Photodeposition of Pd nanoparticles on TiO2 utilizing a channel type quartz reactor

Samira Dadsetan⁎, Saeid Baghshahi⁎⁎, Farshad Farshidfarb, Seyed Mohammad Mehdi Hadavi

⁎ Department of Materials Science and Engineering, School of Engineering, Imam Khomeini International University, Qazvin, Iran
⁎⁎ Biomaterials group, Nanotechnology and Advanced Materials Department, Materials and Energy Research Center, Karaj, Alborz, Iran

ABSTRACT

In this research a channel type quartz reactor with inner diameter of 2.8 mm was utilized for photodeposition of palladium nanoparticles on titania. High surface to the volume ratio of the reactor and a flash irradiation time of 0.5 s per once passing of solution through the reactor are the benefits of utilizing this type of reactor. Samples of Pd@TiO2 with Pd loadings of 0.35, 1.3 and 1.54 wt% were prepared. AAS, IR spectra, XRD, UV–Vis spectroscopy and HR-TEM were utilized for characterization of the samples. Furthermore, the photocatalytic activities of the samples were evaluated by degradation of methylene blue under visible light irradiation. Band-gap reduction from 3.25 to 3 eV as well as enhancement of degradation rate constant from 0.008 to 0.023 1/min for bare and Pd loaded titania respectively, were the main results of this exploration. Data from photodegradation test endorses the notion that higher catalytic activity is achieved by smaller Pd particles with mono size distribution. The sample with mono-dispersed Pd particles all smaller than 8 nm is more photocatalytically active than the sample with higher loading amount but broad Pd particle distribution from 2.5 to 15 nm.

1. Introduction

In the last decade, the photocatalytic properties of TiO2 have been extensively studied for treating precarious chemical wastes. Photo excitation of titania creates electron-hole pairs, which can be transferred towards its surface to act as reductant and oxidant agents. Most organic photodegradation reactions utilize oxidizing power of holes either directly or indirectly [1,2]. However, bare TiO2 suffers from some limitations restricting its practical applicability and efficiency [3,4]. Due to its wide band gap (Eg=3.25 eV), TiO2 is only active under ultraviolet (UV) light, which limits its excitability under natural visible range of solar irradiation. Moreover, high recombination rate of the photo-generated charge carriers results in low photocatalytic efficiency of titania [5–7]. To overcome these limitations, several strategies have been proposed, including doping with other species or deposition of small precious metal clusters such as Pd, Pt, Ag and Au on the surface of TiO2 particle. The former affects band gap by introducing structural vacancy defects and the latter acts as electron trap to decrease charge recombination rate and also provides metallic sites with a higher catalytic reactivity. These promoters can alter the charge transfer properties of TiO2 particle and its surface activity and therefore, shift the photocatalyst absorption edge towards the visible range [6].

Chemical reduction and photodeposition are common methods for deposition of noble metal clusters on the surface of titania. The size and distribution of metal NPs are the most effective parameters on the activity and efficiency of the photocatalyst. Among the mentioned methods, photodeposition is a facile low temperature process with efficient metal-support interaction [8,9].

Herein, to photodeposit Pd nanoparticles on TiO2 surface, a channel type quartz reactor was utilized to flow PdCl2 solutions through the UV light irradiation. A high surface to volume ratio and a flash type irradiation per once passing of particles are the benefits of such a reactor.

2. Experimental

2.1. Materials and methods

Appropriate amounts of commercial Degussa titanium oxide powder (P25, 80% anatase, 20% rutile, BET specific surface area of 50 m²/g) were dispersed in three solutions with PdCl2 (Chimet analytical grade) concentrations of 6.2, 12.5 and 25 ppm to prepare three samples with nominal 0.75, 1.5 and 2.8 wt% of palladium loaded TiO2. Analytical grade methanol was also added as sacrificial electron donor (SED) equal to 2.5 g carbon per 1 g of TiO2. The schematic of the deposition apparatus is shown in Fig. 1. The mixture was circulated for...
8 h by a peristaltic pump at constant flow of 150 ml/min through a quartz tube with inner diameter of 2.8 mm. The length of the UV (LP mercury lamp, 250 W/m²) irradiated part of reactor was adjusted to let irradiation time of 0.54 s per once circulation. The absorption region of the utilized quartz reactor and the P25 powder along with the irradiation wavelength of the LP mercury lamp.

![Fig. 2. UV–Vis absorption of the utilized quartz reactor and P25 powder along with the irradiation wavelength of the LP mercury lamp.](image)

Nitrogen gas was flowing through the solution containing vessel to prevent oxygen entrance. All parts of the system were covered by its thick black texture, except the UV exposing part of the quartz tube reactor. Samples were separated by a 7000 rpm centrifuge for 10 min and then dried at 353 K for 12 h. Three samples were prepared utilizing low (6.2 ppm), medium (12.5 ppm) and high (25 ppm) concentrations of PdCl₂ solutions, named as L, M and H, respectively, implying low, medium and high concentrations.

The surface features of the Pd NPs were studied by FT-IR spectroscopy of the prepared samples separated from the solution are obtained from the plot of modified Kubelka-Munk function [F(R∞) E]¹⁄² versus energy of the absorbed light E(eV) extrapolation to y=0 of the linear regression.

To study Pd NPs surface features, FT-IR spectra of adsorbed CO at 300 K (RT) were recorded by Perkin Elmer 2000. For each spectrum 32 scans were collected in the range of 400–4000 cm⁻¹ with a spectral resolution of 2 cm⁻¹. Self-supporting pellets of the samples were prepared for In-operando setup with a controllable heating chamber equipped with KBr window. Prior to CO purging, the samples were reduced by hydrogen at 393 K to remove any moisture and surface oxides, and then cooled down to room temperature under nitrogen gas flow. Adsorbed CO related FT-IR spectrum was obtained by subtracting acquired spectra after and before CO dosing.

High resolution transmission electron microscopy (HR-TEM) images of the prepared samples were acquired using a JEOL 3010-UHR microscope with an acceleration potential of 300 kV. For this purpose, as prepared samples were ground and dispersed on lacy carbon Cu grids.

### 3. Results and discussion

The photodeposited amounts of Pd on TiO₂ obtained by AAS spectroscopy of the prepared samples separated from the solution are given in Fig. 3. The lower amount of photodeposited palladium in comparison to the nominal amount of the solution was due to the deposition of a black layer on the inner surface of the irradiated part of the reactor. This layer is assumed to be made of Pd@TiO₂, since this layer was not observed when TiO₂ or Pd alone were passed through the tube. It seems that the surface charge carriers of the photo excited titanium oxide particles play the main role in titanium oxide attachment to the quartz surface, and some part of the Pd²⁺ ions were reduced on this layer instead of reduction on the dispersed TiO₂ particles of the solution. This observation is likely to be proposed as a method for deposition of M@TiO₂ (M=metal) layer on glass to enhance its absorption in UV range for applicable products.

Fig. 4 shows XRD patterns of separated Pd@TiO₂ powder, which illustrates successive photodeposition of Pd in the metallic form.
Additionally, anatase and rutile phases of P25 are observed in all samples, which are not affected by the presence of Pd. Recognizable peaks of Pd are observed in XRD patterns of M and H samples, but they do not appear in the L sample with much lower Pd content.

The light absorption properties of the samples were studied by UV–Vis spectroscopy. Diffuse reflectance spectra of the samples in the absorption mode and Kubelka-Munk converted one are shown in Figs. 5 and 6, respectively. It is obvious that there is a broadband absorption from 200 to 350 nm, due to the transition from the O2- antibonding orbital to the lowest empty orbital of Ti4+ [10]. Moreover, the P25 samples with photodeposited palladium show characteristic absorption in the visible region due to the coloration (dark grey) of the powder, which rises by increasing metal loading from 0.35 to 1.54 wt%.

Plotted Kubelka-Munk versus the absorption photon energy show band gap values of 3.23 and 3 for bare P25 and Pd photodeposited P25, respectively, indicating the band gap narrowing due to the Pd loading.

According to the previous reports, the surface plasmon resonance (SPR) peak of Pd nanoparticles is located around 300 nm, which could be shielded by the strong absorption of TiO2 in the UV region [11].

FTIR studies of CO adsorption were performed in order to study the surface features of photodeposited Pd nanoparticles on P25 (Fig. 7).
tri-coordinated (1890–1870 cm\(^{-1}\)) modes\[12\].

CO absorption bands on 0.35 wt% Pd loaded sample are weak, showing two broad band in the regions of 1800–1995 cm\(^{-1}\) and 2027–2106 cm\(^{-1}\), which are related to bridged and linear CO, respectively.

Increasing Pd loading to 1.3 wt% on P25 gives rise to IR absorption intensity of the bridged type CO, besides dividing it into two clear bands with maximum tips at 1987 and 1937 cm\(^{-1}\), which are the characteristics of bridged carbonyls on (100) and (111) faces respectively\[13\]. By further Pd loading to 1.54 wt% on P25, five clear bands at around 1866, 1940, 1984, 2096 and 2112 cm\(^{-1}\) appeared. The last two bands are related to the linear mode adsorption on the closely packed low index faces. According to Bradshaw and Hoffmann \[14\] IR absorption studies on low temperature and high surface area deposited Pd thin film, a linear bonding CO peak appears in the region of 2112 cm\(^{-1}\) (± 2) wavenumber. In the mentioned report, this peak disappears with annealing and is completely absent on films deposited at higher temperatures, which assigns it to linear carbonyl on high defective sites. Similar observation of two linear CO-IR peaks was reported by Junling Lu et al. revealing the existence of both small and large particles\[15\]. Taking into account the mentioned reports, CO-IR bands of 2096 and 2112 cm\(^{-1}\) are related to the large and small Pd particles, respectively.

In Fig. 8 the decomposition curves of MB solution in the presence of photodeposited Pd on TiO\(_2\) samples with three different loading of Pd are compared with bare P25. Also the kinetics of reactions are illustrated in inserted graph of ln(C_0/C)=f(t) in which C_0 and C represent the initial concentration of MB solution and after t(min) of irradiation, respectively. First order reaction kinetics are verified by following linear fitting. Reaction rate constants (k_{deg}) listed in Table 1 are driven from the linear slope of ln(C_0/C)=f(t). All the prepared samples exhibited better photocatalytic activity than the bare titania. The rise in the activity is attributed to the presence of Pd NPs as electron traps with much more reactive surfaces. The sample with 1.3 wt% loaded Pd exhibited the highest photocatalytic decomposition rate constant of 0.023 1/min.

HR-TEM images of the M and H (1.3% and 1.54% Pd@TiO\(_2\)) samples are illustrated in Fig. 9, which clearly shows the growth of Pd NPs at higher concentrations. During the formation of palladium metallic clusters on titanium oxide particles by this method, the primarily deposited metal nuclei act as electron traps, increasing the subsequent reduction rate, resulting in metal particles growth. The largest Pd particles detected in sample M was about 8 nm, which rises to around 15 nm in the sample H with a little bit higher Pd loading. Regarding the sample H, beside large Pd particles with 15 nm in size, several small particles of 2.5 nm were also observed which is in good agreement with double linear CO-IR bands \[15\]. Such broad Pd particle size distribution from 2.5 to 15 nm in the higher Pd loaded sample would be the main reason for its catalytic activity drop. According to EDX results accomplished with TEM test, no trace of chlorides was observed in the samples.

4. Conclusion

Pd photodeposition on TiO\(_2\) was successfully used to reduce the bare P25’s band-gap from 3.25 eV to 3.0 eV, enhancing its photocatalytic activity under irradiation in visible region. Primarily formed palladium particles on TiO\(_2\) acted as electron traps to reduce the remaining Pd ions of the solution resulting in the growth of photodeposited palladium NPs in size. This rendered the size distribution broadening of Pd nanoparticles and catalytic activity drop at the high loadings of Pd@TiO\(_2\).

The formation of a black layer of Pd@TiO\(_2\) as the result of photo excited titanium oxide attachment to the irradiated part of the channel type quartz reactor was also observed which may be due to the surface

---

**Table 1**

Kinetic data of the photocatalytic degradation of MB dye.

<table>
<thead>
<tr>
<th>Pd wt%</th>
<th>k_{deg}×10^2 (1/min)</th>
<th>r_0 (ppm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.54</td>
<td>1.72</td>
</tr>
<tr>
<td>M</td>
<td>1.3</td>
<td>2.35</td>
</tr>
<tr>
<td>L</td>
<td>0.34</td>
<td>1.32</td>
</tr>
<tr>
<td>P25</td>
<td>0</td>
<td>0.82</td>
</tr>
</tbody>
</table>
charge career accumulation on the titanium oxide particles. Photodeposition amount of the metallic palladium on the dispersed titanium oxide particles was diminished due to the formation of this layer.

Acknowledgements

This work was performed at the Department of Chemistry of the University of Torino (Italy), during a 6 months visiting period granted by the Iranian government. Prof. G. Martra, Dr. Elena Groppo and Prof. G. Cerrato are kindly acknowledged for giving access to the experimental and analytical equipment of the NIS Centre facilities.

References