Highly efficient nitrobenzene photoreduction over the amino acid-modified CdS-TiO$_2$ nanostructures under visible light

Mohsen Padervand 1 *, Atefeh Rahmani 2, Sara Rahimnejad 3, Mohammad Reza Gholami 2

1 Faculty of Science, Department of Chemistry, University of Maragheh, Maragheh, Iran
2 Department of Chemistry, Sharif University of Technology, Tehran, Iran
3 Department of Chemistry, Islamic Azad University, Shahr-e-Rey Branch, Tehran, Iran

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ABSTRACT

CdS-coupled TiO$_2$ nanocrystals were prepared by the microemulsion-mediated solvothermal method at pretty low temperatures. The semiconductor nanocrystals were modified with tyrosine, phenylalanine, glycine and glutamate amino acids and then were characterized by BET, SEM, EDX, XRD, UV–Vis spectroscopy, and FTIR analysis methods. The specific surface area and the average pore diameter were found to be about 470 m$^2$ g$^{-1}$ and 2.8 nm, respectively. Moreover, the average size of the CdS-TiO$_2$ particles was evaluated to be 28 nm. The results showed that the modification process with the amino acids improves the adsorption capability and photoactivity of the samples. Among them, tyrosine was determined to be the best choice. According to the results, modification of CdS-TiO$_2$ heterojunction photocatalyst with electron-donating groups is an efficient strategy to increase the photoreduction of nitroaromatic compounds. Reusability experiments were also carried out and confirmed the high capacity of the prepared samples for the photoconversion of nitrobenzene after being repeated for four times.

INTRODUCTION

Nitrobenzene is considered to be a highly toxic aromatic compound which is widely used in explosives, pesticides, prepharmo, dye production, lubricating oils, refinement, soaps or shoe polish production and so on. As a suspected carcinogenic and toxic compound, it poses a high threat to the human health. It may carry a high risk for the environment, even at low concentrations [1]. The strong electron affinity of nitro reduces the electron cloud density of the benzene ring and makes nitrobenzene very stable. Therefore, nitrobenzene is listed as one of the prior pollutants by many countries. Conventional methods for the removal of nitrobenzene from aqueous solutions can be divided into three main categories: physical, chemical and biological treatments [2-5].

Mineralization of nitrobenzene by microorganisms is prevented by the electron-deficient character of the nitro-group. Due to electron-deficiency, oxidation of nitroaromatic compounds is very difficult to achieve [6]. Therefore, conventional biological treatment processes are not effective for the treatment of nitrobenzene-rich wastewater. Nanosized particles of titanium dioxide have remarkable photocatalytic properties and have many applications in medicine, construction and environmental remediation. Lots of efforts have been made to modify titania to enhance the photocatalytic performance and develop multifunctional materials. It has been reported that the composite structure can affect the catalytic activity of catalytic nanostructures [7-15].

CdS–TiO$_2$ is an excellent candidate for photodecomposition of pollutants as result of...
its intrinsic energy band gap. The main drawback of TiO$_2$ is its large band-gap (anatase: 3.2 eV and rutile: 3.0 eV). As a consequence, TiO$_2$ shows the photocactivity only in the near ultraviolet region and can harvest only a small fraction (<5%) of incident solar irradiation [16]. CdS is very unstable against the photocorrosion in aqueous solutions under irradiation unless the solutions contain sacrificial agents, such as S$^2$– and/or SO$_3^{2–}$ [17, 18]. They can compensate the disadvantages of individual component and induce a synergistic effect such as an efficient charge separation and improve the photostability. CdS is a fascinating material having ideal band gap energy. Recently, the surface complexation of TiO$_2$ nanocrystals with some benzene derivatives [19], amino carboxylic acids [20, 21] and arginine [22] resulted in enhancement of adsorption capability of nitroaromatic compounds in order to develop a useful strategy for photocatalytic removal of nitroaromatics from waste water.

The most important advantages of the microemulsion method are to provide a transparent, isotropic and thermodynamically stable synthesis medium. In particular, water-in-oil microemulsions are formed by well-defined nanodroplets of the aqueous phase, dispersed by the assembly of surfactant molecules in a continuous oil phase. These nanodroplets can provide a restricted reaction media to control the shape and size distribution of particles prepared by precipitating.

We used a microemulsion approach to facilitate the direct formation of nanocrystalline TiO$_2$ coupled with the CdS nanocrystals at a considerably lower temperature by the solvothermal method [25]. This method can prevent the oxidation of CdS in CdS/TiO$_2$ nanocomposite during thermal treatment for the crystallization of TiO$_2$ [26]. Afterward, the activities of the prepared samples were evaluated by selective photoreduction of nitrobenzene to aniline under visible light.

**EXPERIMENTAL**

**Materials and methods**

Titanium tetraisopropoxide (TTIP) was used as a titanium source. Cd(NO$_3$)$_2$ and (NH$_4$)$_2$S, which were used as CdS precursors, and nitrobenzene (NB) were purchased from Merck company (Germany). A typical synthesis of (CdS at 3%) involved the use of cyclohexane (0.9 mol) as oil phase, Triton X-100 (0.028 mol) as surfactant and 1-hexanol (0.056 mol) as cosurfactant [25]. Three microemulsions containing 1 mL of water (A), 1.5 mL of 0.3M Cd(NO$_3$)$_2$ solution (B) and 2.5mL of 20 wt% (NH$_4$)$_2$S solution (C) were prepared. Titanium isopropoxide (14.55 mmol) was added to microemulsion (A) under continuous stirring. After titanium isopropoxide was gradually hydrolyzed and condensed in water nanodroplets for 30 min, microemulsion B was mixed with microemulsion A under vigorous agitation and sonicated for 5 min. Microemulsion C was then added into the mixture and sonicated for 5 min. This new microemulsion was stirred for 24 h at room temperature. In this process, cadmium sulfide was incorporated into the TiO$_2$ colloids by simultaneous coprecipitation of Cd(NO$_3$)$_2$ and (NH$_4$)$_2$S in the water nanodroplets. The resulted microemulsion containing CdS and TiO$_2$ particles was placed in a 100 mL Teflon-lined stainless steel autoclave which is initially bubbled with N$_2$ gas for 10 min and then solvothermally treated at 180°C for 16 h.

The obtained yellow slurry was centrifuged and washed with ethanol and water before finally being kept in a desiccator for drying. The modified CdS-TiO$_2$ catalyst (0.5 g) was achieved by soaking the prepared CdS-TiO$_2$ in the amino acid ethanolic solution (50 mL, 0.01 M) and sonicating for 10 min in order to have a well dispersed and homogenous surface at room temperature. It was soaked for 24 h and then dried. Once amino acids were anchored to TiO$_2$ particles, they were strongly bounded to it [27].

**Characterization**

The residual concentration of NB at different times was measured on a GC (Agilent, 6890 series, USA) (60 m HP-5 column, film thickness 1 µm, inside diameter 0.25 mm and FI detector). The X-ray diffraction (XRD) pattern of prepared samples was recorded on Bruker D8 advance X-ray diffractometer with CuKα irradiation (λ= 0.15406). The FTIR spectra were performed on the NB series spectrometer. The specific surface area of photocatalysts was calculated from the N$_2$ adsorption-desorption isotherm at 77 K, using Belsorp apparatus. The average particle size and morphology of photocatalysts were distinguished by scanning electron microscope (SEM) (XL30 model). An OSRAM 125 W lamp was used as a visible source as we can see the emission spectra of the illumination source in Fig. 1. Diffuse reflectance spectroscopy (DRS) analysis was performed.
with a UV spectrophotometer (GBC Cintra40). The specific surface area of photocatalysts was calculated from the $N_2$ adsorption-desorption isotherm at 77 K, using Belsorp apparatus.

**Photocatalytic activity**

The photocatalytic activity measurements for the degradation of NB were performed in a quartz reactor that was placed 10 cm in front of the visible lamp with 125 W and surrounded by a circulating water jacket (Pyrex) to cool the lamp. 0.1 g of the prepared photocatalyst was suspended in a 100 mL aqueous solution of 0.0136 M (NB) whose pH has been adjusted by phosphate buffers. Prior to irradiation, the suspensions were magnetically stirred in the dark for 10 min to ensure the establishment of an adsorption/desorption equilibrium among the photocatalyst. At given irradiation time intervals of 20 to 120 min, 2.5 ml of the suspensions was collected, then centrifuged and filtered to separate the photocatalyst particles.

The aqueous solutions obtained from filtration of the samples were extracted three times with $\text{CH}_2\text{Cl}_2$. The organic extracts were concentrated under a stream of nitrogen and analyzed by GC/MS (Agilent 6890). The oven temperature was programmed as follows: isothermal at 40 °C for 3 min, from 40 °C to 260 °C at 10 °C/min, and isothermal at 260 °C for 1 min. The conversion of NB in the reaction process could be calculated by using the following formula [20]:

$$\text{% Conversion} = \frac{C_0 - C_n}{C_0} \times 100$$

where $C_n$ and $C_0$ are the measured and initial concentration of NB respectively.

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**Fig. 1.** The emission spectra of 125 W mercury lamp.

**Fig. 2.** XRD patterns of CdS-TiO$_2$-Tyrosine (a) after calcination (b) without calcinations.
RESULTS AND DISCUSSION

Characterization

XRD analysis

The XRD patterns of CdS-TiO$_2$-Tyrosine are represented in Fig. 2. Due to the low amount of loaded amino acid, the new diffraction peaks did not appear in the pattern of photocatalyst contained amino acid compared to pure CdS-TiO$_2$ sample. The results reveal that the peaks intensity of crystalline phases of samples has not changed before and after calcination, and it can be seen that there is no obvious difference. The results show that the crystalline phase of TiO$_2$ and CdS has not changed after the modification with Amino acid. The characteristic peaks in 2θ = 25.2°, 37.92° and 48.02° correspond to the anatase TiO$_2$. The additional peaks at 26.5°, 43.9°, 52.1° which can be assigned to the CdS cubic phase (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes, respectively, were also observed in Fig. 2 [25].

FTIR analysis

To understand the details of photocatalytic mechanism of the prepared composites, the FTIR analysis was conducted after the experiments while acidity conditions were changed. Fig. 3 shows the FTIR spectra of CdS-TiO$_2$-Tyrosine after using in acidic and basic conditions.
FTIR spectra of the extracted photocatalyst after being tested in acidic (a) and basic (b) conditions. The peak appearance in 825 cm\(^{-1}\) can be related to the N-H bond and also to the stretching C-N bond. Both peaks indicate that the compounds such as aniline can be adsorbed on the catalyst surface by donating groups and enhancing the photocatalytic activity. We suggest that aniline acts as a hole scavenger and that its presence on the surface decreases the electron-hole recombination and increases the photocatalytic efficiency. The peaks around 3400 cm\(^{-1}\) and 1600 cm\(^{-1}\) are due to O–H stretching and O–H bending modes, respectively. Also, the peaks related to Ti-O and Cd-S appear in the frequencies lower than 700 cm\(^{-1}\).

**SEM analysis**

The SEM images of the prepared nanostructures are shown in Fig. 4. The micrographs show that the distribution of the surface particles is homogenous. The microemulsion synthesis method achieves the homogenous and average small particle size (28 nm), although the surfactant plays the role of controlling particle size and inhibiting the coagulation. Modifying CdS/TiO\(_2\) nanocomposite with amino acid, the surface homogeneity has not changed, however the variation of the average particle size is observed.

The microemulsion method benefits droplet water as the microreactor which can provide the proper media for nucleation and controlling the
growth process of the particles. In the process of modifying by amino acid, the organic solvent such as methanol was used. This organic solvent prevents the agglomeration of nanoparticles. As a result, the average particle size has been increased to 43 nm which is due to the presence of the organic layer (the aminoacids) covered the surface of CdS-TiO$_2$ nanoparticles. The SEM micrograph indicates that the bulk particles have a spherical shape before and after loading the amino acids and a porous structure could be observed in all samples.

**BET analysis**

Table 1 shows the surface area and pore size distribution of CdS-TiO$_2$, CdS-TiO$_2$-Tyrosine photocatalysts. The data demonstrated that modifying CdS-TiO$_2$ by amino acid increased the surface area but did not change the pore volume and the average pore diameter. On the basis of the hysteresis loop, adsorption and desorption branches of CdS-TiO$_2$ and CdS-TiO$_2$-Tyrosine have not changed. The results indicated that modifying with amino acid has not influenced the surface morphology. The MP-Plot (Fig. 5) and BJH (Fig. 6) of the CdS-TiO$_2$, CdS-TiO$_2$-Tyrosine show that the pore diameter was narrow, mainly below 2 nm. BJH plots are not a conventional Gussian curve, indicating the micropore size.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>Mean pore size (nm)</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS-TiO$_2$</td>
<td>423.94</td>
<td>2.8397</td>
<td>0.3010</td>
</tr>
<tr>
<td>CdS-TiO$_2$-Tyrosine</td>
<td>470.74</td>
<td>2.8655</td>
<td>0.3372</td>
</tr>
</tbody>
</table>

*a* BET surface area calculated from the linear part of the BET plot.

*b* Estimated using the BJH desorption branch of the isotherm.

*c* Single point total pore volume of pores at $P/P_0 = 0.97$.

**Table 2. Elemental Analysis of photocatalysts (CdS-TiO$_2$ and CdS-TiO$_2$-Tyrosine)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>W%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS-TiO$_2$</td>
<td>S</td>
<td>3.93</td>
<td>5.84</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>2.52</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>93.55</td>
<td>93.09</td>
</tr>
<tr>
<td>CdS-TiO$_2$-Tyrosine</td>
<td>S</td>
<td>3.72</td>
<td>5.61</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>4.64</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>91.63</td>
<td>92.40</td>
</tr>
</tbody>
</table>

**Fig. 7.** UV–vis absorption spectra of prepared photocatalysts (a: CdS-TiO$_2$-Tyrosine, b: CdS-TiO$_2$)
Energy dispersive X-ray (EDX) analysis

The elemental contents of CdS-TiO\textsubscript{2} and CdS-TiO\textsubscript{2}-Tyrosine composite listed in Table 2 show that Ti, O, Cd and S are mainly elemental contents of CdS-TiO\textsubscript{2} and catalyst purity. The amount of amino acid is so small that no related elemental contents are observed in the EDX analysis, which is consistent with the XRD patterns.

UV–Vis diffuse reflection spectroscopy

The diffused reflectance UV–Vis absorption spectra of the CdS/TiO\textsubscript{2} and CdS-TiO\textsubscript{2}-Tyrosine are shown in Fig. 7. The CdS/TiO\textsubscript{2} sample exhibits the strong absorption peaks in the visible region and the peaks related to CdS-TiO\textsubscript{2}-Tyrosine shift to a longer wavelength. It shows that amino acid as an impurity induces a few levels between the valence and conduction band of the composite. In addition, the edges of the absorption of CdS-TiO\textsubscript{2}-Tyrosine sample were shifted to approximately 472.1 nm, corresponding to band gap energy of 2.62 eV [14, 16]. The absorption onsets were determined by linear extrapolation from the inflection point of the curve to the baseline. To compare, the absorption onsets for CdS-TiO\textsubscript{2} and CdS-TiO\textsubscript{2}-Tyrosine were determined 392.56 and 472.1 nm, corresponding to band gap energies of 3.16 and 2.62 eV, respectively.

Photoconversion of nitrobenzene (NB)

Effect of surface modification on the adsorption capability

It is obvious that in the heterogeneous photocatalysis the efficiency of photocatalytic reaction is affected by the surface adsorption of organic compounds. The adsorption capability of the modified CdS-TiO\textsubscript{2} photocatalysts as a different type of amino acids was investigated and a comparison with CdS/TiO\textsubscript{2} was made. The results showed that the adsorption capability greatly increased in all modified photocatalysts. The hydrogen bonding and the n-π and π-π interactions between the modified TiO\textsubscript{2} and nitrobenzene are responsible for the stronger adsorption capability [2]. The results for this study are shown in Fig. 8.

The effect of modification on the photoconversion efficiency

Fig. 8 shows the results for the conversion of nitrobenzene over different modified CdS-TiO\textsubscript{2} photocatalysts in the aqueous medium. From Fig. 9

![Figure 8](image-url)  
Fig. 8. Effect of surface modification on the adsorption capability (catalyst: 0.1 g, NB: 0.0136 M)

![Figure 9](image-url)  
Fig. 9. The effect of opted amino acid for surface modification on the NB conversion (%) (catalyst: 0.1 g, NB: 0.0136 M, irradiation time: 120 min, pH: neutral).
we can find out that the conversion of modified CdS-TiO₂ was higher than that of bared CdS-TiO₂, while the photoconversion efficiency decreased according to the following: Tyrosine-CdS-TiO₂ > Phenylalanine-CdS-TiO₂ > Glutamate/CdS-TiO₂. Obviously, Tyrosine-CdS-TiO₂ is the most active catalyst in aqueous condition. The results indicate that the reaction is influenced by the surface of TiO₂. In addition, coupling of CdS with TiO₂ can delay the electron hole recombination in titanium dioxide (which is active in the UV region). Different amino acids were taken in to modify CdS-TiO₂ for the positive effect on conversion of NB to Aniline. The loading of amino acids increased both the adsorption of NB and photocatalyst activity. Adding the amino acids can prevent the electron hole recombination, because they have strong electron donating properties and act as a hole trap. In addition, amino acids ameliorate the coupling between NB and CdS-TiO₂, and transferring electrons from the conduction band of CdS-TiO₂ to NB can be conducted with negligible activation energy [3]. The photoactivity yield is highest for the modified photocatalyst with tyrosine due to the presence of the phenyl group in the tyrosine structure which is similar to the NB structure. Therefore, the adsorption of NB increases compared to glysine, phenylalanine and glutamate. In addition, the OH group on the tyrosine structure participates in both hydrogen bonding and π-π interaction between the amino acid and support. This results in an increase in the photocatalytic conversion yield.

Fig. 10. The effect of acidic, natural and basic media on the conversion of NB (%) (catalyst: 0.1 g, NB: 0.0136 M, irradiation time: 120 min)

Fig. 11. The effect of amount of loaded amino acid on the conversion (%) of NB (catalyst: 0.1 g, NB: 0.0136 M, irradiation time: 120 min, pH: neutral)

Fig. 12. Kinetic study of NB photoreduction (catalyst: 0.1 g, NB: 0.0136 M, under optimized conditions)
The effect of pH

The effect of pH on the photoactivity of Tyrosine-CdS-TiO₂ has been studied and the results are shown in Fig. 10. From Fig. 10 we can find out that by increasing the acidity of the medium, the photocatalytic efficiency enhances. This can be related to the structural reformation of the photocatalyst surface. Fig. 3 shows the FTIR analysis for these composites after being used in acidic and basic conditions. The appearance of new peaks at 825, 1245 cm⁻¹ in the acidic medium is related to the amino benzene stretching vibration in the photocatalyst. This observation shows that during the photoreduction conversion of nitrobenzene, a part of products (such as aniline) is strongly bonded to the photocatalyst after being formed. Thus, the photocatalyst surface is being rich of electron donating agents (both amino acid and aniline), the electron hole recombination delays and the efficiency enhances.

The effect of loaded amino acid

The effect of amino acid loading on photoreduction of NB was studied in the range of 5% to 20% of amino acid and the results were compared with pure CdS-TiO₂ presented in Fig. 11. Photoactivity can be related to the availability of active sites on the TiO₂ surface. Increasing the tyrosine amount enhances the photoconversion rate. Tyrosine can enhance the efficiency by trapping the holes from the CdS-TiO₂ photoactivity and reducing the electron-hole recombination. The photoreduction efficiency is enhanced up to 10% of the amount of amino acid, but then decreases due to the covering of active sites of CdS-TiO₂ surface and light scattering. Therefore, we used 10% loaded amino acid as the optimum amount during the next experiments.

Kinetic study

Fig. 12 shows the kinetics of NB (solubility 0.2g/100 ml in water) photoreduction for an initial concentration of 0.0136 M under the optimized conditions with CdS-TiO₂-Tyrosine. The results indicated that the photocatalytic reduction of the NB can be described by the first-order kinetic model, \( \ln(C_0/C) = k_{app} t \).
CONCLUSIONS

The authors declare that there is no conflict of interests regarding the publication of this paper.

REFERENCES


15. Padervand M. Visible-light photoactive Ag-AgBr/[alpha]-
Ag^+ sub 3^\text{+} VO^+ sub 4^\text{+} nanostructures prepared in a water-
soluble ionic liquid for degradation of wastewater. Applied

16. Padervand M, Karanji AK, Elahifard MR. Copper, gold,
and silver decorated magnetic core–polymeric shell
nanostructures for destruction of pathogenic bacteria.

2015;5(14):1500010-n/a.

18. Li G-S, Zhang D-Q, Yu J-C. A New Visible-Light Photocatalyst:

19. Padervand M, Tasviri M, Gholami M. Effective photocatalytic
degradation of an azo dye over nanosized Ag/AgBr-modified

20. Elahifard M, Padervand M, Yasini S, Fazeli E. The effect of
double impurity cluster of Ni and Co in TiO2 bulk; a DFT

21. Padervand M, Reza Elahifard M, Vatan Meidanshahi R,
Ghasemi S, Haghighi S, Reza Gholami M. Investigation of
the antibacterial and photocatalytic properties of the zeolitic
nanosized AgBr/TiO2 composites. Materials Science in

Photocatalytic Degradation of 4-Nitrophenol in Aqueous
Suspension by Using Polycrystalline TiO2 Impregnated with
Lanthanide Double-Decker Phthalocyanine Complexes. The

23. Ramazani A, Hamidi S, Morsali A. A novel mixed-ligands
holodirected two-dimensional lead(II) coordination
polymer as precursor for preparation lead(II) oxide
nanoparticles. Journal of Molecular Liquids. 2010;157(1):73-
7.

24. Wu L, Yu JC, Fu X. Characterization and photocatalytic
mechanism of nanosized CdS coupled TiO2 nanocrystals
under visible light irradiation. Journal of Molecular Catalysis

CdS/TiO2 photocatalyst with high stability and activity:
Effect of mesoporous substrate and bifunctional linking
molecule. Journal of Materials Chemistry. 2011;21(13):4945-
52.

photoreduction of nitrobenzene to aniline on TiO2
nanoparticles modified with amino acid. Journal of

27. Fardood ST, Ramazani A, Moradi S. Green synthesis of
Ni–Cu–Mg ferrite nanoparticles using tragacanth gum
and their use as an efficient catalyst for the synthesis of
polyhydroquinoline derivatives. Journal of Sol-Gel Science