(\alpha h\nu)^{1/2}$ versus photon energy, as illustrated in Fig. 4. While the bandgap energy of TiO₂ is 3.20 eV [13,26,27], it was calculated as 3.05 eV for Au@PW-TiO₂, 2.90 eV for Pt@PW-TiO₂, and 2.95 eV for Ag@PW-TiO₂. It indicates the lowest bandgap energy for Pt NPs anchored to TiO₂, confirming the additional electron-hole pairs on the Pt@PW-TiO₂ surface. Additionally, it can result in higher photocatalytic activity of the Pt@PW-TiO₂ nanohybrid under simulated sunlight irradiation for RB19 dye degradation.

3.2. Photocatalyst study

The photocatalytic performances of M@PW-TiO₂ were studied in the degradation of RB19 under different conditions. Photocatalyst activity is significantly influenced by the pH of the initial solution [27–29]. On the other hand, the net surface charge of photocatalytic materials depends on their isoelectric point (IEP) and chemical composition [16]. IEP refers to the pH value at which the molecule carries no electrical charge [30]. According to zeta potential studies, as a commonly used parameter to determine the surface charge of nanostructure, M@PW-TiO₂ has an IEP of about 3.8, so the surface charge is different by pH value. Consequently, M@PW-TiO₂ is protonated and positively charged at lower pH values, and negatively charged at higher ones [27,31]. Its effect on RB19 photodegradation in the presence of M@PW-TiO₂ was studied using different values of initial pH (3.8 ± 0.5 , 6.7 ± 0.5 , and 9 ± 0.5). From the results, indicated in Fig. 5a – c, the significant impact of this parameter on the process can be concluded. As seen, the highest RB19



Fig. 5. Effect of pH on RB19 photodegradation in the presence of (a) Au@PW-TiO₂, (b) Pt@PW-TiO₂, and (c) Ag@PW-TiO₂ nanohybrids.

Table 2

Effect of different dosages of (a) Au@PW-TiO₂, (b) Pt@PW-TiO₂, and (c) Ag@PW-TiO₂ on photodegradation of RB19 after 120 min (pH 3.8, room temperature).

Sample	Photodegradation efficiency (%)		
	2 mg	5 mg	10 mg
Au@PW-TiO ₂ Pt@PW-TiO ₂	14.9 59.8	20.6 67.7	94.1 99.9
Ag@PW-TiO ₂	30.6	59.7	97.0

photodegradation efficiency using M@PW-TiO₂ was occurred at acidic media (i.e 3.8 ± 0.5) under simulated sunlight irradiation. At 120 min, the maximum photodegradation efficiencies were obtained 92.63 %, 99.99 %, and 96.52 %, in the presence of Au@PW-TiO₂, Pt@PW-TiO₂, and Ag@PW-TiO₂ respectively. This result can be attributed to the electrostatic attraction between RB19 molecules and M@PW-TiO₂ surfaces at lower pH values [26,27]. On the other hand, the basic dye medium contains lots of hydroxyl free radicals, which were produced from the photooxidation of OH⁻ by photoexcited holes on the surface of M@PW-TiO₂. As a result of the alkaline condition, the photo-excited holes are reduced and deactivated. Thus, increasing hydroxyl radical

Adsorption in

dark condition

production can reduce RB19 photocatalytic degradation efficiency. Furthermore, dispersive forces can reduce dye photodegradation efficiency due to the negative charge on M@PW-TiO₂ surfaces in alkaline media. These findings are consistent with results from literature demonstrating that the discoloration of RB19 is higher in acidic media [32]. Therefore, 3.8 was chosen as the optimum pH condition for further experiments.

The effect of M@PW-TiO₂ dosage (2, 5, and 10 mg) was also studied on RB19 photodegradation and the results are summarized in Table 2. It shows that the photodegradation efficiency was improved with an increasing amount of nanohybrids. This may occur because of a higher number of active sites, which increased the rate of reaction and efficiency. Due to the increased amount of nanohybrid, there are additional active sites that can be accessed, increasing the efficiency. The active sites in a photocatalyst play a crucial role in initiating and facilitating photocatalytic reactions. The nature of active sites in metal nanoparticles doped on PW-TiO₂ can be attributed to surface defects and catalytic site on metal nanoparticles, TiO₂, and metal-support interactions. By increasing the number of available active site, besides the greater overall surface area available for interaction with light, the probability of incident photons will be absorbed by the nanohybrids. It



Fig. 6. Visualization of RB19 concentrations in photodegradation using (a) Au@PW-TiO₂, (b) Pt@PW-TiO₂, and (c) Ag@PW-TiO₂. (Down) comparison chart of photodegradation efficiency using nanohybrids at different times and optimum conditions.

Time (min)



Fig. 7. Fitting the experimental data with first-order kinetic model in the presence of nanohybrides.

can resulted in enhancing the light adsorption capacity. Therefore, electron-hole pair production can be facilitated at higher amount of photocatalyst, resulting to improve the photocatalytic degradation efficiency. The results also revealed that RB19 photodegradation in the presence of $Pt@PW-TiO_2$ was significantly higher than that of other nanohybrids at all photocatalyst dosages.

beyond this point. As a result, the optimal reaction time utilizing $Pt@PW-TiO_2$ was considered to be 60 min, where they showed an increasing trend with two other nanohybrids until 120 min. Kinetic studies have been conducted to determine the photodegradation rate using a pseudo-first order model, as shown in the following equation:

$$Ln\frac{C}{C_0} = -K_1 t \tag{7}$$

3.3. Kinetic study

Photodegradation of RB19 in the presence of M@PW-TiO₂ was monitored over the 120 min irradiation time, while the pH and nanohybrid dosage were kept fixed. The results are illustrated in Fig. 6. As seen, the photodegradation efficiency increased until 60 min after the introduction of Pt@PW-TiO₂, but no significant changes were observed where K₁, t, C₀, and C are first-order rate constant (min⁻¹), irradiation time (min), initial dye concentration, and dye concentration given time, respectively. Fig. 7 depicts the linear relationship between $\text{Ln}\frac{\text{C}}{\text{C}_0}$ and irradiation time. The apparent rate constants were calculated from the slopes as 0.0203 min⁻¹, 0.0802 min⁻¹, and 0.0250 min⁻¹ for Au@PW-TiO₂, Pt@PW-TiO₂, and Ag@PW-TiO₂, respectively. These results also



Scheme 2. Plausible mechanism of RB19 photocatalytic degradation in the presence of M@PW-TiO₂ nanhybrids.

show that the highest rate constant was obtained using $Pt@PW-TiO_2$, demonstrates its highest photocatalytic activity in RB19 degradation, compared to other hybrid nanomaterials. These findings are in agreement with those reported in the literature [19]. For example, the same trend has been observed by Pearson et al. [33] in the photodegradation of Congo red dye and by Hu et al. [34] in the photocatalytic hydrogen evolution reaction, in which the platinum doped TiO₂ displayed superior photocatalytic behavior to the Ag and Au. There are, however, a number of parameters that can be considered for the next steps or analyses in this study, including the concentration of the doped metal nanoparticles, the TiO₂ morphology, and the doping of bi-metal nanoparticles.

3.4. RB19 photodegradation mechanism

An illustration of the possible mechanism of photodegradation of RB19 dye using M@PW-TiO₂ is provided in Scheme 2. One of the excellent inherent properties of noble metals is the surface plasmon band (SPB), which can be observed at about 560 nm [35,36]. Visible light can be exploited for the excitation of SPB in noble metal NPs during the inserting of electrons into the TiO₂ conduction band [37,38]. Local deposition of metal nanoparticles using PW interlinks can accelerate the charge transfer rate between the TiO₂ support and metal NPs inside the nanocomposite structure.

In the photocatalytic mechanism depicted in Scheme 2, the electron/ hole recombination phenomenon can be considered as rate restriction [19]. Upon incident photons, the stimulation process is initiated and electrons move up from the valence band (VB) to the conduction band (CB). Such transformation provides a significant driving force to recombine the electrons and the newly created hole [39]. Despite the questionable effectiveness of metal nanoparticle deposition on TiO₂ surfaces for photocatalytic oxidative reactions [40], different Fermi levels may explain the increased photocatalytic activity of the fabricated nanohybrid. The conduction band edge of TiO₂ is often higher than the Fermi level energy for noble metals [41]. Thus, the metal nanoparticles trap electrons stimulated by light, but the holes produced by light simply remain in the semiconductor valence band [42]. Due to the variation in Fermi levels of metals (Au, Pt, and Ag) and metal oxides (TiO₂), electrons are persistently transferred from the surface of titania to MNPs to reach an equilibrium state of Fermi energy levels [43,44]. As a result, electrons are distributed between MNPs and TiO2 surface. Consequently, loaded metal nanocomposites try to transfer photo-induced electrons from TiO₂ conduction to adsorbed O₂ by forming a Schottky barrier at their interfaces [43-45].

Additionally, the charge recombination process can be further inhibited by the situation of a qualified electron-transferable molecule such as PW on the TiO₂ surface and noble metal NPs (see Scheme 2). In general, two possible phenomena might be accomplished over the stimulation of the nanohybrid under light irradiation: (i) the photonmediated separation of holes and electrons inside the TiO₂ structure, and (ii) the UV-mediated reduction of PW molecules between the titania and MNPs [13,19]. Comparatively to pristine TiO₂, the second one, which is attributed to TiO₂ in conjunction with PW and MNps, is most likely play the major role in terms of photocatalytic performance. Due to the high electron transferability of PW, its reduced state (PW*) is keen to receive electrons and, therefore, provides an easy pathway for electrons to move from TiO₂ to PW*, which will be continuously regenerated during the process.

4. Conclusion

A comparative study was conducted here between PW-modified TiO_2 , which was anchored by different metal nanoparticles (Au, Ag, and Pt). In addition to locally reducing metal ions on the TiO_2 surface and the interconnection of Titanian and metal nanoparticles, the presence of PW can considerably promote the photocatalytic performance of TiO_2 -based nanohybrids under simulated sunlight. Different methods

were used to characterize the prepared nanomaterials, which confirmed that the polyoxometalates and metal nanoparticles were successfully introduced onto TiO_2 . TEM analysis demonstrated the formation of metal NPs in the range of 20 nm on TiO_2 surface without contamination by free metal NPs. The photocatalytic efficacy of prepared nanohybrids was investigated in RB19 dye photodegradation under solar light irradiation under different conditions. The optimum degradation performance was found at pH of 3.8, wherein the maximum and minimum photocatalytic activity was associated with $Pt@PW-TiO_2$ and $Au@PW-TiO_2$, respectively.

CRediT authorship contribution statement

Shakiba Bahrami: Investigation, Data curation, Formal analysis, Methodology. Ali Ahmadpour: Supervision, Conceptualization, Writing – review & editing. Tahereh Rohani Bastami: Conceptualization, Methodology. Ali Ayati: Supervision, Conceptualization, Writing – review & editing. Shohreh Mirzaei: Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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