



Visible-Light Photocatalytic Conversion of Carbon Monoxide to Methane by Nickel(II) Oxide**

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Research in the area of “solar fuels” obtained photocatalytically by sunlight is actual and active because these fuels are sustainable and CO₂-neutral. Although H₂ generation from H₂O is the most widely studied photocatalytic process for solar fuel production, the technical problems associated with H₂ storage and fuel-cell efficiency make also attractive other chemicals obtained from CO₂ such as CH₃OH, CH₄, and CO.^[1–7]

The production of solar fuels requires efficient photocatalysts with high visible-light photoresponse. While TiO₂ is the most widely studied photocatalyst,^[8–10] this semiconductor shows activity only upon UV-light exposure and a considerable effort aims at developing TiO₂ photocatalysts with visible response.^[11–15] In contrast, the use of p-type semiconductors absorbing visible light such as NiO, CuO_x, FeO_x, and CoO_x has been less explored in photocatalysis, because of their presumably lower stability compared to TiO₂.^[16] In particular, NiO has been frequently employed as co-catalyst in combination with titanates or other photocatalysts for visible-light splitting of H₂O rather than as active photocatalyst. In the present report, we describe that p-type semiconducting metal oxides, specifically NiO and FeO_x, show high visible and sunlight photocatalytic activity for the reduction of CO by H₂O vapor or H₂ leading to the formation of substantial amounts of CH₄, with almost complete selectivity at full CO conversion. NiO can be reused without change in the XRD pattern, supporting its photostability. The novelty of our study derives from the consideration of two points: 1) the unprecedented room-temperature photocatalytic CO reduction by H₂O or H₂ to CH₄, and 2) the possibility of using sunlight and visible light to activate the process.

Preliminary experiments using TiO₂ as photocatalyst showed that this n-type semiconductor leads mainly to oxidation of CO by H₂O vapor, forming quasi-stoichiometric amounts of CO₂ and H₂ [Eq. (1)],



accompanied by detectable, amounts of CH₄, and traces of

ethane. Formation of CO₂ can be understood as arising from photooxidation of CO by positive holes generated in the charge separation on the semiconductor. The conversion of CO using TiO₂ promoted by solar light was very small (see Table 1) in agreement with the well-documented low photocatalytic activity of TiO₂ at solar light irradiation.^[15]

Then we tested other first-row transition-metal oxides that can absorb visible light, though they are generally

Table 1: Photocatalytic activity for CO conversion, carbon content, and formation of H₂, CO₂ and CH₄ in the presence of metal-oxide semiconductors.^[a]

Photocatalyst ^[b]	CO Conversion [%]	C [%] ^[c]	Production [μmol g ⁻¹ cat.]		
			H ₂	CO ₂	CH ₄ ^[d]
TiO ₂ ^[e]	3	0.1	260	650	4 (0.5)
NiO ^[e]	95	3.3	820	12 200	1700 (10.2)
CuO ^[e]	14	0.5	20	2900	270 (7.5)
Co ₃ O ₄ ^[e]	91	1.2	1000	12 300	600 (4.3)
Co ₂ O ₃ ^[e]	93	3.1	990	12 500	200 (1.3)
Fe ₃ O ₄ ^[e]	59	0.1	3620	8200	900 (9.8)
Fe ₂ O ₃ ^[e]	68	2.5	3760	10 400	20 (0.2)
NiO ^[f]	96	2.2	— ^[g]	11 240	8387 (39.1)
Fe ₃ O ₄ ^[f]	49	3.6	— ^[g]	6590	733 (7.1)
NiO ^[h]	99.5	1.8	— ^[g]	711	17 266 (87)
Fe ₃ O ₄ ^[h]	28	0.5	— ^[g]	943	580 (28.2)
NiO ^[i]	99.4	1.9	— ^[g]	450	20 799 (92)
NiO ^[j]	99.0	1.8	— ^[g]	87	16 030 (97)
NiO ^[k]	16	1.0	— ^[g]	1386	1379 (38.3)

[a] Blank controls: 1) illumination in the absence of any solid, 2) contact to the solid and gas phase in the dark or 3) irradiation of the photocatalyst in N₂ did not lead to any product, C mass balances were higher than 95 %. [b] See the Supporting Information for the origin and characterization data of these commercially available photocatalysts.

[c] Weight percentage of carbon on the solid after the photocatalytic experiment. [d] The number in brackets corresponds to the selectivity of the process to CH₄ defined as number of moles formed of CH₄ divided by moles of converted CO in percentage. [e] Irradiation conditions: Mixture of N₂ (19.6 mmoles), H₂O (2.5 mmol), and CO (20%, 4.9 mmol), irradiation time 22 h, photocatalyst mass 250 mg, irradiation source solar simulator (1000 W m⁻²). [f] Reaction conditions: Mixture of CO (20%, 5 mmol), H₂ (5 mmol), Ar (1.1 mmol), and N₂ (13.9 or 0.125 mmol); photocatalyst mass 250 mg, reaction time 3 h, light source solar simulator. [g] Reagent. [h] Reaction conditions: Mixture of CO (20%, 5 mmol), H₂ (18.75 mmol), Ar (1.1 mmol), and N₂ (13.9 or 0.125 mmol); photocatalyst mass 250 mg, reaction time 3 h, light source solar simulator. [i] Second test under conditions indicated in [h] and activation of NiO at 450 °C with air for 5 h. [j] Third test under conditions indicated in [h] and activation of NiO at 450 °C with air for 5 h.

[k] Irradiation with the solar simulator equipped with a cut-off filter (λ > 400) under conditions indicated in [h].

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considered much less efficient photocatalysts than TiO₂. The results obtained for the p-type metal-oxide semiconductors are summarized in Table 1, whereas Figure S1 (see the Supporting Information) shows the temporal evolution of CH₄ upon irradiation in the presence of the p-type semiconductors using simulated solar light.

In contrast to experiments performed in the dark, where no products are formed (see footnote [a] in Table 1), or in contrast to the generation of CO₂ using TiO₂, p-type semiconducting metal oxides of Ni, Cu, Fe, and Co afford significant amounts of CH₄ in the gas phase upon sunlight irradiation. Equation (2) provides the presumed stoichiometry of the CH₄ formation for the photocatalytic CO



reduction by water using simulated solar light. While TiO₂ is a white powder, all the rest of the transition metals in Table 1 are colored, the visible absorption bands being responsible for the notable sunlight photoactivity (up to 33 times that of TiO₂). Particularly notable is the performance of NiO and Fe₃O₄ (in its most abundant α -polymorph)^[17] where the production of CH₄ is the highest (10.2% in the gas-phase mixture in the case of NiO). These differences in photocatalytic activity in the series of p-type metal-oxide semiconductors are unlikely to arise from differences in their surface area, since they show similar values (see Table S1). It is more reasonable to attribute the results to the intrinsic photocatalytic properties (redox potentials of electrons and holes, efficiency of charge separation and lifetime of charge separation among other parameters to be considered) of the semiconductor.

Figure 1 shows the temporal evolution of the CO conversion and the formation of CO₂, CH₄, and H₂ using NiO as photocatalyst and H₂O as reducing agent under simulated sunlight irradiation. As can be seen in Figure 1, H₂ is formed as primary, but unstable product and its proportion grows in the first hour of irradiation, but subsequently decreases

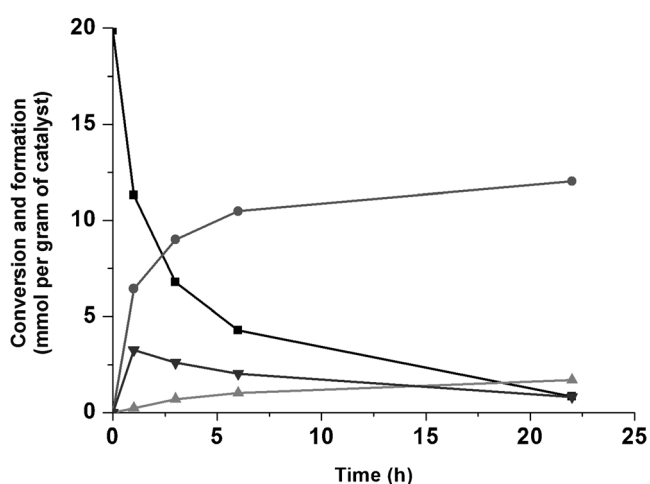


Figure 1. Photocatalytic CO (■) conversion and formation of CO₂ (●), CH₄ (▲) and H₂ (▼). Reaction conditions: gas-phase irradiation of a moisture-saturated mixture of N₂ (80%) and CO (20%, 4.9 mmol), NiO 250 mg, irradiation source solar simulator (1000 W × m⁻²).

gradually. CH₄ exhibits an induction period at initial times and is formed as a secondary product. These temporal profiles, particularly the fact that the rate of H₂ decrease is about one half that of the CH₄ growth, provide kinetic support to a CH₄ formation mechanism involving prior generation of H₂ from H₂O vapor and subsequent reaction of H₂ to form CH₄.

With regard to Table 1, it is worth commenting on the high percentage of carbon present on the solid photocatalyst, particularly in the cases of NiO, Co₂O₃, and Fe₂O₃. This carbonaceous residue adsorbed on the photocatalyst was characterized by Raman and X-ray photoelectron spectroscopy (XPS; see Figures S2 and S3), both spectra being compatible with the assignment of this residue to graphitic carbon generated in the photocatalytic process. The fresh photocatalysts do not show any carbon-related Raman peak. However, after irradiation, the characteristic 2D, G, and D bands of carbon appearing between 2500–2900 and at 1600 and 1350 cm⁻¹ were observed.

XPS of the photocatalyst after being used shows the presence of a peak at 285.12 eV that can be deconvoluted in three major components corresponding to sp² graphene C atoms (67%), sp² C atoms bonded to O (25%), and sp³ C atoms (8%), respectively. The percentage of carbonaceous residue deposited on each material before and after irradiation was determined by combustion elemental analysis of the solid. The carbon content of the fresh photocatalysts was negligible, whereas it was necessary to consider the amount of carbon deposited on the photocatalyst after the reaction, together with the CH₄ and CO₂ formed in the gas phase to calculate satisfactorily the C mass balance (>95%) in all cases. This indicates that CO is converted not only into gas-phase products, but it also forms carbon deposits on the solid. In agreement with the presence of carbon on the used photocatalyst, the colored metal oxides after the reaction become in some cases visually black (see the inset in Figure S2 for NiO).

The behavior observed for p-type semiconductors (formation of large CH₄ percentages in the gas phase and carbon residues on the solid) sharply contrasts with the photocatalytic activity of TiO₂ commented earlier [Eq. (1)]. Additional tests using CeO₂ as photocatalyst, another n-type semiconductor, also show the preferential formation of CO₂. Sunlight conversion of CO using TiO₂ and CeO₂ is about 30 times lower than the conversion achieved by p-type metal oxides. This low activity of TiO₂ and CeO₂ at solar light irradiation is well-known and derives from their limited visible-light photoresponse of these wide-bandgap semiconductors. Besides the advantageous photoaction spectra of n-type semiconductors arising from the visible-light absorption of these materials, the different photocatalytic behavior of p- and n-type semiconductors could derive from the higher conduction-band potential in p-type semiconductors (+0.8 V versus the normal hydrogen electrode, NHE, for Ni)^[18] compared to TiO₂ (−0.1 V versus NHE at pH 0)^[19] and CeO₂ (−0.1 V).^[12] A high conduction band potential favors the reduction of CO to C and CH₄ with respect to the oxidation of CO to CO₂ which is almost the sole process observed for TiO₂ and CeO₂.

To establish if the photocatalytic reduction of CO to CH₄ using p-type photocatalyst can be further favored using H₂ instead of H₂O as reducing agent present in the system, additional experiments with simulated sunlight where NiO or Fe₃O₄ were illuminated in contact with an atmosphere that contains CO and H₂ were carried out. H₂ could be obtained independently from steam reforming and the water-gas shift reaction or generated photocatalytically from water. The results obtained using two different CO/H₂ molar ratios are summarized in Table 1 (footnotes [f] and [h]), whereas the corresponding time conversion plots are shown in Figure 2. The photocatalytic CH₄ formation increases considerably using H₂ as reducing agent. The high CO conversions

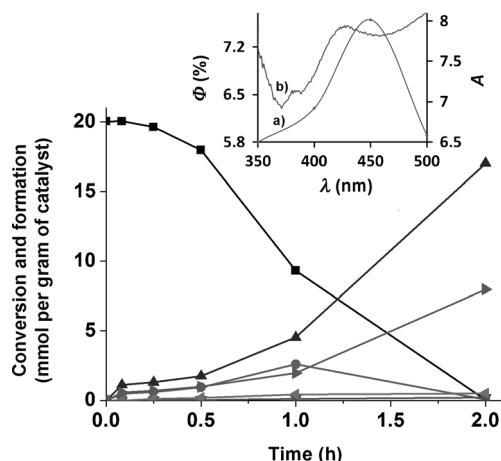
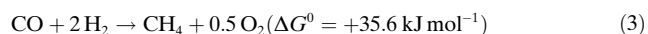


Figure 2. CO (■) conversion and formation of CO₂ (●) and CH₄ (▲), O₂ (◆), ethane (◄) and propane (►). Reaction conditions: Mixture of CO (20%, 5 mmol), H₂ (18.75 mmol), Ar (1.1 mmol), and N₂ (13.9 or 0.125 mmol); photocatalyst mass 250 mg, reaction time 3 h, light source solar simulator, illumination source solar simulator (1000 W × m⁻²). The inset shows the apparent quantum yields (Φ) for the CH₄ formation (a) and the UV/Vis absorption spectrum of NiO (b; A = absorbance).

achieved using H₂ allow the quantification of the O₂ evolution, which shows a trend similar to the temporal profile of the CH₄ evolution (Figure 2) according Equation (3).



Both in the absence and presence of H₂, formation of CO₂ is observed although with considerably lower yields when H₂ is present (see Table 1 and Figure 2). This higher activity using H₂ as reducing agent can be easily understood considering the high endoergonicity of the reaction using H₂O as reducing agent [Eq. (2)] and the more complex reaction mechanism using H₂O that requires prior H₂ generation. The percentage of elemental carbon deposited on NiO is reduced by one half when the irradiation is carried out using H₂ as reducing agent compared to H₂O vapor.

For the formation of CH₄ two equivalents of H₂ should be consumed. Thus, for those irradiation reactions where H₂ and CO are present in a 1:1 molar ratio, the generation of CH₄ reaches asymptotically a value that does not grow further

when the reaction time is prolonged (Figure S4). When the irradiation is carried out in H₂ excess, the CH₄ production is higher, the consumption of CO is complete, and the percentage of CO₂ formed is considerably lower.

Comparison of the photocatalytic activity of NiO and Fe₃O₄ indicates that the former is more efficient for the CH₄ formation (Table 1). The highest CH₄ yield achieved herein was 17.26 mmol per gram of catalyst, corresponding to a reaction carried out using NiO as photocatalyst with a 3.5-fold excess of H₂. Under these optimal conditions in excess of H₂ using simulated sunlight with a nominal power of 1000 W × m⁻², the yield of CO₂ is 24 times lower than the global amount of alkanes. This efficiency using simulated solar light is remarkable and without precedent.

To assess the visible-light photoactivity of NiO, the photoaction spectrum for the CH₄ generation was determined (see the inset in Figure 2). The overlay of the apparent quantum yield for the CH₄ generation based on the incident photon conversion (maximum Φ_{app} 7.5% at 450 nm) with the NiO absorption band shows a notable coincidence, although the efficiency of the photocatalytic CH₄ generation at long wavelengths is much lower compared to the NiO absorption spectrum. This could be related to the higher efficiency of the ligand-to-metal electronic transition appearing around 410 nm with respect to the less efficient Ni²⁺-centered d-d absorption characteristic of transition-metal ions with incomplete d shell appearing at longer wavelengths in the visible region.

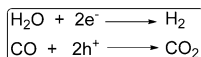
In cases in which H₂ is present together with CH₄, significant amounts of ethane and propane are also formed. Formation of these light alkanes decreases somewhat the CH₄ selectivity. This behavior is reminiscent of the Fischer-Tropsch process, where a mixture of CO and H₂ gives rise to the formation of linear hydrocarbon molecules at elevated temperatures using Ni or Fe catalysts. It is, however, pertinent to remind that the current process is performed at temperatures below 36 °C.

Formation of elemental carbon on the photocatalyst corresponds to CO reduction and this elemental carbon could act as an intermediate in the formation of CH₄. In order to verify this possibility, a test was carried out in which CO diluted in N₂ was submitted to irradiation until the NiO photocatalyst became visually black. At this time, the irradiation was stopped and the photoreactor outgassed to remove CO. Sampling of the photocatalyst revealed 1.7 wt % carbon content. Then, H₂ was admitted into the photoreactor and the irradiation continued. CH₄ evolution was observed in the gas phase in the absence of CO. This experiment can be easily interpreted considering that upon irradiation in the absence of H₂ carbon deposits are formed on the NiO surface. Subsequently, this carbon residue is able to react photocatalytically with H₂ to form CH₄, regardless of the absence of CO. A control experiment following an identical protocol in the dark shows that no CH₄ is formed.

A mechanistic proposal for the photoreduction of CO by H₂ using a p-type photocatalyst is shown in Scheme 1. According to this proposal, CO can act as a hole-trapping agent, leading to the formation of CO₂. If another electron donor agent, such as H₂O or H₂, is also present, then these

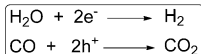
A) n-Type semiconductors

CO oxidation

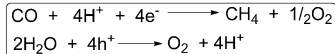


B) p-Type semiconductors

CO oxidation



CO reduction



Scheme 1. Contrasting photocatalytic behavior of n- and p-type semiconductors based on the product distribution observed.

compounds will compete with CO for oxidation. CO can alternatively undergo reduction by the semiconductor conduction-band electrons, forming elemental C and O₂. This CO reduction process will be more favorable as the reduction potential of the conduction-band edge of the photocatalyst increases (case of p-type semiconductors), as has been observed in related precedents.^[20] Thus, one of the main factors influencing the outcome of the photocatalytic CO reduction should be the position of the semiconductor conduction-band edge.

In agreement with this rationalization, a stoichiometric growth in the concentration of molecular O₂ was detected when H₂ is the reducing agent. When H₂O is used as electron donor, the lower formation of CH₄ makes the quantification of O₂ uncertain because of the air contamination. Elemental carbon is deposited on the surface of the photocatalyst as evidenced visually (inset in Figure S2) and determined by combustion chemical analysis (Table 1). Elemental carbon undergoes efficient photocatalytic H₂ reduction, giving rise to CH₄.

To provide some support to the mechanistic proposal, additional experiments were carried out. A mixture of CO and H₂ was irradiated in the presence of methanol as sacrificial electron donor agent, whereby total inhibition of the formation of CO₂ was observed, while CH₄ was still formed. This is in accordance with the proposed origin of CO₂ arising from the photooxidation of CO on the surface of the semiconductor as indicated in Scheme 1.

The photocatalytic irradiation of CO and H₂ using simulated sunlight was also performed in the presence of CH₄ and NiO as photocatalyst, and under these conditions ethane as primary irradiation product was observed, similar to the Fischer–Tropsch mechanisms and the reported photocatalytic CH₄ conversion.^[21]

One of the main reasons frequently invoked to disregard p-type semiconducting metal oxides as photocatalysts is their presumed lack of stability and the occurrence of corrosion. Photocorrosion tests have been carried out mainly in liquid water. Since these conditions are different from those employed in the present study in the gas phase, we have verified the stability of the photocatalytic activity of NiO by performing three consecutive tests of the same sample. After each test, the NiO sample was submitted to calcination at 450 °C in air to effect the combustion of possible carbonaceous residue. As can be seen in Table 1, a minor decay in the CO conversion (from 99.5 to 99 %) and even an increasing

CH₄ selectivity (from 87 to 97 %) were measured after the three tests. Moreover, XRD of the NiO sample before and after the three tests was also coincident, ruling out changes in the crystal structure of NiO. XPS, which is a specific surface analysis technique, did not show differences in the binding energy related to the Ni 2p peaks (Figure S5). This information indicates the stability of NiO as photocatalyst under the present conditions. A similar stability was observed by XPS for Fe₃O₄ and Co₃O₄ (Figures S6–S8).

The previous photocatalytic experiments were carried out using simulated sunlight containing about 5 % UV radiation. The high photocatalytic activity in terms of CO conversion using NiO as catalyst compared to TiO₂ or CeO₂ has been attributed to the visible-light photoresponse of NiO in accordance to the photoaction spectrum. Additional experiments on the photocatalytic reduction of CO to CH₄ by H₂ using NiO were also carried out under visible-light irradiation using a filter that cuts off radiation wavelengths shorter than 400 nm (see the spectrum of the cut-off filter in Figure S9). The results of the visible-light photocatalytic activity of NiO (see Table 1) show that although a large percentage of the catalytic activity of NiO is related to the UV region, NiO is still active under visible-light illumination.

In conclusion, here we have shown that p-type transition-metal oxide semiconductors are efficient photocatalysts for the visible-light or solar-light, room-temperature reduction of CO to CH₄, provided that H₂O vapor or H₂ are present as reducing agents. This photochemical behavior contrasts with that of TiO₂ and CeO₂ (n-type semiconductors) that promote under the same conditions highly selectively the oxidation of CO to CO₂. Formation of elemental carbon deposited on the photocatalyst surface is also observed. NiO was the most efficient photocatalyst among the series of first-row transition-metal oxide semiconductors. Under optimal conditions using simulated sunlight and molecular H₂ as reducing agent, a selectivity towards the formation of CH₄ of 97 % at complete CO conversion was obtained. Our results open new opportunities for the photocatalytic production of solar fuels at high conversion and selectivity.

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- [1] G. R. Dey, *J. Nat. Gas Chem.* **2007**, *16*, 217.
- [2] S. Navalón, A. Dhakshinamoorthy, M. Álvaro, H. Garcia, *ChemSusChem* **2013**, *6*, 562.
- [3] J.-S. Hwanga, J.-S. Changa, S.-E. Parkb, K. Ikeuec, M. Anpo, *Top. Catal.* **2005**, *35*, 311.
- [4] T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* **1979**, *277*, 637.
- [5] K. Koci, L. Obalová, L. Matejová, D. Plachá, Z. Lacný, J. Jirkovský, O. Solcová, *Appl. Catal. B* **2009**, *89*, 494.
- [6] W. Leitner, *Angew. Chem.* **1995**, *107*, 2391; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207.
- [7] K. Mori, H. Yamashita, M. Anpo, *RSC Adv.* **2012**, DOI: 10.1039/c2ra01332k.
- [8] M. A. Fox, M. T. Dulay, *Chem. Rev.* **1993**, *93*, 341.

- [9] M. R. Hoffmann, S. T. Martin, W. Y. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, 95, 69.
- [10] D. W. Bahnemann, *Res. Chem. Intermed.* **2000**, 26, 207.
- [11] A. Primo, A. Corma, H. Garcia, *Phys. Chem. Chem. Phys.* **2011**, 13, 886.
- [12] A. Primo, T. Marino, A. Corma, R. Molinari, H. Garcia, *J. Am. Chem. Soc.* **2011**, 133, 6930.
- [13] S. Sakthivel, M. Janczarek, H. Kisch, *J. Phys. Chem. B* **2004**, 108, 19384.
- [14] S. Sakthivel, M. V. Shankar, M. Palanichamy, B. Arabindoo, D. W. Bahnemann, V. Murugesan, *Water Res.* **2004**, 38, 3001.
- [15] C. G. Silva, R. Juarez, T. Marino, R. Molinari, H. Garcia, *J. Am. Chem. Soc.* **2011**, 133, 595.
- [16] J. M. Herrmann, *ACS Symp. Ser.* **1986**, 298, 200.
- [17] G. Carraro, C. Maccato, A. Gasparotto, T. Montini, S. Turner, O. I. Lebedev, V. Gombac, G. Adami, G. Van Tendeloo, D. Barreca, P. Fornasiero, *Adv. Funct. Mater.* **2013**, n/a.
- [18] M. P. Dare-Edwards, J. B. Goodenough, A. Hamnett, N. D. Nicholson, *J. Chem. Soc. Faraday Trans. 2* **1981**, 77, 643.
- [19] M. Grätzel, *Nature* **2001**, 414, 338.
- [20] Y. P. Xie, G. Liu, L. Yin, H.-M. Cheng, *J. Mater. Chem.* **2012**, 22, 6746.
- [21] L. Yuliati, H. Yoshida, *Chem. Soc. Rev.* **2008**, 37, 1592.