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Visible light motivated synthesis of polyhydroquinoline derivatives using CdS nanowires

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Abstract In this article, we report the synthesis of one-dimensional cadmium sulphide nanowires (CdS NWs) by chemical synthesis approach. These as-synthesized materials were characterized by ultraviolet–visible spectroscopy, X-ray diffraction, scanning electron microscopy with energy dispersive spectroscopy, and transmission electron microscopy analysis. These nanowires have an average diameter of $\sim$20 nm and length up to several micrometres. CdS NWs are highly stability and are found to be a very efficient recyclable/reusable (minimum four times without any significant loss) photocatalyst for polyhydroquinoline synthesis under visible light (Halogen lamp, 70 W) at room temperature. This system offers a mild, efficient, and highly economical alternative to the existing protocols in its catalytic activity under visible light irradiation ($\lambda \geq 420$ nm). These findings will open up new opportunities for developing low-cost efficient photocatalyst synthesis of value added intermediates.

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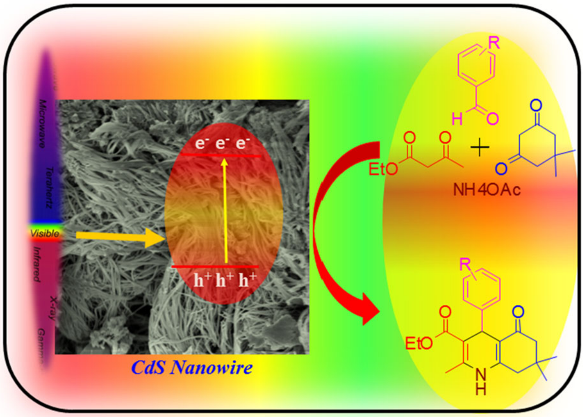
Graphical abstract



Keywords CdS nanowires · Photocatalyst · Polyhydroquinoline · Visible light · Green approach

Introduction

Nowadays, photocatalysis is of promising significance for the purpose of environmental protection/remediation. However, heterogonous photocatalysis by semiconductor materials has been gaining increasing interest due to its promising potential towards solar energy renovation [1–5]. Conventional chemical processes use hazardous reagents that are concerning considering the environmental crises. Moreover, transition metal complex-based homogenous photocatalysts also ultimately generate secondary toxic wastes. To overcome these issues, developing an alternative semiconductor based heterogenous photocatalyst that is new, efficient, stable, eco-friendly, clean, and by greener approach, as well as its sustainable are a great challenge to the chemist.

Furthermore, the most commonly studied semiconductors, such as TiO_2 and ZnO, with band-gap 3.2 and 3.4 eV, respectively, absorb ultraviolet photons that account for less than 5% of solar light [6]. In contrast to this, cadmium sulfide (CdS), a typical II–VI semiconductor, has been extensively explored and become an alternative in the field of photocatalysis due to its having a shorter and suitable band-gap (2.4 eV) corresponding well with the spectrum of sunlight. Because of the larger surface area (high surface to volume ratio), high capacity for absorbing solar light, and many active sites, CdS semiconductors offer wide applications in H_2 generation reactions [7], photochemical reduction of CO_2 [8], solar cells [9], photolytic cells [10], and also in organic transformations [11–14]. Compared to bulk CdS and its nanoparticles (NPs), one-dimensional (1D) CdS nanowires (NWs) have recently attracted special attention due to their firm and prolonged distance electron transportation based on its exclusive 1D geometry.

However, it has extraordinary (enhanced) light absorption/interaction capacity and scattering due to the high length-to-diameter/width ratio of CdS NWs [15–18]. Hence, it is of substantial interest to examine the potential applications in organic transformation of 1D CdS NWs as a heterogeneous photocatalyst [19–22].

Significantly, among the *N*-heterocyclic intermediates, polyhydroquinoline has attracted much attention because of its diverse pharmacological and therapeutic properties such as vasodilation, bronchodilation, anti-mutagenic, anti-atherosclerotic, anti-hypertensive, hepatoprotective, antitumor, geroprotective, and anti-diabetic [23]. The polyhydroquinoline derivatives are found in many drugs such as nifedipine, nitrendipine, and nimodipine, which explain the important efforts devoted to the synthesis of these heterocycles [24]. Several methods have been reported for the preparation of the polyhydroquinoline using various catalysts such as molecular iodine [25], iron(III) trifluoroacetate [26], L-proline [27], ceric ammonium nitrate [28], heteropoly acid [29], Sc $(OTf)_3$ [30], baker's yeast [31], p-TSA [32], trimethylsilyl chloride (TMSCl) [33], Yb $(OTf)_3$ [34], MgO, and Fe_3O_4 nanoparticles [35, 36]. Unfortunately, most of these methods have several disadvantages such as the use of high temperature, expensive metal precursors, environmentally harmful catalyst, and harsh reaction condition. Interestingly, smaller nanoparticles with their high active surface area (larger active sites for use) coupled with visible light as a source of energy is the best alternative for conventional methods. Moreover, as previous literature shows, Das et al. [37] have been reported the synthesis of the 2-substituted benzothiazoles using CdS nanosphere in visible light. However, (from this report) we focus on the catalytic activity of CdS nanospheres in condensation reaction for the synthesis of benzothiazoles, which encourages us to check the catalytic activity of as-synthesised 1D CdS nanowires as catalyst for the synthesis of potent biologically active polyhydroquinoline in the presence of visible light as an energy source.

Synthesis of CdS bulks

Briefly, the preparation method of CdS bulks involves initially $3CdSO_4{\cdot}8H_2O$ (0.5 mmol) dissolved in 40 mL DI water mixed with thiourea (1 mmol) in the 20 mL DI water, and the pH of the solution was adjusted to 9–10 by slow addition of aqueous ammonium hydroxide under stirring. This resulting mixture was stirred further for 1 h at 70 °C without addition of any external reducing and capping agent. A yellow precipitate was obtained, which was separated by centrifugation and washed with ethanol and water several times. The product was then dried in a vacuum oven at 120 °C for 3–4 h.

Synthesis of CdS nanowires (NWs)

CdS nanowires were synthesised using tetrabutyl ammonium bromide (TBAB) as a capping agent. In brief, the above prepared aqueous solution of $CdSO_4$ (50 mL) was mixed with an aqueous solution of thiourea (20 mL) and the pH of the solution was adjusted to 9–10 by slow addition of dilute ammonium hydroxide solution. Another 0.5 g TBAB was added, which acts as a capping agent to avoid the further aggregation of the nanoparticles. In continuation of this, the reaction mixture was then stirred for 1 h at 70 °C. A yellow precipitate was obtained, indicating the formation of CdS nanowires. This yellow precipitate was separated from the reaction mixture by centrifugation and washed several times with ethanol and water to remove excess/unbound capping agent and other side products. The product was then dried in a vacuum oven at 120 °C for 3–4 h. Further, the formation of CdS nanowires along with their morphology and wire size was proven by SEM and TEM images at different magnifications. Accordingly, Fig. 1a shows low magnification scanning electron microscope (SEM) image of as-synthesised 1D CdS NWs, and Fig. 1b shows low magnification TEM image with 20 nm size and insets of the surface morphology of single CdS NWs. Fig. 2a shows high magnification CdS NWs with uniform 20 nm size; Fig. 2b shows the TEM image taken after four cycles. XRD analysis was further carried out to investigate the crystallinity of these as-synthesised CdS NWs and also to evaluate their size distribution. Figure 3a shows the XRD patterns with peaks of 2θ values are assigned to (100), (002), (101), (102), (110), (103), (201), (203), (114), and (105) crystal planes, respectively, corresponding to hexagonal phase crystal structure and is in good agreement with the previous reports [38, 39]. Moreover, there are slight differences observed in the orientation, FWHM, and intensity, which might be due to their 1D growth along the c-axis and controlled dimensions in the nano regime. Moreover, the XRD of bulk CdS is also shown in Fig. 3b. In addition to this, Fig. 4 shows the UV–visible absorption spectrum of as-synthesised CdS NWs and bulk CdS, respectively. It shows the absorption of the CdS NWs observed at 413 nm, while the bulk CdS absorption is observed at 415 nm. The absorption edge of CdS NWs is slightly blue shifted; this slight shifting in the absorption edge is the outcome of the quantum confinement effect of the CdS NWs, which is slightly distinct from CdS bulk (absorption). The CdS NWs were further characterized by the spot EDS mapping to prove the local elemental composition (Fig. 5), and it confirms the CdS compound

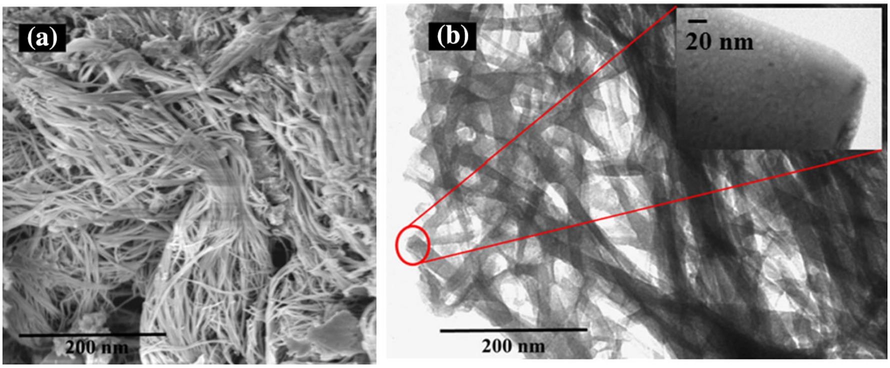


Fig. 1 **a** Low magnification scanning electron microscope (SEM) image of as-synthesised 1D CdS NWs, **b** transmission electron micrographs (TEM) of as-synthesised CdS NWs at low magnification and insets of the surface morphology of single CdS NWs

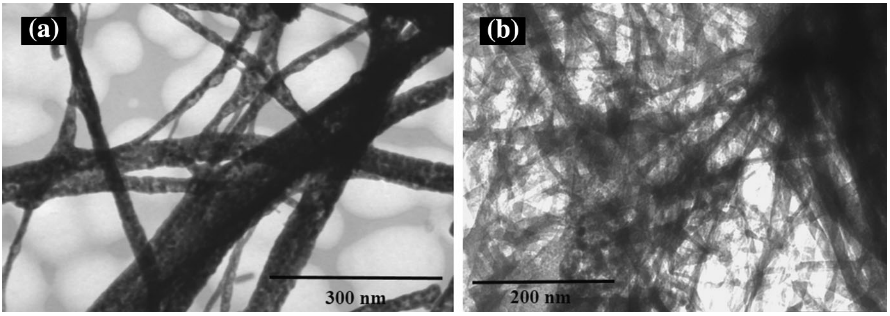


Fig. 2 **a** High magnification TEM image of CdS NWs having average particle diameter of the 20 nm, and **b** TEM analysis after four cycles

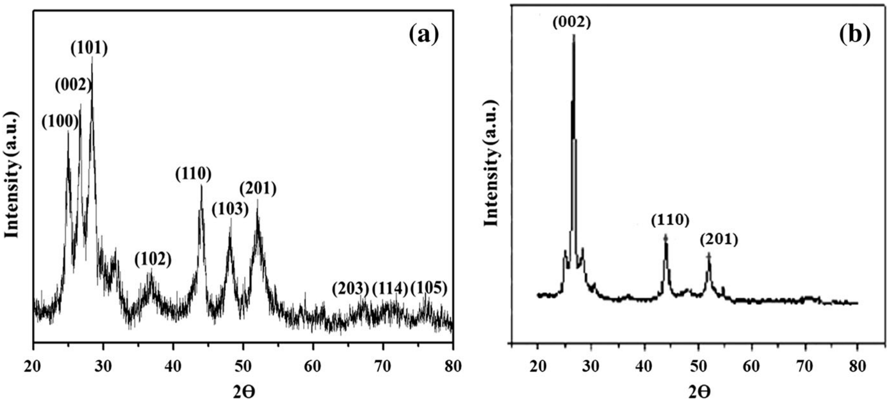
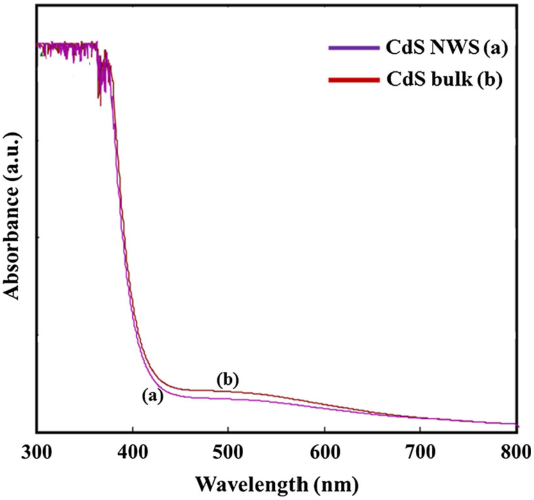


Fig. 3 **a** X-ray diffraction (XRD) pattern of as-synthesised CdS NWs using Cu-Kα (1.54 Å) radiations. **b** X-ray diffraction (XRD) pattern of bulk CdS

Fig. 4 UV–visible absorbance spectra of as-synthesised (*a*) CdS NWs and (*b*) bulk CdS



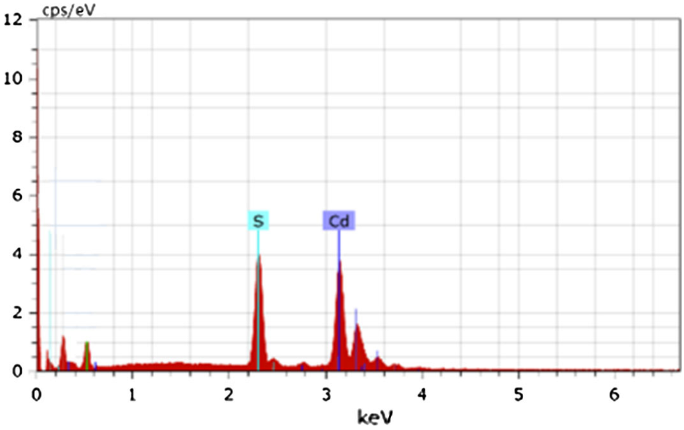


Fig. 5 EDS spectrum of CdS NWS

formation and homogenous distribution of Cd and S in CdS NWs. These results were in good agreement with morphological studies shown in Fig. 1b. These above as-synthesized and well-characterized catalytic CdS NWs were further tested for photocatalytic synthesis of polyhydroquinoline derivatives.

General procedure for the photochemical synthesis of polyhydroquinolines

A mixture of aldehyde 1a (0.002 mol), dimedon 2 (0.002 mol), ethyl acetoacetate 3 (0.002 mol), ammonium acetate 4 (0.003 mol), and CdS NWs (8 mg) was taken in the 50 mL double-walled quartz photoreactor with continuous flow of water to maintain the room temperature of the reaction vessel. The reaction was exposed to visible light (70 W, Halogen lamp with range 400–700 nm) equipped with cut off filter ($\lambda > 420$ nm) was used as visible light source for an appropriate time under constant stirring. The progress of the reaction was monitored by thin layer chromatography (TLC) using ethylacetate: *n*-hexane (4:6) composition. After completion of the reaction the catyalyst was recoved by the filtration and obtained crude products were filtered and recrystalised from ethanol to afford polyhydroquinoline.

Spectral data for the representative compound

Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahy-droquinoline-3-arboxylate (Table 5-5e)^1**H NMR** (400 MHz, $CDCl_3$) δ ppm: 0.81 (s, 3H, $–CH_3$), 0.93 (s, 3H, $–CH_3$), 1.11 (t, 3H, $J = 7.3$ Hz, $–CH_3$), 2.04 (dd, 2Hn,$–CH_2–$), 2.12 (dd, 2H, $–CH_2–$), 2.26 (s, 3H, $–CH_3$), 3.95 (q, 2H, $J = 7.2$ Hz, $–OCH_2–$), 4.93 (s, 1H, –CH–), 7.07 (d, 2H, $J = 9.1$ Hz, Ar–H), 7.15 (d, 2H, $J = 9.2$ Hz, Ar–H), 7.91

(brs, 1H,–NH);**^{13}CNMR** (100 MHz, $CDCl_3$): δ14.7, 18.6, 26.5, 29.5, 31.4, 36.3, 41.1, 50.5, 60.3, 75.8, 104.3, 110.2, 125.5, 129.8, 132.6, 143.2, 149.6, 165.1, 192.9., **(ES-MS)** = 396.07 $[M + Na]^{+\cdot}$

Results and discussion

Experimental

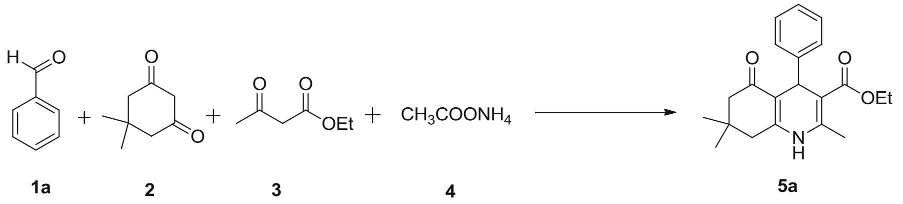
Chemicals and instruments

All reagents were purchased from Merck and Aldrich and used without any further purification. The particle size and morphology of the synthesized catalysts were characterized with a scanning electron microscopy (SEM, JSM-6400) transmission electron microscopy (TEM, PHILIPS, CM 200, 20–200 kv Resolution: 2.4 Å). X-ray diffraction (XRD) measurements were performed using a Bruker AXS Company, D8 ADVANCE diffractometer (Germany). Infrared (IR) spectra were recorded on a Thermo Nicolet AVATAR-370. ^{1}H NMR spectra were recorded on a Bruker DRX 400 spectrometer respectively.

To find out the better catalytic systems for the polyhydroquinolines derivatives, optimisation of the reaction condition was carried out by taking benzaldehyde 1a (0.002 mol), dimedon 2 (0.002 mol), ethylacetoacetate 3 (0.002 mol), and ammonium acatate (0.003 mol) as a model substrates (Scheme 1).

In order to understand the nature of catalyst amount, here we have studied the effect of CdS NWs at different loadings (amount) on model reaction.

In brief, in search of better percentage yield of polyhydroquinoline, CdS NW photocatalyst at different amount (loadings) has been carried out at 4, 8, 10 and 12 mg, respectively, but 8 and 10 mg of catalyst was sufficient to offer the excellent yield. Moreover, the same product yield (94%) has been found at different catalyst amounts, i.e. 8 and 10 mg (Table 1, entry 1). Furthermore, a model reaction has been performed at a minimum catalytic amount of 4 mg and maximum at 12 mg to find the exact amount of the catalyst that resulted in 85 and 94% yield, but there was not a considerable difference found in product yield at the highest catalyst loading, i.e. the catalyst was unable to offer the expected yield at 12 mg catalyst. Finally, catalytic activity of CdS NWs was compared to that of bulk CdS, $CdSO_4$, and $CdCl_2$ (Table 1). The application of bulk CdS (entry 2), $CdsO_4$ (entry 3), and $CdCl_2$ (entry 4) as a catalyst at 4, 8, 12 mg loadings, respectively, did not give



Scheme 1 Standard model reaction for the synthesis of polyhydroquinolines

Table 1 Screening of the catalysts with concentrations

Entry	Catalyst	Catalysts loading (mg)	Yield[a] (%)
1	CdS NWs	4	85
		88 (in dark)	94 No condensation
		10	94
		12	94
2	CdS bulk	4	40
		8	45
		12	47
3	$CdSO_4$	4	No condensation
		8	No condensation
4	$CdCl_2$	4	No condensation
		8	No condensation
5	No catalyst	–	No condensation

Reaction conditions: 1a (0.002 mol), 2 (0.002 mol), 3 (0.002 mol), 4 (0.003 mol), stirred under visible light (70 W, Halogen lamp) in ethanol solvent (5 mL) for 35 min

[a] Isolated yield

condensation under our experimental conditions, in ethanol as a solvent. The only bulk CdS system that led to some conversion as 47% of 5a was produced in ethanol with 12 mg loading (entry 2).

Herein, we applied potential, recoverable, and reusable CdS NWs as heterogenous catalyst for carrying out the synthesis of polyhydroquinolines by condensation of various aromatic aldehydes with dimedone, ethylacetoacetate, and ammonium acetate. The experiments began with the purpose of optimizing the reaction conditions for this multicomponent reaction by varying solvents and keeping the energy source and reaction time constant. To determine the most effective solvent for this condensation reaction using CdS NWs as catalyst, we screened the various protic and aprotic solvents shown in (Table 2 entry 1–7). But the ethanol was found to be the best solvent system for this condensation reaction with CdS NWs catalyst (Table 2, entry 2). At room temperature with 8 mg of the CdS NWs catalyst, the

Table 2 Screening of solvent

Entry	Solvents	Time (min)	Yield[a] (%)
1	Water	35	80
2	Ethanol	35	94
3	THF	35	70
4	DCM	35	60
5	Acetonitrile	35	74
6	Methanol	35	89
7	1,4-Dioxane	35	45

Reaction conditions: 1a (0.002 mol), 2 (0.002 mol), 3 (0.002 mol), 4 (0.003 mol), CdS NWs (8 mg) stirred under visible light (70 W, Halogen lamp) in solvent (5 mL) for 35 min

[a] Isolated yield

reaction appeared to proceed very well to provide the desired product in an excellent yield (i.e. 94%) in 35 min.

Model reaction has been performed under the following different conditions: conventional, unconventional, and photocatalytic (under visible light), which acts as activation energy source (Table 3). In more detail, the model reaction (Scheme 1) performed at reflux condition using CdS NWs as a catalyst (8 mg) offered 65% yield in 70 min (Table 3, entry 1). Furthermore, the same model reaction was carried out under ultrasound irradiation at 80 °C, which offered 80% yield of 5a in 50 min (Table 3, entry 2). Both conditions (conventional and ultrasonication) applied on model reaction at room temperature for better comparison run of photocatalyst but not expected yield observed. Finally, when the same model reaction was stirred under visible light (70 W, Halogen lamp) at room temperature, excellent yield (i.e. 94%) was obtained in only 35 min (Table 3, entry 3). In this entire course of conventional and non-conventional experimental conditions, the model reaction was found to proceed effectively under visible light within a very short reaction time, delivering the desired product in excellent yield. Inspired by this, it was decided to synthesize a number of derivatives following the developed reaction condition by photochemical method.

One of the advantages of using a heterogeneous catalyst is the possibility to recycle the catalyst, thus reducing the cost and environmental impact of the process. To investigate this key feature, four successive condensations of 1a were performed with the same CdS NW sample, which was recovered by the simple method described as follows.

The reaction mixture was filtered through Whatman 40 filter paper. The insoluble catalyst remained as residue and was collected and dried. The filtrate was extracted with ethyl acetate. The collected CdS NWs (catalyst) were dried and put into a round bottomed flask, and a reaction was carried out with the same amount of starting material. No significant decrease of the catalytic activity was observed throughout the different condensation reactions. As a result, quinoline was produced in nearly constant yield. However, after a third cycle slight loss of the catalytic activity was observed, which may be due to the deactivation or personal loss of the catalyst during the course of the reaction and recovery process. At the fourth reuse the catalyst also offered 89% in 45 min (Table 4).

Table 3 Study of catalytic activity of catalyst under conventional and unconventional conditions

Entry	Conditions	Catalyst	Temp. (°C)	Time (min)	Yield[a] (%)
1	Conventional	CdS NWs	Reflux	70	65
			RT	70	30
2	Ultrasound	CdS NWs	80	50	80
			RT	50	40
3	Photocatalysis	CdS NWs	RT	35	94

Reaction conditions: 1a (0.002 mol), 2 (0.002 mol), 3 (0.002 mol), 4 (0.003 mol), CdS NWs (8 mg) stirred in ethanol solvent (5 mL)

[a] Isolated yield

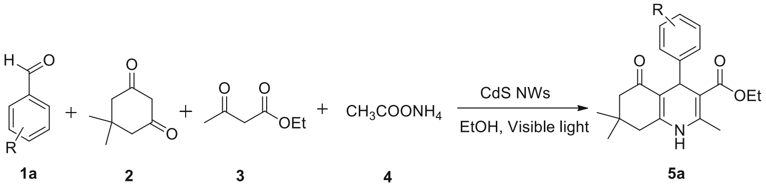
Table 4 Recycling experiment

Entry	Cycle	Time (min)	Yield[a] (%)
1	Fresh	35	94
2	1st reuse	35	93
3	2nd reuse	35	90
4	3rd reuse	35	88
5	4th reuse	45	89

Reaction conditions: 1a (0.002 mol), 2 (0.002 mol), 3 (0.002 mol), 4 (0.003 mol), CdS NWs (8 mg) stirred under visible light (70 W, Halogen lamp.) in ethanol (5 mL) for 35 min

[a] Isolated yield

Table 5 Synthesis of polyhydroquinoline derivatives



Entry	Comp.	R	Time (min)	Yield[a] (%)	M.P. (°C)	
					Found	Literature
1	5a	2-Cl	45	90	207–209	208–210
2	5b	4-OH,3-OCH_3	40	88	211–213	210–212
3	5c	3-NO_2	37	90	176–178	177–178
4	5d	3-OH	30	92	220–223	220–222
5	5e	4-Cl	30	92	244–246	245–246
6	5f	4-OH	35	88	232–234	232–234
7	5g	4-NO_2	40	85	240–242	242–244
8	5h	H	35	94	203–205	204–205
9	5i	4-CH_3	45	89	259–262	261–262
10	5j	4-OCH_3	30	94	257–260	258–259
11	5k	CH_2=CH–	40	84	205–207	206–207
12	5l	4-Br	35	90	256–257	254–255
13	5m	2-Furyl	40	80	248–250	248–249
14	5n	2-Thienyl	50	87	240–241	241–242
15	5o	4-$N(CH_3)_2$	45	89	234–236	233–234

Reaction conditions: 1a (0.002 mol), 2 (0.002 mol), 3 (0.002 mol), 4 (0.003 mol), CdS NWs (8 mg) stirred under visible light (Halogen lamp, 70 W) in solvent (5 mL) for 35 min

[a] Isolated yield

Model reaction has been performed using CdS NWs as a potential photo catalyst in the presence of visible light (70 W, Halogen lamp) as an energy source. In this experiment, the model reaction was found to proceed effectively within very short

Table 6 Comparative study of CdS NWs (our studies) and other catalysts reported for synthesis of polyhydroquinoline derivatives

Entry	Catalyst	Time (min)	Yield (%)	References
1	$NaHSO_4$–SiO_2	300–480	75–90	[43]
2	Silica–sulfuric acid	45	92	[44]
3	Cellulose sulfuric acid	120–300	78–92	[45]
4	*P*-Toluene sulfonic acid	120	93	[46]
5	Molecular iodine	30	93	[47]
6	Yb $(OTf)_3$	300	90	[48]
7	PPh_3	120–300	72–96	[49]
8	CdS NWs	35	90–94	(This work)

reaction time delivering the desired product in excellent yield. Inspired by this, it was decided to synthesize a number of derivatives following the developed reaction condition with visible light as a green energy source (Table 5). With that result in hand, we optimized the reaction parameters. We generalized the applicability of this method for the synthesis of a series of polyhydroquinolines starting from various aromatic aldehydes. The aldehyde with both the electron donating and electron withdrawing substituents didn't show any significant effect on the product yields. Furthermore, we also tried catalytic activity for the checkout yield of heterocyclic polyhdydroquinolines starting from 2-furyl and 2-thienyl heterocyclic aldehydes (Table 5, entry 14, 15). Our conclusive finding says that aldehydes with no substituent on phenyl ring reacted smoothly and products were obtained in excellent yield 94% (Table 5, entries 8). Furthermore, the polyhydroquinoline products were isolated and characterised, and their melting points were found to be in good agreement with those reported in the literature [40–42]. To show the merits of this work over the methods reported in the literature, comparison of results obtained by use of CdS NWs with different catalysts such as [bmim][PF_6], PEG400, Bi $(SCH_2COOH)_3$, $HClO_4$–SiO_2, Silica gel, Saccharomyces cerevisiae are shown in Table 6.

The cyclocondensation reaction of the polyhydroquinoline seems to be very feasible it may be due to the electrophilic-like character of holes generated in the CdS NWs on irradiation of the visible light. The visible light having the capacity to excite the electron from valence band to conduction band and resulting holes (h^+) within the CdS NWs may responsible for the condensation of reactant and accelerate the rate of reaction.

Conclusion

In summary, 1D CdS NWs was found to be a promising photocatalytic system to perform the synthesis of polyhydroquinoline in the presence of visible light (Halogen lamp, 70 W). Some attractive features of our methodology are (1) the mildness of the reaction conditions as polyhydroquinoline were formed at room temperature (2) the very low catalytic loading (8 mg) (3) the possible recyclability of the catalyst and (4) the scope of CdS NWs photocatalytic system was also applied in a one-pot three-component system (condensation reaction). The results obtained in the context of this study thus compared favourably to previous reports in terms of overall efficiency.

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