Novel Au NPs/Preyssler acid/TiO2 nanocomposite for the photocatalytic removal of azo dye

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Abstract
In this study, we introduced a novel nanocomposite consisting of Au nanoparticles decorated TiO2 and Preyssler acid as a multifunctional photocatalyst linker molecule, in which gold ions reduced locally on the TiO2 surface. The obtained nanocomposite has been characterized using Fourier Transform Infra-red (FTIR), X-ray Diffraction (XRD), Electron Dispersive X-ray (EDX) Spectroscopy, Transmission Electron Microscopy (TEM) and Scanning Electron Microscope (SEM). Also, their photocatalytic activity has been studied for the degradation of model organic azo dye Malachite Green under UV light irradiation.

1. Introduction
In the recent years, the synthesis and photocatalytic application of TiO2 and its composite materials have attracted growing interest due to the low-cost, availability, nontoxicity, small crystal size, high specific surface area and highly porous structure of mesoporous titanium dioxide [1–4]. The large band gap of TiO2 (Eg: ~3.2 eV [5]) and its massive recombination of photogenerated charge carriers are the most significant drawbacks of titania, which results in a low quantum yield and poor photocatalytic efficiency [6]. Loading of noble metal nanoparticles such as Au, Ag, Pt on the TiO2 surface is one of the most effective strategies to overcome the large band gap of titania [7,8] by reducing the fast recombination of the photogenerated charge carriers. Metal nanoparticles store electrons and act as a sink for the interfacial charge transfer processes.

Among various metal nanoparticles, the Au/TiO2 nanocomposites have received particular attention because of interesting phenomena occurring at the Au NPs and TiO2 interface, such as effective passivation of surface states as well as electric field amplification at their interfaces upon SPR excitation [9,10]. Recently, many researchers have found that the excitation of Au nanoparticles (NPs) can contribute significantly to the photocatalytic performance of TiO2. When Au NPs deposit on the TiO2 surface, they decrease the band gap energy of TiO2 to a value less than the common band gap energies of titania in the bulk form [11], which causes the stronger interaction between Au and titania [11]. Also, it leads to considerable enhancement of photocatalytic activity of TiO2 due to increasing the charge separation between the excited electron (e−) and hole (h+) [12–14]. Consequently, the synthesis method and photocatalytic application of Au NPs/TiO2 nanocomposite is an emerging research area [10,15,16].

The deposition of Au NPs over the surface of pre-synthesized or commercial TiO2 have been carried out through different photodeposition and chemical techniques [17–19]. In the most of chemical paths for the deposition of Au NPs on the TiO2 surface, the gold ions reduction step leads to the formation of both Au/TiO2 and free Au NPs in the solution [20]. Actually, the presence of free nanoparticles in the product is undesirable. So, locally the reduction of gold
ions on the surface of TiO2 particles can be a strategy to overcome this drawback to formation of Au NPs-decorated TiO2 without any free Au NPs contamination [21].

In this regards, polyoxometallates (POMs) can be introduced as green candidates for localized reducing agents. POMs are a unique class of molecularly defined inorganic metal–oxide clusters with exceptional properties [22]. Their structures remain unchanged under stepwise and multielectron redox reactions, and they can easily be reduced by photochemical and electrochemical procedures with suitable reducing agents [23]. Recently, the green synthesis of metal NPs using POMs as photocatalysts, mild reductants and stabilizers has also been comprehensively studied [24–28]. In the previous works, we have introduced the Preyssler type POM (H14[NaP5W10O31], Preyssler) as an excellent reducing agent and stabilizer for the synthesis of Au NPs under UV irradiation [29–31]. Preyssler is a remarkable POM because of: strong Brønsted acidity with 14 acidic protons, high thermal and hydrolytic (pH 2–12) stability, reusability, non-corrosiveness, high oxidation potential and greenness [32]. To the best of our knowledge, this is the first study on the use of Preyssler acid as a photocatalytic linker molecule of locally reduced metal ions on the surface of TiO2. On the other hand, because of the photocatalytic ability of Preyssler [33], it can affect the photocatalytic activity of Au/TiO2.

In this study, we investigated the unique capability of Preyssler bounded anatase TiO2 particles to act as a highly localized reducing agent for the photosynthesis of Au NPs/Preyssler/TiO2 nanocomposite. So, this facile photoreduction approach leads to the formation of nanocomposite particles without any free gold contamination in the solution via independent nucleation. The obtained Au NPs/Preyssler/TiO2 nanocomposite has been characterized using different methods. Also, its photocatalytic activity has been studied for the degradation of model organic azo dye Malachite Green under visible light irradiation.

2. Experimental

2.1. Chemicals and instruments

Titanium dioxide (TiO2, anatase, 99.8%), gold (III) chloride trihydrate (HAuCl4·H2O, ≥ 99.9%) were obtained from Sigma Aldrich. All the chemicals for the synthesis of Preyssler acid and also, 2-propanol (≥ 99.8%) were purchased from Merck Company and were used as received. H14[NaP5W10O31] was prepared according to our earlier work [34]. Also, the N,N,N,N-Tetramethyl-4,4-diaminotriphenylcarbenium oxalate (Malachite Green, MG, Scheme 1) was purchased from Sigma Aldrich (Dye content ≥ 90%). The FTIR spectra of the prepared powders were measured by the ATR method with a VERTEX-70 infrared spectrometer. The samples were analysed by X–ray powder diffraction (XRD) using a PANalyticalX’Pert PRO diffractometer equipped with primary beam Johansson monochromator to generate pure Cu Ka1 radiation (1.5406 Å; 45 kV, 30 mA). Samples were prepared on to silicon-made zero-background sample holder using petrodatum jelly as an adhesive. X’Celerator detector in a continuous scanning mode was used to collect the data in 2θ range of 10–120° with a step size of 0.017° and counting time of 960 s per step.

The Hitachi S-4800 Ultra-High Resolution Scanning Electron Microscope was used for SEM analysis. It is equipped with EDAX analysis for determination of elemental analysis. The EDAX model and its detector type were S4800(I) and 7747/17-ME, respectively. Moreover, the nanocomposite sample for TEM analysis were prepared by drop coating the solution onto a carbon-coated copper grid, followed by TEM measurements using a JEOL-2200FS FEG(Japan) instrument.

The concentration of azo dye MG was measured by its UV visible spectra using JASCO V-670 spectrophotometer (Japan). 2.2. Synthesis of Au/Preyssler/TiO2

For synthesis of the nanocomposite, we prepared Preyssler/TiO2 by impregnation method. So, 100 mg of TiO2 was dispersed in the 40 mL solution of Preyssler acid (10 mM) and left under stirring to dry at 30 °C. In this composite, Preyssler acid is bounded to the TiO2 surface and it is called Preyssler/TiO2. For decoration of the composite, 20 mL of dispersed composite (20 mg/mL), 10 mL HAuCl4 solution (5 × 10–4 M) and 2 mL 2-propanol were mixed in a quartz reactor cell and purged with nitrogen gas for 20 min. The mixture was irradiated by UV light (15 W low pressure mercury vapor lamp) under continuous stirring for an hour and the temperature was fixed by setting the temperature of water circulating around the cell. The resulting nanocomposite was separated using centrifugation (5000 rpm) and dried at 60 °C for 6 h.

2.3. Photocatalytic degradation of Malachite Green

The photocatalytic performance of synthesized nanocomposite was investigated by degradation of an organic azo dye Malachite Green (MG) under UV light irradiation.

In a typical reaction, in a quartz glass reactor equipped with a magnetic stirrer, 30 mg of nanocomposite was added to 100 mL of MG (10 ppm) and fully dispersed in ultrasonic bath. The mixture was purged with nitrogen for 15 min and stirred in a dark place for 20 min. Then, it was irradiated under the low pressure mercury lamp(15 W) as a UV light source at room temperature and the liquid samples were withdrawn at given irradiation time intervals. The catalyst can be easily separated by centrifugation (4000 rpm). Then, the absorbance of the remaining solution was examined by UV–vis spectroscopy.

3. Results and discussion

When the Preyssler/TiO2 was used for the reduction of gold ions, the bounded Preyssler to the TiO2 surface was reduced (Preyssler*)under the UV irradiation and in the presence of 2-propanol which plays the role of sacrificial agent [31].

\[
\text{Preyssler}^* + \text{Au}^{3+} \rightarrow \text{Au}^{0}/\text{Preyssler}/\text{TiO}_2
\]

(1)

Due to the ability of Preyssler* for transferring electrons efficiently to gold ions, the color of solution turns gradually from milky to magenta which indicated the formation of Au NPs and simultaneous oxidation of Preyssler* to Preyssler, following the Eq. (2):

\[
\text{Preyssler}^* + \text{Au}^{3+} \rightarrow \text{Au}^{0}/\text{Preyssler}/\text{TiO}_2
\]

(2)
So, the Au NPs were formed locally on the surface of TiO$_2$ and meanwhile, Preyssler acts as molecular bridge. The above two equations were occurred in a one-pot system at ambient temperature.

We have followed the binding of Preyssler to TiO$_2$ surface and Au NPs by FTIR analysis. The spectra are shown in Fig. 1. As it can be seen in Fig. 1a TiO$_2$ does not have any significant band in the range of 600–1300 cm$^{-1}$. It is indicated in Fig. 1b that the characteristic bands of Preyssler structure are three bands due to P–O stretching at 1158, 1084 that are consistent with a C$_{5v}$ symmetry anion and 1020 cm$^{-1}$, and two bands attributed to W–O–W at 935 and 902 cm$^{-1}$, a band at 694.7 cm$^{-1}$ corresponding to W=O.

By the investigation on the shifts in the vibrational modes of oxygen atom, we could find the bands of Preyssler to TiO$_2$ surface and Au NPs (see Fig. 1c and d). With the Preyssler functionalization of TiO$_2$, a blue shift in the characteristic band of W–O–W is observed from 902.5 to 910.8 cm$^{-1}$ with little shifts in the other vibrational modes which confirmed that the Preyssler binds to the TiO$_2$ surface through the oxygen atoms.

For the prepared nanocomposite, by the synthesis of Au NPs, there is a further blue shift in the W–O–W vibrations from 910.8 to 915 cm$^{-1}$ in the asymmetric stretching vibrational mode of the terminal oxygen atoms. This suggests that Preyssler interacts strongly with the Au NPs and binds to it through the terminal oxygen atoms in the W–O–W positions.

The XRD pattern of the obtained nanocomposite is displayed in Fig. 2. It shows that three distinct phases can be identified, those are minor fraction of gold phase, major component which is TiO$_2$ in anatase form, and smaller fraction of TiO$_2$ in rutile form. By careful observation, it can be found that the peaks emerge at $2\theta = 38.2^\circ$, 44.4$^\circ$, 64.6$^\circ$ and 77.6$^\circ$, which can be attributed to the diffraction peaks of (111), (200), (220) and (311) lattice planes of polycrystalline Au, respectively [19], although the latter two ones are very weak.

The broader peak profiles of less crystalline Au phase are clearly distinguishable from the sharper peaks of more crystalline anatase and rutile phases. Also, the isolated diffraction peaks at $2\theta$ angles of 64.57$^\circ$ (200) and 77.55$^\circ$ (311) (wherein there are no assignation interfering anatase or rutile peaks) are clear indications for the presence of Au phase. The crystal size of Au particles is rather tricky to evaluate, as its peaks are severely overlapped with peaks originating from titania.

Preyssler which was bound to the TiO$_2$ surface did not change the intensity of diffraction peaks arising from anatase. This can be due to the formation of only a thin coating of POM on the TiO$_2$ surface and thus the majority of the observed signals are related to the crystal phases of anatase TiO$_2$ [20].

Decoration of the Preyssler modified TiO$_2$ surface with Au NPs is demonstrated by SEM analysis which images are shown in Fig. 3. It is seen that Au nanoparticles' localization can be clearly demonstrated, wherein the quasi-spherical nanoparticles appear in the range of 15–20 nm in diameter, and those are well dispersed and on the surface of the titania.

Moreover, EDX analysis (Fig. 4) was employed to confirm the presence of Au NPs and Preyssler in the prepared nanocomposites as well as to semiquantitatively assess its elemental composition to determine the loading amount of Au NPs (0.48% w/w) on the TiO$_2$ surface. The characteristic energy line at 1.7 keV corresponding to W MR confirms the binding of Preyssler onto the TiO$_2$ surface. As it can be seen in the figure, in addition to characteristic energy line of Ti and O which are related to the TiO$_2$, this analysis confirmed the presence of gold metal in nanocomposites. It displays a characteristic energy line corresponding to Au M$_{4\alpha}$ at 2.29 keV.

Fig. 5 shows the TEM images of Au/Preyssler/TiO$_2$ nanocomposite. The decorated quasi-spherical Au NPs are seen as dark contrasts; dispersed on the surface of TiO$_2$ support without aggregation and their size are about 10–20 nm. Because the gold is heavier than TiO$_2$, the image of gold is significantly darker than that of titanium dioxide. Interestingly, the TEM image of this nanocomposite did not show the formation of any free gold NPs. So, it confirms that Preyssler acts as a localized reducing agent for the synthesis of Au NPs on the surfaces of the Preyssler-functionalized TiO$_2$ particles.

### 3.1. Photocatalytic performance of the obtained nanocomposites

For the investigation of nanocomposite photocatalytic activity, we have compared the photodegradation rate of organic azo dye

![Fig. 1. FTIR spectra of (a) anatase TiO$_2$, (b) Preyssler, (c) Preyssler/TiO$_2$ and (d) Au/Preyssler/TiO$_2$.](image)

![Fig. 2. XRD pattern of prepared nanocomposite. Characteristic Bragg peak positions of Au (red), TiO$_2$ anatase (blue) and rutile (green) are indicated by the tick marks with heights corresponding to their reference intensity ratios.](image)
Malachite Green by TiO2, Preyssler, Preyssler/TiO2 and Au NPs/Preyssler/TiO2, in the presence of visible light by TiO2. For the kinetic rate of reaction we have used Langmuir–Hinshelwood model which is usually applied to describe the kinetics of photocatalytic reactions of aquatic organics. It involves a three-step mechanism for the catalytic degradation of substrates including the adsorption on the surface \([35]\). It presents the rate of photodegradation \((r)\) and the concentration of organic compound \((C)\), which is expressed as follows:

\[
 r = -\frac{dC}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C}
\]

where \(k_r\), \(K_{ad}\) and \(t\) are the intrinsic rate constant \((\text{M/min})\), dye adsorption equilibrium constant on the catalyst particle \((\text{M}^{-1})\) and irradiation time \((\text{min})\), respectively. At very low organic concentration, Eq. (3) can be simplified to the following first-order kinetics with an apparent first-order rate constant \(k_{app}\) \((\text{min}^{-1})\):

\[
 \ln \left( \frac{C}{C_0} \right) = -k_{app} t = -k_{app} t
\]

So, pseudo first-order kinetics is applicable in the plot of \(-\ln(C/C_0)\) versus \(t\) which yield a straight line as indicated in Eq. (4) and \(k_{app}\) is the slope of the plot. For \(C_0\) and \(C\), we have used the intensity of the characteristic absorbance maxima of MG solution \((\lambda = 617 \text{ nm})\) at time \(t = 0\) and \(t = t\), respectively.

Fig. 6 shows the degradation of MG using pristine anatase TiO2, as a wide band gap semiconductor material, under photo irradiation. Also, the MG degradation during photoexcitation in the presence of photocatalysts could be easily followed by the kinetic plots which are shown in Fig. 7, for the first 60 min. However, Preyssler is an efficient photocatalyst \([36]\, but it did not show high activity in the degradation of MG \((K_{app} = 0.0019)\) in comparison to TiO2.
(\(K_{app} = 0.0203\)). As expected, binding of Preyssler to TiO\(_2\) and formation of Preyssler/TiO\(_2\) resulted in an increase in the photodegradation of MG and \(K_{app}\) increased to 0.0263 which might be due to the cocatalytic activity of Preyssler and TiO\(_2\).

Interestingly, by introducing of Au NPs to the Preyssler/TiO\(_2\) composite, the photocatalytic performance enhanced in which \(K_{app}\) increased to 0.0773. Therefore, it indicates that the photocatalytic performance rate of nanocomposites shows 3.8-fold and 2.9-fold increase in the photoactivity of anatase TiO\(_2\) and Preyssler/TiO\(_2\), respectively.

The possible mechanism of Au NPs/Preyssler/TiO\(_2\) for degradation of MG under UV light irradiation is shown in Scheme 2.

One of the most remarkable properties of Au-NPs is the existence of a visible band at around 560 nm denoted as surface plasmon band (SPB) due to the collective excitation of electrons confined in the metal NPs [37–39]. In principle, the injection of electrons on the TiO\(_2\) conduction band could be possible using light to excite this SPB of Au-NPs [40]. Because of photocactivity of Preyssler molecules and their strong electron transferability, the bridging layer of Preyssler between TiO\(_2\) and Au NPs may provide an additional driving force to facilitate the charge transfer between them.

A major rate-limiting factor in the photocatalytic performance of TiO\(_2\)-based materials is the phenomenon of electron/hole recombination [20]. The excitation by incident photons leads to the promotion of electrons from valence to conduction band across the band gap, where a large driving force exists to recombine the electron and newly generated hole [41]. Although, the effective role of TiO\(_2\) supported Au-NPs in photocatalytic oxidative reactions is still under debate [42], the enhancement of photocatalytic activity of Au NPs/TiO\(_2\) can be attributed to the different Fermi levels [43]. Usually, the energy of Fermi level of noble metals is lower than the conduction band edge of TiO\(_2\). So, the photo-promoted electrons can be captured by the noble metals, while photo produced holes remain in the semiconductor valence band [2].

The difference in the Fermi levels of gold and TiO\(_2\) make a continuous electron transfer from titania to Au NPs to achievement of the same Fermi energy levels is achieved. By formation of Schottky barrier at the interface of Au and TiO\(_2\) [44], loaded gold desires to transfer photo-induced electrons from TiO\(_2\) conduction to adsorbed O\(_2\) which leads to the reduction of decreasing the recombination rate of photo-induced electrons and holes and consequently improvement of photocatalytic activity [45].

By addition of Preyssler layer as a redox molecule with high electron transfer ability between Au NPs and TiO\(_2\) surface, charge recombination process could be blocked further [20]. Actually, two phenomena could happen on the excitation of the nanocomposite under UV light: (1) the photon-mediated separation of holes and electrons within TiO\(_2\) and (2) the UV-mediated reduction of Preyssler molecules between the TiO\(_2\) surface and Au NPs [20]. By migration of electron to from TiO\(_2\) to Preyssler (Preyssler'), the Au NPs at the other side of Preyssler molecules will act as an electron sink. Therefore, the electrons transferred from TiO\(_2\) to Preyssler' will transfer from Preyssler to the Au NPs. So, the molecules will be regenerated during the process, continuously.

Since the deposition of Au NPs showed significant enhancement in the photocatalytic activity of Preyssler/TiO\(_2\), the recyclability and stability of photocatalyst, which is very important from the application point of view, was investigated. After the reaction completion (cycle I), the nanocomposite was separated by centrifuge and utilized in cycles II and III under the similar reaction conditions. Our results showed that the \(K_{app}\) slightly decreased about 3% and 5% in cycles II and III (in comparison with cycle I), respectively, pointing the stability and retention capability of photocatalyst.

4. Conclusion

In the present work, we employed Preyssler acid as a multifunctional photocatalyst linker molecule and a highly localized UV-switchable reducing agent to synthesis a new class of smart gold nanoparticles decorated TiO\(_2\) nanocomposite. The FTIR analysis confirmed the binding of Preyssler to TiO\(_2\) surface and Au NPs. Also, the TEM and SEM analysis show the formation of Au NPs-decorated TiO\(_2\) without any free Au NPs contamination. The photocatalysis results have shown that the novel introduced nanocomposite is a UV light active material and acts as a triple photocatalysts system that shows a high photocatalytic performance and can be employed for the efficient photodegradation of organic pollutants such as azo dyes. Also, the possible mechanism involved in improving the photocatalytic performance of these materials has been proposed, in which the bridging layer of photoactive Preyssler, with strong electron transferability, between TiO\(_2\) and Au NPs, may provide an additional driving force to facilitate the charge transfer between them. However, the Au NPs deposition on the TiO\(_2\) surface, the band gap energy of pristine TiO\(_2\) decrease to a value less than its common band gap energies in the bulk form.

Fig. 7. kinetic rate of MG Photodegradation in the presence of: (a) Preyssler, (b) anatase TiO\(_2\), (c) Preyssler/TiO\(_2\) and (d) Au/Preyssler/TiO\(_2\) (30 mg/100 mL).

Scheme 2. Schematic representation of the possible mechanism for the photocatalytic activity of Au NPs/Preyssler/TiO\(_2\) nanocomposites.


