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1. Introduction

In the recent years, many attempts have been devoted to developing a heterogeneous photocatalysts with high activity for the environmental applications, including water disinfection, water purification, air purification and hazardous waste remediation [1, 2]. Among the various metal oxide semiconductor photocatalysts, TiO\(_2\) has shown to be the most suitable for environmental purposes due to its strong oxidizing power, chemical inertness, long-term stability, and cost effectiveness [3, 4]. The primary event occurring on the TiO\(_2\) surface after irradiation is generation of electrons (e\(_{-}\)) and holes (h\(_{+}\)). In these reactions, the organic pollutants are oxidized (decomposed) by the photo-generated h\(_{+}\) or by the reactive oxygen species (OH\(^*\) and O\(_2\)\(^*\) radicals) formed onto the illuminated TiO\(_2\) surface. However, the practical application of TiO\(_2\) is limited by two main factors: first, due to wide band gap of TiO\(_2\) (3.2 eV for anatase, 3.0 eV for rutile phase) [5], it is can only absorb UV portion of solar light (λ<387 nm) which is up to 5% of solar light [6]. Therefore, in order to extend its practical application, many efforts have been made to design second-generation TiO\(_2\)-based photocatalysts which would be able to induce photocatalysis under visible light irradiation. Secondly, the low rate of photocatalytic decomposition using TiO\(_2\) photocatalyst is attributed to the charge recombination of photogenerated electron-hole pairs (charge carriers).

In order to overcome these problems, several approaches have been proposed: metal doping [7, 8], metal ion doping [9-11], nonmetal doping [12-14], dye-sensitizing of TiO\(_2\) (e.g., thionine) [15, 16], making composites of TiO\(_2\) with other semiconductor owning narrow band gap energy (e.g. CdS particles) [17], and doping TiO\(_2\) with up-conversion luminescence agent [18]. Among them, metal doping has been proved to be a very promising approach due to greatly extending the light absorption of TiO\(_2\) and significantly improving the trapping efficiency of change carriers [19-22]. Raftery et al., reported that doping of TiO\(_2\) nanoparticles with vanadium cations could extend the photoresponse of TiO\(_2\) to visible light region (396–450 nm) and also temporarily trap the photogenerated electrons (e\(^-\)) and holes (h\(^+\)), and thus suppress the charge recombination of the charge carriers [23]. Wu and Chen found that V-doped TiO\(_2\) exhibits photoactivity in visible light region and show a “red shift” in the UV–Vis spectra [24]. Choi et al., reported that doping of V\(^{5+}\) into TiO\(_2\) at V/Ti ratio of 0.1–0.5 %wt, can significantly increase the TiO\(_2\) photoreactivity due to the improved interfacial charge transfer [25]. Wang et al., observed that by introducing In ions into TiO\(_2\) structure, not just new energy states emerge between the TiO\(_2\) band gap which results in considerable red-shift in absorption, but also the ions facilitate the charge separation [26]. The same results were reported by other group [27]. They analyzed the photocatalytic activity of In-doped TiO\(_2\) under visible light illumination. It was demonstrated that the In doping improve visible light response of TiO\(_2\) catalyst and enhance the charge carriers separation, which the factors combined leads to the significant improvement in photocatalytic performance of TiO\(_2\) under visible light illumination. Modification of TiO\(_2\) by binary doping of metal ions is a novel process for enhancing the optical efficiency of TiO\(_2\). The synergic effect of codoping can further improve the photocatalytic activity of...
semiconductor can be excited and then generate electrons ($e^-$) and holes ($h^+$) in the conduction band (CB) and valence band (VB), respectively, if the energy of the photons of the incident light is greater than the band gap of the semiconductor [34]. The metal ion dopants influence the photo-efficiency of TiO$_2$ by acting as electron or hole trap centres within band gap of TiO$_2$ and alter the e/$h^+$ pair recombination rate [32], through following process. The photo-reduction of the metal ions (Eq. 1) is accompanied by the elimination of photo-generated holes using water oxidation (Eq. 2):

$$M^{n+} + ne^{-} \rightarrow M^n$$

(1)

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

(2)

In-doped TiO$_2$ with various metal content were prepared as follows:

To prepare In-doped TiO$_2$, first different molar percent of InCl$_3$ (0.1, 0.2, 0.4, 0.6, 1.0% of V to Ti molar ratio) as indium source was added to 100 ml of aqueous solution containing certain amount of pure TiO$_2$ particles synthesized by sol-gel and hydrothermal processes. Then, the resulting solution was purged with high-purity N$_2$ atmosphere while stirring. Afterward, the resulting solution was transferred to a quartz reactor with its head covered and was put under UV irradiation for 12 hours, under vigorous stirring. After this stage, the precursor was filtered by centrifugation and washed with deionized water for several times. The resulting powders were dried at 100 °C for 12 h.

To prepare In-V-codoped TiO$_2$, the same method for synthesis of In-doped TiO$_2$ was adopted using both InCl$_3$ (0.1, 0.2, 0.4, 0.6, 1.0% of V to Ti molar ratio) as indium source and VCl$_3$ (0.1, 0.2, 0.4, 0.6, 1.0% of V to Ti molar ratio) as vanadium source.

2.4. Characterization of the Prepared Catalysts

Crystalline phases of the prepared samples were analysed by X-ray powder diffractometer (XRD, Bruker D8 Discover X-ray Diffractometer). The morphology was revealed by a transmission electron microscope (TEM, Hitachi H-7650) and scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive X-ray detector (EDAX). UV-Vis DRS spectra of the samples were recorded by a Shimadzu 1800 spectrometer. UV-Vis absorption spectra of MO degradation were measured by UV-Vis spectrophotometer (Perkin Elmer Lambda25, Germany). XPS test was monitored by Omicron XPS/UPS system with Argus detector which uses Omicron’s DAR 400 dual Mg/Al X-ray source.

2.5. Photocatalytic Performance Analysis

The photocatalytic activity of the prepared catalysts was analyzed by MO degradation under UV and visible lights irradiation. Each time, 0.1 gr photocatalyst was dispersed into 100 ml MO aqueous solution with a concentration of 10 mg l$^{-1}$ held in a quartz reactor (with a dimension of 12cm × 5cm, height and diameter, respectively). Two 400W Osram lamps provided the visible and UV sources, located 40 cm and 25 cm away from the reactor, respectively. The reaction system was stirred in dark for 30min to achieve absorption equilibrium, before irradiation.

3. Results and Discussions

3.1. X-ray Diffraction Patterns

Figure 1 shows the XRD patterns of parent TiO$_2$ and In, V-codoped TiO$_2$ catalysts. (101), (004), (200), (105), (211), (204), (116) diffraction peaks were proved anatase phase for the pure TiO$_2$ [35]. A main peak for anatase phase around 2θ = 25.2º (101) has tetragonal form [35]. Also no rutile phase diffraction peak was detected in the samples. Furthermore, the XRD pattern did not show any In or V phase (as in metallic or metal oxide state) and it was concluded that In and V ions were uniformly loaded onto the TiO$_2$ surface. There is also relatively small shift in In, V-codoped TiO$_2$ compared to parent TiO$_2$, which shows slight distortion in the TiO$_2$ structure.
Debye–Scherrer formula was used for measuring the average crystallite size of the prepared catalysts as follows:

$$D = \frac{K \lambda}{\beta \cos \theta} \tag{3}$$

Where $k$ is the constant which is taken as 0.9 here, $\lambda$ is the wavelength of the X-ray radiation ($\lambda= 0.1541$ nm), $\beta$ is the corrected band broadening (FWHM) full-width at half-maximum) after subtraction of equipment broadening and $\theta$ is the Bragg angle [35]. By using mentioned equation on the anatase phase ($2\theta= 25.2, 48.2, 55.2^\circ$) the average particle size was calculated for pure TiO$_2$ synthesized via hydrothermal method to be about 18.75 nm. The particle size of In, V-codoped TiO$_2$ with 0.2% mol metal content was estimated to be 14.3 nm. As it is obvious, we found that doping of TiO$_2$ by In and V ions results in decreases of TiO$_2$ catalyst particle size.

Indeed, the formation of Ti–O–In or Ti–O–V inhibits transition of the TiO$_2$ phase and blocks Ti–O species at the interface with TiO$_2$ domains, and thus preventing agglomeration of TiO$_2$ particles. Hence, doping of TiO$_2$ by In and V minimizes the charge carrier recombination during the photocatalytic decomposition of MO, and as results, it is expected that In, V-codoped TiO$_2$ show a higher photocatalytic activity compared to the pure TiO$_2$.

### 3.2. SEM-EDX Analysis

Figure 2 shows SEM micrographs of pure TiO$_2$ and 0.2% In-0.2% V/TiO$_2$ catalysts. The SEM micrographs show that the particles consist of uniform, global and slightly agglomerated particles, and the doped metal ions had not obvious influence on the morphology of the samples. Further observation indicates that the morphology of samples is very rough and maybe beneficial to enhancing the adsorption of dye due to its great surface roughness and high surface area [36]. Both narrow size distribution of nanoparticles and well dispersion are in favour of photoactivity.

The EDX measurement was carried out to verify the formation of In and V nanoclusters onto the TiO$_2$ surface after photochemical reduction. As it is obvious from Figure 3, new peaks are appeared in the TiO$_2$ spectra after metal deposition which confirms the presence of In and V in the prepared In, V/TiO$_2$ sample.

### 3.3. TEM Analysis

TEM images of pure TiO$_2$ and 0.2% In-0.2% V/TiO$_2$ catalysts are shown in Figure 4. Based on the images, the particle size of 0.2% In-0.2% V/TiO$_2$ sample was estimated to be around 11-13 nm which is in a good agreement with the particle size estimated from Debye–Scherrer formula ($12-15$ nm). Also, HRTEM image shows that the peak located at 2theta= 25 matches well with the (101) plane of anatase TiO$_2$ (JCPDS Card No. 01-065-9124), indicating the formation of anatase TiO$_2$ [37].
3.4. XPS Study of In, V-codoped TiO$_2$ Catalyst

XPS test is carried out to determine the oxidation states of In and V in In$_x$V$_y$-codoped TiO$_2$ catalyst. Figure 5 shows the XPS spectrum for In 3d and V 2p of In$_x$V$_y$-codoped TiO$_2$. As shown in Figure 5, XPS spectrum in Ti 2p region of In$_x$V$_y$-codoped TiO$_2$ shows peaks at around 456 eV (Ti 2p3/2) and 462 eV (Ti 2p1/2), which is corresponding to Ti$^{4+}$ ions in TiO$_2$ lattice [38]. The O 1s peak of the prepared In$_x$V$_y$-codoped TiO$_2$ can be seen in binding energy of around 527 eV, which is attributed to crystal lattice oxygen (O$^{2-}$) of In$_x$V$_y$-codoped TiO$_2$ (Ti–O–Ti; Ti–O–In; Ti–O–V) [38]. Our findings show that In element in In$_x$V$_y$-codoped TiO$_2$ exist in oxidation state of 3, In(III), showing peaks around 444.8 eV (In 3d$_{5/2}$) and 450.6 eV (In 3d$_{3/2}$), which is in agreement with previous reports [39]. Regarding to presence of V element in the In$_x$V$_y$-codoped TiO$_2$ catalyst, we have witnessed peak for V 2p3/2 which consists of two peaks, one at around 516 eV, related to V$^{4+}$ and around 517 eV, related to V$^{5+}$ [38].

3.5. UV-Vis DRS Analysis of In, V-codoped TiO$_2$ Catalysts

It is well-known that the photocatalytic performance of metal oxide semiconductor is closely related to its band gap structure. The UV–Vis absorbance spectra of the pure and metal doped TiO$_2$ samples are shown in Figure 6. By considering the absorbance spectra of pure TiO$_2$, the onset of the absorption appears at 380 nm, which matches well with intrinsic band gap of the anatase TiO$_2$ (3.2 eV). Also, it is obvious that there is a considerable shift in the absorption toward higher wavelength for the In, V-codoped TiO$_2$ catalyst compared to the pure TiO$_2$. The reason for that might be attributed to appearance of the new electronic energy state in the middle of TiO$_2$ band gap, which result in gap reduction between conduction band (CB) and valence band (VB) of the TiO$_2$, allowing TiO$_2$ to absorb visible light [36].
Methyl orange (MO) was used as probe environmental pollutant to study photocatalytic activity of the pure TiO$_2$ and doped TiO$_2$ catalysts. Table 1 and Table 2 show the degradation results over In-doped TiO$_2$ with various metal content synthesized via hydrothermal-assisted photochemical reduction and sol-gel assisted photochemical reduction, respectively, and Figures 7 and Figures 8 demonstrate photocatalytic performance of In,V-codoped TiO$_2$ with various metals content synthesized via sol-gel assisted photochemical reduction and hydrothermal-assisted photochemical reduction, respectively. Before shining UV or visible light on the catalysts, the MO solution containing the catalysts were stirred in dark for half an hour. Our detection results exhibited that the MO concentration showed negligible decrease due to slight absorption on the photocatalysts surface, which showed that there was almost no MO decomposition in the absence of light irradiation.

### Table 1. The photocatalytic results of MO degradation using In-doped TiO$_2$ nanoparticles with various In(III) content, prepared via hydrothermal assisted photochemical deposition.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>37.32</td>
<td>59.77</td>
<td>81.07</td>
<td>90.80</td>
</tr>
<tr>
<td>0.05</td>
<td>43.91</td>
<td>59.78</td>
<td>75.71</td>
<td>82.56</td>
</tr>
<tr>
<td>0.1</td>
<td>35.42</td>
<td>48.58</td>
<td>67.82</td>
<td>82.68</td>
</tr>
<tr>
<td>0.2</td>
<td>52.41</td>
<td>71.72</td>
<td>86.51</td>
<td>95.09</td>
</tr>
<tr>
<td>0.5</td>
<td>46.28</td>
<td>81.99</td>
<td>88.66</td>
<td>98.47</td>
</tr>
<tr>
<td>0.8</td>
<td>45.21</td>
<td>78.47</td>
<td>88.12</td>
<td>96.17</td>
</tr>
<tr>
<td>1</td>
<td>38.16</td>
<td>60.69</td>
<td>81.53</td>
<td>92.18</td>
</tr>
<tr>
<td>2</td>
<td>44.67</td>
<td>64.37</td>
<td>81.23</td>
<td>92.87</td>
</tr>
</tbody>
</table>

### Table 2. The photocatalytic results of MO degradation using In-doped TiO$_2$ nanoparticles with various In(III) content, prepared via sol-gel assisted photochemical deposition.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>15</th>
<th>30</th>
<th>90</th>
<th>120</th>
<th>150</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>23.85</td>
<td>34.18</td>
<td>48.15</td>
<td>62.98</td>
<td>69.38</td>
</tr>
<tr>
<td>0.05</td>
<td>26.15</td>
<td>45.56</td>
<td>60.15</td>
<td>74.21</td>
<td>79.81</td>
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<tr>
<td>0.1</td>
<td>28.66</td>
<td>48.89</td>
<td>70.81</td>
<td>93.55</td>
<td>98.89</td>
</tr>
<tr>
<td>0.2</td>
<td>28.89</td>
<td>46.07</td>
<td>61.63</td>
<td>77.63</td>
<td>82.78</td>
</tr>
<tr>
<td>0.5</td>
<td>9.18</td>
<td>22.36</td>
<td>36.15</td>
<td>47.48</td>
<td>52.72</td>
</tr>
<tr>
<td>0.8</td>
<td>8.02</td>
<td>19.51</td>
<td>29.63</td>
<td>41.52</td>
<td>48.21</td>
</tr>
<tr>
<td>1</td>
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<td>37.18</td>
<td>51.48</td>
<td>66.07</td>
<td>72.13</td>
</tr>
<tr>
<td>2</td>
<td>26.89</td>
<td>43.11</td>
<td>58.59</td>
<td>73.19</td>
<td>78.32</td>
</tr>
</tbody>
</table>

By using the following equation, band gap values of the pure TiO$_2$ and In, V-codoped TiO$_2$ catalysts were calculated [40]:

$$E_g = \frac{h c}{\lambda}$$  

where, $E_g$ = band gap energy, $h = \text{Planck’s constant in eV (4.135 \times 10^{-15} \text{ eV})}$, $C = \text{velocity of light (3 \times 10^8 \text{ m/s})}$, $\lambda = \text{wavelength of the corresponding catalysts}$. We found that the band gap values were lower for the doped catalysts (below 3 eV) compared to the pure TiO$_2$ catalyst (up to 3 eV).

Furthermore, the V 3d energy state and In 4d energy state play important roles in interfacial charge transfer and elimination of charge recombination. Thus, transition metal ions (V and In) would act as an efficient electron scavenger to trap the electrons of CB state of TiO$_2$ [35]. Accordingly, it can be presumed that the In, V-TiO$_2$ photocatalyst may demonstrate higher photocatalytic activity under visible light irradiation, compared to the pure TiO$_2$.

### 3.6. Photocatalytic Performance of In, V-codoped TiO$_2$ Catalysts

Methyl orange (MO) was used as probe environmental pollutant to study photocatalytic activity of the pure TiO$_2$ and metal-doped TiO$_2$ catalysts. Table 1 and Table 2 show the degradation results over In-doped TiO$_2$ with various metal content synthesized via hydrothermal-assisted photochemical reduction and sol-gel assisted photochemical reduction, respectively, and Figures 7 and Figures 8 demonstrate photocatalytic performance of In,V-codoped TiO$_2$ with various metals content synthesized via sol-gel assisted photochemical reduction and hydrothermal-assisted photochemical reduction, respectively.

![UV-Vis DRS absorption spectra of as-prepared TiO$_2$ and In, V-codoped TiO$_2$ nanoparticles with different metal content.](chart1.png)

![Fig. 6.](chart2.png)
As it is apparent from Table 1, all In-doped TiO₂ nanoparticles are visible light active. The optimal dosage of indium ion to get highest photocatalytic activity for MO decomposition was found to be 0.1% (hydrothermal-assisted photodeposition) and 0.2% (sol-gel assisted photodeposition) under visible light and 0.5% (hydrothermal-assisted photodeposition) and 2% (sol-gel assisted photodeposition) under UV light illumination.

Our findings regarding to In, V-codoped TiO₂ catalyst prepared with sol-gel assisted photodeposition technique (Figures 7), illustrate no improvement in photocatalytic performance in comparison to pure TiO₂. But in case of In, V-codoped TiO₂ catalyst prepared with hydrothermal-assisted photodeposition technique (Figures 8), we found that TiO₂ catalyst with 0.2% metal content achieved the higher rates of MO decomposition compared to the pure TiO₂ catalyst. Indeed, in the In, V-codoped TiO₂ catalyst the metal could acts as electron trapper and thus reduce the charge recombination rate which is in favour of photocatalytic activity enhancement. The improvement of pollutant degradation was initially increased with the increase of metal content, but it was declined while the metal content reached a high level [41-43]. As matter of fact, in In, V-codoped TiO₂ catalysts with metal content of higher than 0.2%, the metal ions acts as electron-hole recombination center which as result decreases the photo-efficiency and photocatalytic activity.

To investigate the In³⁺ doping effect on the photocatalytic performance of TiO₂, it was found that loading indium ions onto TiO₂ particles prevent the particle growth and In³⁺ change to In²⁺ as electron trapper by forming a low energy level between CB and VB of TiO₂. In absence of light irradiation, In²⁺ ions convert to In³⁺ and atmospheric O₂ traps released electron as electron acceptor and produce O₂⁻. The process mechanism is shown below:

\[
\begin{align*}
\text{TiO}_2 + h\nu &\rightarrow \text{e}^-_{\text{cb}} + h^+_{\text{vb}} \quad (9) \\
\text{Ti}^{4+} + \text{e}^-_{\text{cb}} &\rightarrow \text{Ti}^{3+} \quad (10) \\
\text{M} + \text{e}^-_{\text{cb}} &\rightarrow \text{M}^- \quad (11) \\
\text{Ti}^{4+} + \text{M} &\rightarrow \text{Ti}^{4+} + \text{M}^- \quad (12)
\end{align*}
\]

where \( h\nu \) represents the light irradiation energy, \( \text{e}^-_{\text{cb}} \) and \( h^+_{\text{vb}} \) represent the photogenerated electrons in CB and holes in the VB.
of TiO$_2$, respectively. Ti$^{3+}$ and M$_x$ represent the titanium ions or atoms in the TiO$_2$ crystal and metal atoms or ions in the metallic clusters, respectively. The number of electrons in the bulk TiO$_2$ is reduced; thereby the possibility of recombination (Eqs. (13) and (14)) is declined:

\[ e^{-} + h^{+} \rightarrow \text{recombination} \]  
\[ \text{Ti}^{3+} + h^{+} \rightarrow \text{Ti}^{4+} \]  

In general, most of the photogenerated electrons and holes recombine through Eqs. (13) and (14) processes, and only a small number remain for the photocatalytic reactions. By using IR spectroscopic, it was reported that electron transfer from the TiO$_2$ support to the deposited metal clusters is the bottleneck of the photocatalytic reactions [44].

Based on our findings, there is a significant potential to enhance efficiency of photocatalytic reactions through improving charge separation and charge transfer using proper metal nanoclusters loading over TiO$_2$ catalysts.

4. Conclusions
In the current study, a series of novel In, V-codoped TiO$_2$ catalysts with different In and V contents were synthesized by photochemical reduction technique and were used as photocatalyst to decompose MO as probe pollutant in aqueous solution. XRD and EDAX analysis didn’t show any peaks to confirm the appearance of unwanted impurities. SEM analysis confirmed that all samples are uniform, global and slightly agglomerated and TEM analysis confirmed the results diagnosed from SEM and XRD analysis. The photocatalytic activity of pure TiO$_2$ is greatly improved in presence of loaded metal nanoclusters with 0.2% In and 0.2% V content. The high visible-light-driven photocatalytic activity of In and V modified TiO$_2$ is ascribed to the synergetic effects of (1) decreased particle size; (2) improved visible-light harvesting ability due to formation of subenergy levels in TiO$_2$ structure, and (3) improved efficiency in separation of photo-generated charge carriers. This investigation contributes to the understanding effects of the complex ion doping on TiO$_2$ photocactivity and thus, provides a reference for improving its environmental application.

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References