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Photocatalytic degradation of nitrobenzene by gold nanoparticles decorated polyoxometalate immobilized TiO_2 nanotubes

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ABSTRACT

In this study, the gold nanoparticles were deposited on the surface of tungstophosphoric acid immobilized TiO_2 nanotubes, in which tungstophosphoric acid plays the roles of highly localized UV-switchable reducing agent and multifunctional photocatalyst linker molecule. The prepared novel nanocomposite was characterized with FTIR, XRD, EDX and TEM and showed high photocatalytic efficiency in nitrobenzene removal. The results demonstrated that by introducing of AuNPs, the photocatalytic performance significantly enhanced, where the photocatalytic rate of using Au/HPW/TiO_2-NTs nanocomposites was 4.1-fold increase compared to TiO_2 nanotubes. The photocatalytic mechanism was proposed.

1. Introduction

Nitrobenzene (NB) as a highly toxic aromatic compound, is frequently discharged from the petroleum industry, dyes, herbicides, fungicides, wood and explosives manufacture effluents [1–3]. It is a skin and eyes irritant and affects the central nervous and cardiovascular systems and also, is suspected to be possible carcinogenic or mutagenic agent [3]. The maximum allowable concentration is reported 1 mg L^{-1} in wastewaters [4]. In this regard, several treatment processes were reported for the nitrobenzene effective removal, such as ozonation [5], adsorption [6], catalytic [1] and photocatalytic degradation [7]. Among these methods, the latter process is largely studied due to the complete mineralization of organic pollutants to nontoxic or significantly less toxic inorganic compounds.

Design of effective hybrid materials using the semiconductors has attracted growing interest for photocatalysis [8,9]. Titanium dioxide (TiO_2) is one of the most widely studied semiconductor which has unique chemical and physical properties including its availability, low cost, nontoxicity, small crystal size, high specific surface area, highly porous structure [10–12]. TiO_2 is well-known to exhibit photocatalytic activity due to the photo-generated charge carriers [10,13]. It is demonstrated that the TiO_2 nanotubes as nanoparticulated forms of TiO_2 possess higher photocatalytic activity in comparison to colloidal forms of TiO_2, due to large specific surface area and pore volume [10,14] that can significantly increase the number of reaction sites.

The most important drawbacks of bulk TiO_2 and also, TiO_2 nanotubes are their large band gap (Eg: 3.0–3.2 eV) which requires its exposure to ultraviolet irradiation for potential photocatalysis applications and its massive recombination rate of photogenerated electron(e−)–hole (h+) pair which hinders its photocatalytic efficiency [15,16]. It is of great interest to develop TiO_2 based photocatalyst with improved photocatalytic activity.

Doping the TiO_2 surface with noble metals, which act as electron acceptors, is one effective strategy to improve its photocatalytic activity. Among the noble metals, gold NPs deposition has attracted significant interest [17,18]. The charge separation between the excited electron (e^-) and hole (h^+) resulting the strong interaction between gold and TiO_2 [19] which decreases the band gap energy of TiO_2 and enhances its photocatalytic activity [18,20].

On the other hand, it is demonstrated that the combination of the Polyoxometalate (POMs) and TiO_2 can enhance the

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photocatalytic efficiency of TiO_2-catalyzed reaction, due to the synergistic photocatalytic effect between these two components [21,22]. POMs as a molecularly defined inorganic metal–oxide clusters [23] can be easily reduced by photo/electro chemical procedures and their structures remain unchanged under stepwise and multielectron redox reactions. Because of these properties, they have been used as efficient photocatalysts, mild reductants and stabilizers in the green synthesis of metal NPs [24–27].

In our recent study [28], we applied Preyssler acid, as a POM structure, for the locally deposition of gold NPs on the TiO_2 surface, wherein it played the role of interlink between the AuNPs and TiO_2. The local decoration of AuNPs on the TiO_2 surface prevents the formation of free non linked AuNPs in the solution and also, the formation of a novel nanocomposite composed of AuNPs, TiO_2 and POM. In this study, we investigated the deposition of AuNPs on the tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) immobilized TiO_2 nanotubes surface. The HPW (a Keggin type of POM) have attracted significant attention in catalysis and photocatalysis due to its low cost, low environmental impact, interesting electron and proton transfer, high thermal stability and storage characteristics [23]. We studied the photocatalytic activity of prepared nanocomposite for the degradation of nitrobenzene under simulated visible light irradiation.

2. Experimental

2.1. Chemicals and instruments

Titanium dioxide (TiO_2, anatase, 99.8%), Tetrachloroauric acid ($HAuCl_4{\cdot}H_2O$, ⩾99.9%), HPW and nitrobenzene (⩾99.0%) were obtained from Sigma Aldrich. The 2-propanol (⩾99.8%) was purchased from Merck Co.

The prepared powders were analyzed by the ATR method with a VERTEX-70 infrared spectrometer to study their FTIR spectra. The XRD measurement was carried out using PANalytical Empyrean powder diffractometer by Cu Ka radiation. Also, the EDAX analysis was used for elemental analysis which model and detector type were S4800(I) and 7747/17-ME respectively. The TEM measurement was performed by a Hitachi HT7700 instrument.

2.2. TiO_2 nanotubes preparation

The hydrothermal method has been used for the preparation of TiO_2 NTs [10]. For this aim, 4 g of commercial anatase TiO_2 powder was dispersed in NaOH aqueous solution (10 M) and transferred into a Teflon-lined autoclave. The autoclave was heated at 393 K for 24 h and then cooled to room temperature. The obtained mixture was washed with deionized water and HCl solution (0.1 M) till the solution reached the pH = 7. The prepared TiO_2 NTs were dried in a vacuum oven at 353 K, followed by calcination at 573 K for 4 h in the furnace.

2.3. Preparation of AuNPs/HPW/TiO_2 NTs

Firstly, HPW was deposited on the TiO_2 NTs surface by dispersion of 100 mg TiO_2 in 40 mL solution of HPW (10 mM), followed by stirring at room temperature for 24 h. It was separated by centrifugation (4000 rpm), washed with water three times and dried in an oven for 8 h at 60 °C. This composite is called HPW/TiO_2-NTs. Then, for the decoration of obtained composite, 1 mL $HAuCl_4$ solution (10^{-3} M) was added to 20 mL of dispersed obtained composite (20 mg/mL), and mixed with 1 mL 2-propanol in a quartz reactor cell. The suspension was purged with nitrogen gas for 15 min. Afterwards, the mixture was irradiated by a 15 W low pressure mercury vapor lamp, as UV light source, under continuous stirring for an hour. The color of suspension was changed from milky to purple, indicating the formation of gold NPs. The obtained nanocomposite was separated using centrifugation (4000 rpm), washed with water and dried at 60 °C for 6 h.

2.4. Photocatalytic degradation of nitrobenzene

The photocatalytic activity of AuNPs/HPW/TiO_2-NTs nanocomposite film was evaluated by the degradation of nitrobenzene aqueous solution under visible light irradiation. For the photocatalytic reaction, 20 mg of nanocomposite was added to the nitrobenzene solution (40 ppm), purged with nitrogen for 15 min and magnetically stirred in the dark for 30 min to reach adsorption/desorption equilibrium. During the photoreaction, the samples were collected at given time intervals and centrifuged (4000 rpm) to separate the nanocomposite particles. Then, the solution was subsequently analyzed by UV–vis spectroscopy (A JASCO V-670 spectrophotometer (Japan)) at λ_{max} = 268 nm, through Beer–Lambert law in which the absorbance value versus concentration obeys a linear relationship [29].

3. Results and discussion

3.1. Mechanism of nanocomposite formation

The present HPW molecules bonded to TiO_2 NTs in the HPW/TiO_2-NTs composites were used for local reduction of gold ions on the surface of TiO_2 NTs. By the UV irradiation of HPW/TiO_2-NTs composites in the presence of 2-propanol, the bounded $[PW_{12}O_{40}]^{3-}$ can be easily reduced to $[PW_{12}O_{40}]^{4-}$ by the following equation [30–32]:

$$[PW_{12}O_{40}]^{3-}/TiO_2\text{-NTs} + (CH_3)_2CHOH \xrightarrow{h\nu} [PW_{12}O_{40}]^{4-}/TiO_2\text{-NTs} + (CH_3)_2C{=}O + 2H^+ \quad (1)$$

$[PW_{12}O_{40}]^{4-}$ is highly active to transfer electrons efficiently to metal ions, and acts as reducing agent for the reduction of metal ions. So, in the contact with the gold ions, the $[PW_{12}O_{40}]^{4-}$ simultaneously oxidize to $[PW_{12}O_{40}]^{3-}$ and gold nanoparticles form according to Eq. (2):

$$[PW_{12}O_{40}]^{4-}/TiO_2\text{-NTs} + Au^{3+} \rightarrow Au^0/[PW_{12}O_{40}]^{3-}/TiO_2\text{-NTs} \quad (2)$$

Actually, the HPW plays the role of reducing agent and molecular bridge between AuNPs and TiO_2 NTs.

3.2. Nanocomposite characterization

The binding of HPW and AuNPs to TiO_2 were followed by FTIR analysis, as shown in Fig. 1. As it can be seen, the TiO_2 NTs does not have any significant band in the range of 600–2000 cm^{-1}. On the other hand, the HPW ($H_3PW_{12}O_{40}$), as Keggin structure of POMs, consists of a cage of tungsten atoms which are linked by oxygen atoms and a phosphorus atom is at the center of the tetrahedral [33]. There are four main peaks inferred signatures due to the oxygen atoms which form four chemically distinct bonds. The 1080 cm^{-1} is related to the P—O at the center of the HPW structure, 800 and 897 cm^{-1} corresponding to the vibration modes of W—O_a—W due to the oxygen atoms along the edges and W—O_b—W due to oxygen atoms at the corners of Keggin structure respectively. Also, the W=O corresponds to the asymmetric stretching of terminal oxygen atoms reflected at 971 cm^{-1} [34].

By deposition of HPW to the surface of TiO_2 NTs (HPW/TiO_2-NTs), a red shift in the W—O_b—W bending vibrations appeared from