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Nano-CdS by polymer-inorganic solid-state reaction: Visible light pristine photocatalyst for hydrogen generation

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Abstract

We have explored the possibility of using environmentally stable nano-CdS embedded in thermally stable polymer matrix as an efficient photocatalyst for the hydrogen generation by photodecomposition of hydrogen sulphide under visible light irradiation. Initially, we restricted our attempt to the usage of nano-CdS synthesized by novel polymer-inorganic solid-state reaction between cadmium iodide and polyphenylene sulphide (PPS). The structural study revealed the formation of nanocrystallites of CdS with the particle size ranging from 6 to 28 nm entrapped in modified (cyclized) PPS matrix. A quantum yield of 19.7% for the H_2 generation was accomplished with CdS–PPS nanocomposite in pristine state, which appears to be superior in comparison to that of the conventional Pt loaded CdS. We believe that this straightforward approach can be extended to synthesise other nano-metal sulphides in polymer network for photocatalytic and allied applications.

Keywords: A. Semiconductor; A. Polymer; D. Catalytic properties

1. Introduction

The dream to harvest energy from sunlight for electric power generation or chemical fuels such as hydrogen is yet to be realized at economically viable large scale. Photocatalytic production of hydrogen from water, H_2S and organic waste using semiconductors is one of the potential strategies for converting the sunlight energy into chemical energy. Conventionally, various metal sulphides, particularly CdS have been used as photocatalyst [1–3]. However, these metal sulphides are prone to photocorrosion. To overcome the problem of photocorrosion, attempts are being made to use highly stable metal oxides as visible light photocatalyst. Unfortunately, most of the oxides have wide band gap and absorb very little of the visible light [4,5]. Therefore, the improvement in the stability of CdS based photocatalysts utilizing visible range of the spectrum is a great challenge. Organic compounds as sacrificial promoter [6] and mesoporous silica [7,8] have been reported to increase the stability and enhance the photocatalytic activity of CdS. Also, many researchers have reported the use of various transition metal doping methods for the preparation of CdS for their improved photocatalytic activity [9–11]. The uses of nanocrystalline semiconducting

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CdS powders with uniform particle size and large surface area for the photocatalytic decomposition of H_2S have also been reported [12–14]. Synthesis of nano-CdS in hetero-matrices has been a subject matter of immense interest owing to their distinctive optical, electrical and opto-electronic properties [15]. The use of organic material in the synthesis of hetero-matrices also provides an interface for the charge transfer resulting in the increase of photocatalytic efficiency [16–19]. Recently, we have demonstrated the synthesis of nano-CdS in hetero-matrices by a polymer-inorganic solid-state reaction where the polymer served a dual-purpose of a reactant (sulphur source) and a stabilizing agent [20].

In this communication, we report the photocatalytic performance of such nano-CdS–PPS composites in the photodecomposition of hydrogen sulphide for hydrogen generation under visible light irradiation. This is a unique attempt in which nano-CdS in hetero-matrices (where one of the matrices also acts as a reactant) has been used in order to study the photocatalytic activity.

2. Experimental

2.1. Synthesis and characterization of CdS photocatalyst

Polyphenylene Sulphide (PPS) having an average molecular weight of 10,000 and cadmium iodide were obtained from Aldrich (99% purity) and used as received. The nanocrystalline CdS in polymer matrix was prepared as per the procedure reported in our recent paper [20]. The admixture of PPS and CdI_2 (1:1 or 10:1 molar ratio) was heated at the melting temperature of PPS (285 °C) for 48 h in a platinum crucible. The CdS-polymer powder thus obtained was characterized by powder X-ray diffractions pattern recorded on Philips PW-1729 X-ray Diffractometer using Cu Kα radiation with Ni filter. Transmission electron microscopy (TEM) was performed using Jeol-2100X TEM. The surface morphology and particle size were determined using a Field Emission Scanning Electron Microscope (FESEM, JEOL-JSM6700F). Spectroscopic study of the product was carried out using UV–vis (SHIMADZU UV-2450 diffuse reflectance mode) spectrophotometer. In the present study, the CdS–PPS nanocomposite prepared using the admixture of PPS and CdI_2 with mole ratio 1:1 is denoted as CdS-NC-1:1 and that with mole ratio 10:1 is denoted as CdS-NC-10:1.

2.2. Photocatalytic measurement

About 0.5 g nano-CdS-polymer powder (CdS-NC-1:1/CdS-NC-10:1) dispersed in an aqueous solution of KOH (0.5 M, 250 ml) was introduced into cylindrical pyrex photochemical reactor with quartz window having a thermostatic water-jacket. This dispersion was purged with argon for 1 h followed by bubbling of hydrogen sulfide (2.5 ml/min) for about 1 h at 25 °C. The undercomposed hydrogen sulphide was trapped in NaOH solution and the amount of evolved hydrogen was measured using a graduated gas burette. It was subsequently characterized by using a gas chromatograph (Shimadzu GC-14B, MS-5 Å column, TCD, Ar as a carrier gas). A Xe lamp (Oriel) of intensity 450 W with cut-off filter (>420 nm) was used as a light source. Photocatalytic activity of all samples was measured for 4 h.

3. Results and discussion

3.1. Crystal structure and particle morphology

Two different concentrations of precursors were used in this novel solid-state reaction for the synthesis of CdS nanocrystallites in the polymer network. Fig. 1(a–c) represents the X-ray diffractograms corresponding to PPS, CdS-NC-1:1 and CdS-NC-10:1, respectively. X-ray diffractogram corresponding to CdS-NC-1:1 (Fig. 1b) reveals mainly occurrence of mixture of cubic and hexagonal phases of CdS [21]. The presence of hexagonal phase of CdI_2 can also be noticed [22]. In case of CdS-NC-1:1 (Fig. 1b), although mixed phases of CdS were formed, hexagonal phase was found to be more dominant than cubic phase in this product The peaks pertaining to PPS were absent in this system implying that the PPS has been completely utilized to incorporate CdS in its matrix. X-ray diffractogram corresponding to CdS-NC-10:1 (Fig. 1c) reveals the presence of PPS, cubic CdS and hexagonal CdI_2.

The average particle size of the resultant CdS nanocrystallites as derived from Scherrer's formula was found to be 15 nm for CdS-NC-1:1 and 12 nm for CdS-NC-10:1.

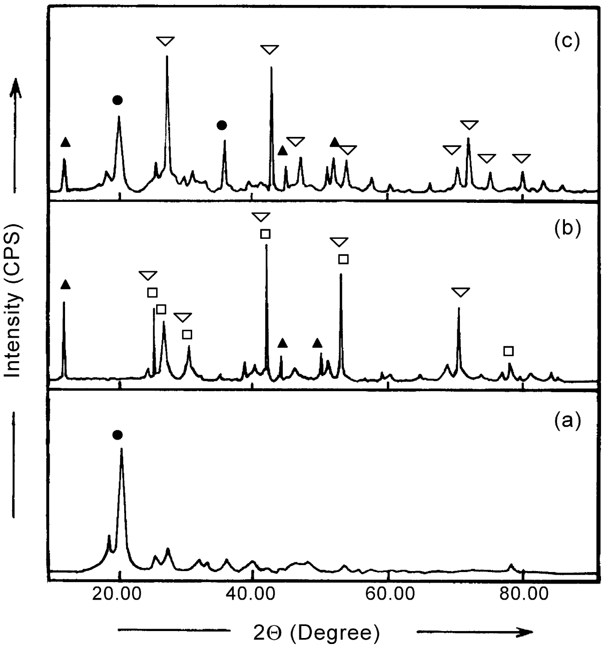

Fig. 1. X-ray diffractograms corresponding to (a) PPS, (b) CdS-NC-1:1 and (c) CdS-NC-10:1 (●: PPS, ▲: hexagonal-CdI_2, ▽: cubic-CdS, □: hexagonal-CdS).

The FESEM photomicrographs corresponding to PPS, CdS-NC-1:1 and CdS-NC-10:1 are presented in Fig. 2(a–c), respectively. The clumpy and chunk-like morphological features were observed for PPS (Fig. 2a). However, such features were absent in the photomicrograph of CdS-NC-1:1 powder (Fig. 2b), indicating the formation of CdS in the cyclized polymer matrix. While in case of CdS-NC-10:1 nanocomposite (Fig. 2c), the presence of a chunk like morphology (associated with PPS) indicates the probable retention of the polymer network even after heating at 285 °C. This observation is in agreement with the pertinent XRD data (Fig. 1, pattern (a) and (c)).

Fig. 3 shows TEM images recorded for samples corresponding to (a) CdS-NC-1:1 and (b) CdS-NC-10:1 nanocomposite powders. The uneven spherical shaped dark black regions (Fig. 3a) plausibly indicate the presence of nano-CdS particles. The nearly spherical and irregular shaped dark black regions (Fig. 3b) can be associated with nano-CdS particles as SAED pattern associated with these spots (Fig. 4) reveals occurrence of cubic CdS in close agreement with XRD data. The SAED rings evidently indicate the polycrystalline nature of the product whereas the spots imply the single crystalline nature of the product. Thus, it can be inferred that the as formed CdS nanocrystallites are randomly positioned between polycrystalline and single crystalline lattices. In close agreement with XRD results, the average size of the CdS nanocrystallites were in the range of 15–28 nm in case of CdS-NC-1:1 while it was in the range of 6–20 nm for the CdS-NC-10:1. TEM micrograph of CdS-NC-10:1 nanocomposite powder shows that the polymer was retained in the product whereas it was missing in the case of CdS-NC-1:1 nanocomposite powder.

3.2. Electronic band structure by DRS

Fig. 5(a–c) shows the UV–vis diffuse reflectance spectra of the PPS, CdS-NC-1:1 and CdS-NC-10:1 nanocomposite powders. The DRS of the PPS (Fig. 5a) has absorption edge cut-off at 370 nm with corresponding band gap of 3.35 eV, while DRS of CdS-NC-1:1 (Fig. 5b) nanocomposite powder showed the broad adsorption edge cut-off in the visible region. The similar kind of behaviour was observed in CdS-NC-10:1 nanocomposite powder (Fig. 5c). The broad absorption edge shoulder reveals the formation of CdS incorporated in cyclized polymer matrix. The presence of uneven shape and size of nanocrystals (Fig. 3) of CdS in PPS matrix could also be one of the reasons for the broad absorption peak [5].

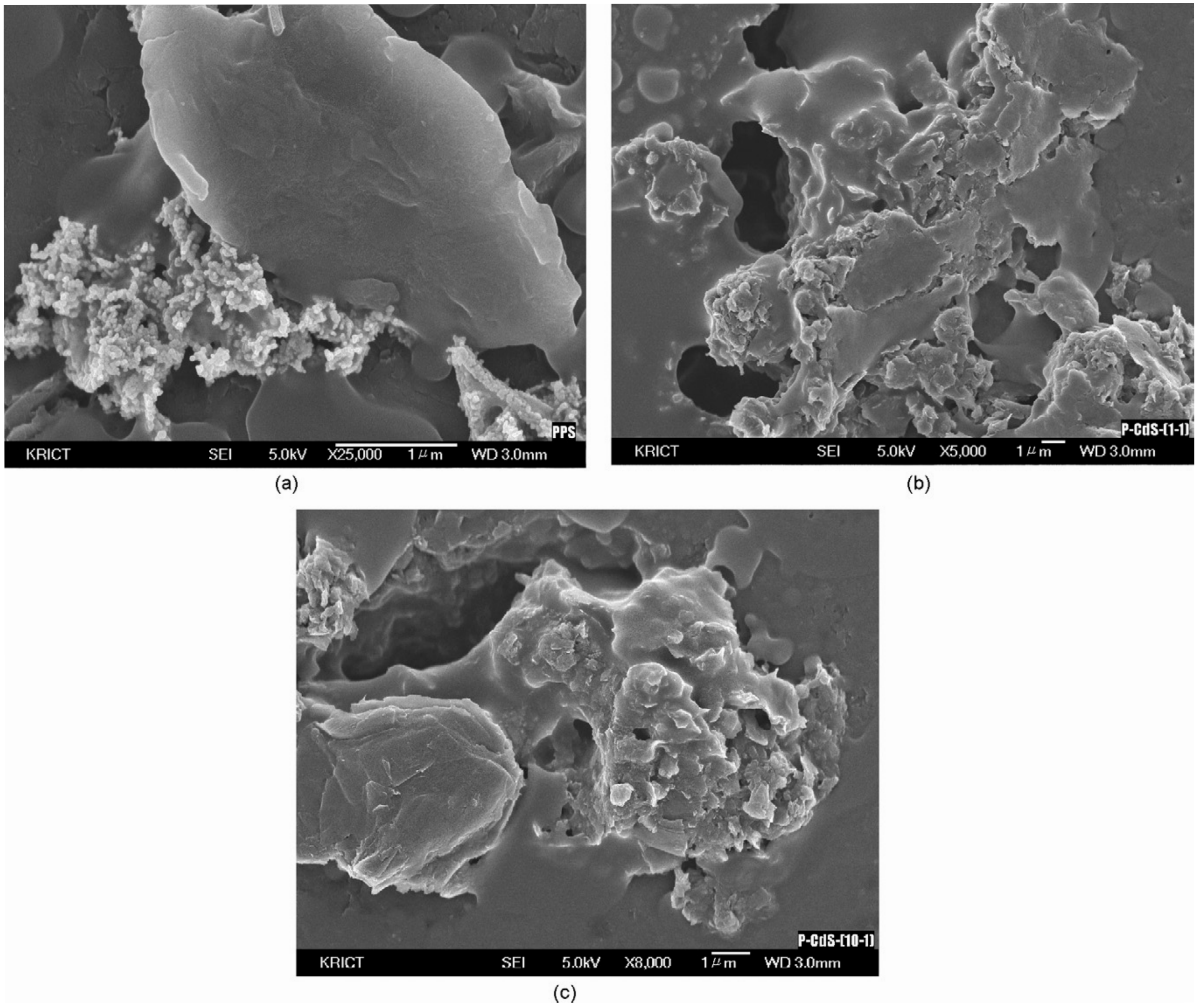

Fig. 2. FESEM micrographs: (a) PPS, (b) CdS-NC-1:1 and (c) CdS-NC-10:1 nanocomposite powder.

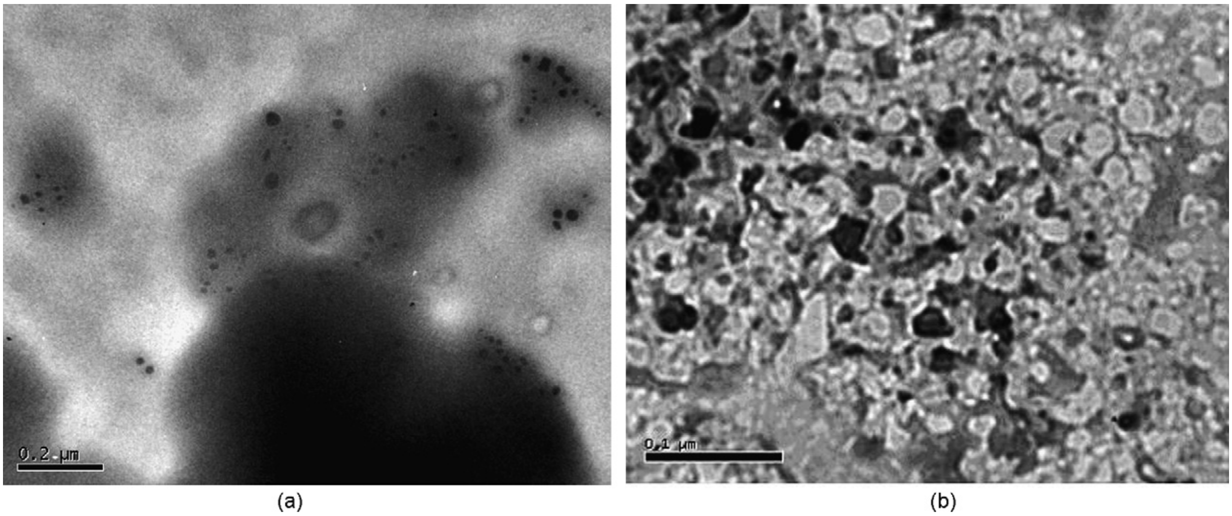

Fig. 3. TEM micrographs of (a) CdS-NC-1:1 and (b) CdS-NC-10:1.

3.3. Photocatalytic activities of CdS embedded in PPS matrix

The photocatalytic production of hydrogen using PPS, CdS-NC-1:1 and CdS-NC-10:1 nanocomposite powders as catalyst for the decomposition of hydrogen sulfide was carried out under the specified conditions and the relevant data is reproduced in Table 1. An excellent photocatalytic activity was observed for CdS-NC-1:1 nanocomposite powder. The maximum hydrogen production rate achieved was 3926 μmol/h without using any doping agent which, in turn, implies that the nanocomposite in pristine state is an active photocatalyst for hydrogen sulfide decomposition under visible light irradiation. Nevertheless, with CdS-NC-10:1 the hydrogen production rate achieved was to the tune of 2838 μmol/h. The PPS matrix showed negligible photocatalytic evolution of hydrogen. Photocatalytic activity of all samples was measured for short term (i.e.4 h) as limited by our experimental facility. The samples were re-used for photodecomposition three times over a period of 24 h and we achieved the same results. The CdS-NC-1:1 and CdS-NC-10:1 nanocomposite powders gave 19.7% and 11.7% quantum yields at 500 nm, respectively for the H_2 evolution. It is worthwhile to note that CdS-NC-1:1 nanocomposite powder offers higher photocatalytic activity under visible light irradiation in comparison to reported data [23–27]. It also showed good stability under the experimental conditions used for the photodecomposition of H_2S. The CdS-NC-10:1 nanocomposite powder showed relatively less photocatalytic activity as compared to CdS-NC-1:1 because of the

Spot#	d-Spacing (nm)	Rec. Pos.(1/nm)	Degrees to Spot 1
1	0.3686	2.713	0.00
2	0.2670	3.745	63.06
3	0.2145	4.661	31.15
4	0.1839	5.437	62.42
5	0.1208	8.275	59.10

Fig. 4. SAED pattern of CdS-NC-10:1 powder.

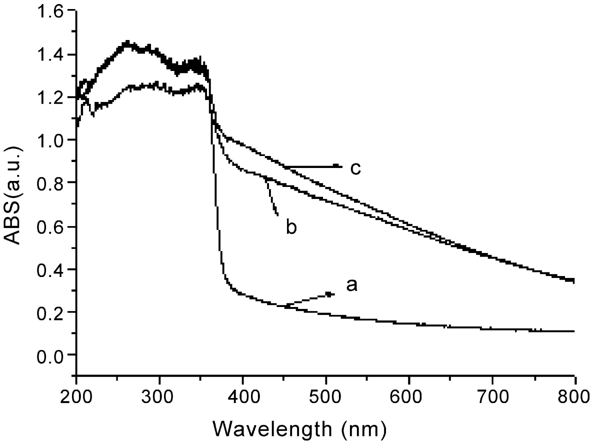

Fig. 5. UV–vis diffuse reflectance spectra of (a) PPS, (b) CdS-NC-1:1 and (c) CdS-NC-10:1 nanocomposite powder.

Table 1
Photocatalytic activities of various catalysts for H_2S splitting[a]

Catalyst	H_2 evolved (μmol/h)
CdS-NC-1:1	3926
CdS-NC-10:1	2838
Pt-CdS	1517

[a] Catalyst, 0.5 g; 250 ml (0.5 M aqu.KOH); H_2S (2.5 ml/min); 450 W Xe lamp (Oriel) with cutoff filter ($\lambda \geq 500$ nm).

prevalence of cubic CdS in the polymer matrix. It is quite well known that the CdS particles having hexagonal crystal structure are more efficient as photo-catalysts for hydrogen production than their counter part with cubic crystal structure [28]. Apart from the high surface area, good degree of crystallanity is very important for better photocatalytic activity. While material with high surface area may exhibit good photocatalytic activity initially but is prone to fast deactivation. Therefore, for the overall efficiency of a photocatalyst, its good crystalline nature is more important than its surface area [28,29]. To this effect, CdS-NC-1:1 nanocomposite powder showed better activity than CdS-NC-10:1. To compare our results with well-known system, we carried out experiments using Pt-CdS as photocatalyst for the decomposition of H_2S under same experimental conditions that gave hydrogen evolution rate of 1517 μmol/h (Q.Y. 7.7%). This suggests that CdS–PPS nanocomposite has much higher photocatalytic activity than the nanocrystalline Pt-CdS.

In the present case (nano-CdS in cyclized PPS matrix), PPS matrix may also be contributing in suppressing the photocorrosion of CdS. Hence, good stability of the nanocomposite is quite explicable. Bard and co-workers [30] also made similar observations pertaining to the polymer matrix while reporting the photocatalytic hydrogen production using CdS particles embedded in Nafion polymer.

4. Conclusion

We have demonstrated that a polymer-inorganic solid-state method for the synthesis of nano-CdS crystallites (size, 6–28 nm) embedded in the PPS network can be advantageously used for its generic application in the photodecomposition of H_2S for hydrogen generation under visible light irradiation. The photocatalytic activity examined for such CdS–PPS nanocomposite (in the pristine state) was much higher than that of commonly used Pt-CdS. XRD data of the nanocomposite revealed the existence of hexagonal and cubic crystal structure of the CdS. The hexagonal nano-CdS present in the nanocomposites may be responsible for good photocatalytic activity. Our preliminary work may open up an enormous possibility of synthesizing variety of nano-metal sulfide in polymer network for photocatalytic and allied applications.

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References

[1] T. Kida, G. Guan, N. Yamada, T. Ma, K. Kimura, A. Yoshida, Int. J. Hydrogen Energy 29 (2004) 269.
[2] A. Koca, M. Sahin, Int. J. Hydrogen Energy 27 (2002) 363.
[3] A.S.K. Sinha, N. Sahu, M.K. Arora, S.N. Upadhyay, Catal. Today 69 (2001) 297.
[4] A. Kudo, H. Kato, I. Tsuji, Chem. Lett. 33 (2004) 1534.
[5] B.B. Kale, J.O. Baeg, J.S. Yoo, S.M. Lee, S.J. Moon, H. Chang, Can. J. Chem. 83 (2005) 527.
[6] S. Kambe, M. Fujii, T. Kawai, S. Kawai, F. Nakahara, Chem. Phys. Lett. 109 (1984) 105.
[7] L. Nguyen, R. Kho, W. Bae, R. Mehra, Chemosphere 38 (1999) 155.
[8] T. Hirai, K. Suzuki, I. Komasawa, J. Coll. Int. Sci. 244 (2001) 262.
[9] T. Kida, G. Guan, A. Yoshida, Chem. Phys. Lett. 371 (2003) 563.
[10] W.F. Shangguan, A. Yoshida, J. Phys. Chem. B 106 (2002) 12227.
[11] S.A. Naman, Int. J. Hydrogen Energy 22 (1997) 783.
[12] A. Eychmuller, J. Phys. Chem. B 104 (2000) 6514.
[13] L.E. Brus, J. Phys. Chem. 90 (1986) 2555.
[14] A.P. Alivisatos, Science 271 (1996) 933.
[15] H. Chang, K. Kong, Y. Choi, E. In, Y. Choi, J.O. Baeg, S. Moon, Chem. Phys. Lett. 398 (2004) 449.
[16] U. Wendy, J. Janke, J. Dittmer, A.P. Alivisatos, Science 295 (2002) 2425.
[17] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789.
[18] L.S. Roman, M.R. Andersson, T. Yohannes, O. Inganas, Adv. Mater. 9 (1997) 1164.
[19] J.J. Dittmer, E.A. Marseglia, R.H. Friend, Adv. Mater. 12 (2000) 1270.
[20] K.G. Kanade, R.R. Hawaldar, R. Pasricha, S. Radhakrishnan, T. Seth, U.P. Mulik, B.B. Kale, D.P. Amalnerkar, Mater. Lett. 59 (2005) 554.
[21] ASTM card No. 06-0314 and ASTM card No. 02-0454.
[22] JCPDS Card No. 33-239.
[23] Z. Zou, J. Ye, K. Sayama, H. Arakawa, Nature 414 (2001) 625.
[24] M. Matsumura, Y. Saho, H. Tsubomura, J. Phys. Chem. 87 (1983) 3807.
[25] I.B. Rufus, B. Viswanathan, V. Ramkrishnan, J.C. Kuriacose, J. Photochem. Photobiol. A: Chem. 91 (1995) 63.
[26] L. Borrell, S. Cervera-March, J. Gimenez, R. Simartto, J.M. Andjar, Solar Eng. Mater. Solar Cells 25 (1992) 25.
[27] N. Serpone, E. Borgarello, M. Gratzel, J. Chem. Soc., Chem. Commun. (1984) 342.
[28] M. Ashokkumar, Int. J. Hydrogen Energy 23 (1998) 427.
[29] D. Beydoun, R. Amal, G. Low, S. McEvoy, J. Nanopart. Res. 1 (1999) 439.
[30] A.W.H. Mau, C.B. Huang, N. Kakuta, A.J. Bard, A. Campion, M.A. Fox, J.M. White, S.E. Webber, J. Am. Chem. Soc. 106 (1984) 6537.