CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000703

Anthraquinone Sulfonate Modified, Layered Double Hydroxide Nanosheets for Dye-Sensitized Solar Cells

Jong Hyeon Lee, Juyeon Chang, Ji-Hyun Cha, Duk-Young Jung,* Sung Soo Kim, and Ji Man Kim[a]

Dye-sensitized solar cells (DSCs) have been extensively investigated for solar energy conversion by using various combinations of inorganic semiconductors and organic sensitizers because of their low cost, easy production, and high efficiency.[1] For efficient visible-light absorption, various organic dyes have been intensively exploited because of their advantages, such as their high molar extinction coefficients and tunable optical bands,[2] in which they are anchored on mesoscopic TiO_2 semiconductors. Recently, inorganic semiconducting materials, such as quantum dots (CdSe,[3] CdS,[4]) and organometal perovskites,[5] have been proposed as inorganic sensitizers in photovoltaic cells to overcome some drawbacks of the organic dyes such as their relatively low heat stability and narrow absorption bands. One possible approach to improving the inherent light-harvesting ability of the organic dyes is to hybridize them with nanosized multifunctional inorganic materials such as layered double hydroxides (LDHs), which can provide a stable chemical environment, higher heat or photostability, and are environmentally friendly. The LDHs, also known as anionic or hydrotalcite-like clays,[6] are useful in new multifunctional systems such as biological carriers,[7] catalysts,[8] and hybrid optical layers.[9] Recently, Duan et al.[10] reported an ultrathin hybrid film consisting of LDH nanosheets and luminescent polyanions, in which the LDH nanosheets induced a well-defined photoluminescence of polymer monolayers that are individually separated by the exfoliated LDH nanosheets.[11] Moreover, the LDHs provide a stable chemical environment to increase the photochemical function and thermal stability of the intercalated organic photochromic dyes.[12] In this study, LDH nanosheets are suggested as the inorganic matrix in an attempt to induce an intense photochromic function of the organic photochromic dyes, anthraquinone sulfonate anion (AQS),[13] that are chemically immobilized on the surface of the LDH nanosheets. Herein, we report a new hybrid light sensitizer for DSCs, in which the AQS anion is selected as the organic sensitizer and the LDH nanosheets as the inorganic host. This is believed to be the first example of hybrid LDH/organic nanosheets used as a light sensitizer in photovoltaic devices.

The chemical structure and photochromic behavior of the LDH−AQS nanosheets in formamide are shown in Figure 1a. The powder X-ray diffraction (XRD) pattern of LDH−AQS microcrystals indicated a well-crystallized rhombohedral hydrotalcite-like, $3R_1$ phase with lattice parameters of $a=3.05$ and $c=60.0$ Å. An antiparallel arrangement of the AQS would be the best model by assuming that the length of the AQS anion was 12.9 Å.[14] Notably, a transparent solution was obtained by ultrasound treatment for 10 min, indicating the successful exfoliation of the platelike LDH−AQS microcrystals. Typical Tyndall light scattering of the resulting solution demonstrated the presence of exfoliated LDH nanosheets[11] as shown in Figure 1a. Interestingly, the suspension showed a strong photoinduced coloration that was not seen in the AQS–formamide solution. In (4) of Figure 1b, the UV/Vis absorption spectra for the irradiated suspension of the LDH−AQS nanosheets show extremely enhanced absorption bands in the range of 400–600 nm, where the absorption bands at 435 and 525 nm are characteristic signals for the reduction state of anthraquinone sulfonate (AQS^{2-})[15] that have a long-term stability in a high pH condition,[16] whereas formamide (the solvent) might be oxidized during the photoreaction.[17] Under continuous irradiation of the exfoliated LDH−AQS solution shown in (2) of Figure 1b, the band intensities gradually increased as a function of the irradiation time and then decreased after the light was cut off. The rate constants for photocoloration and decay were 0.072 and 0.059 min^{-1}, respectively. This may be

---

[a] Dr. J. H. Lee, J. Chang, J.-H. Cha, Prof. D.-Y. Jung, S. S. Kim,
Prof. J. M. Kim
Department of Chemistry-BK21 and Sungkyunkwan
Advanced Institute of Nanotechnology
Institute of Basic Sciences, Sungkyunkwan University
Suwon, 440-746 (Korea)
Fax: (+82) 31-290-7075
E-mail: dyjung@skku.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000703.

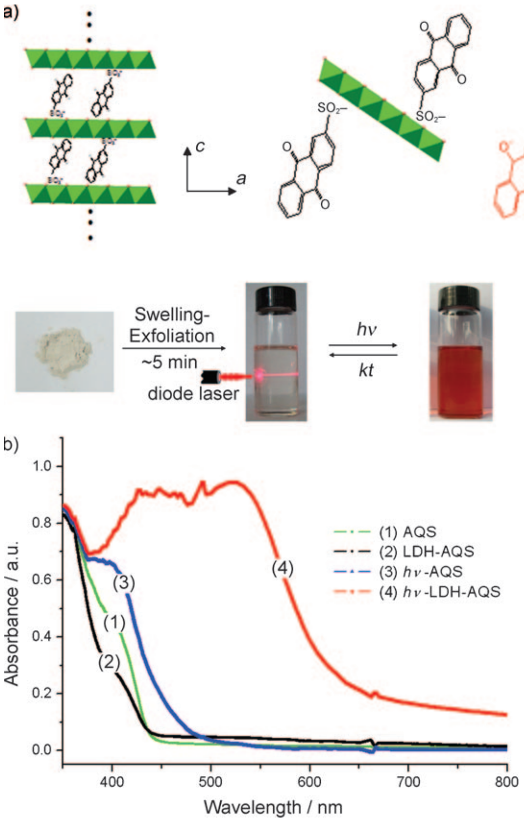

Figure 1. a) Chemical structures of the LDH–AQS nanosheets, photographs of the LDH–AQS powder, and the Tyndall light scattering and light-induced coloration of the exfoliated LDH–AQS nanosheets suspension; b) UV/Vis absorption spectra for the solutions of AQS (1, 3) and the exfoliated LDH–AQS nanosheets (2, 4). Spectra corresponding to the 3 and 4 were obtained by measuring each solution after 10 min of light soaking.

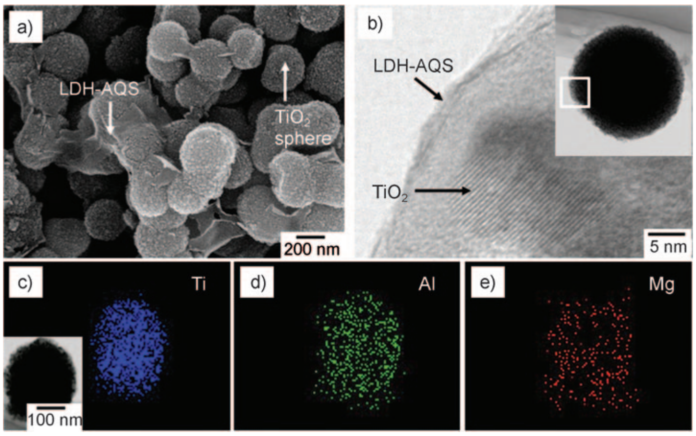

Figure 2. a) SEM image, b) HRTEM image, and c)–e) elemental maps for the LDH–AQS nanosheets self-organized on a TiO_2 sphere. The SEM image was obtained from a TiO_2 electrode on FTO glass.

due to the fact that the reactive hydroxide surfaces of the LDH framework provide a high pH environment that stabilizes the photoexcited $AQS^{\cdot -}$ or the AQS^{2-}.[16] Full characterizations and spectroscopic results are given in the Supporting Information.

The LDH–AQS nanosheets were deposited on the nanoporous TiO_2 electrode by using a self-organization process with the solution of the exfoliated LDH–AQS (1 mg/1 mL) in formamide, then rinsed with ethanol and dried at 70 °C. The top view of the field-emission scanning electron microscopy (FESEM) image in Figure 2 a revealed that the nanosheets were deposited on the top layer of the TiO_2 spheres. For further observation, a colloidal sample of the LDH–AQS nanosheets with monodispersed TiO_2 spheres was prepared and characterized by high-resolution transmission electron microscopy (HRTEM). The HRTEM image in Figure 2 b clearly indicated the existence of a continuous 2 nm thick layer of LDH–AQS nanosheets on the outside surface of the TiO_2 spheres that had a well-developed nanoporous structure.[17] The TEM image in the inset of Figure 2 b shows the colloidal sample, which consists of tightly wrapped LDH nanosheets on the surface of the TiO_2 sphere. The elemental maps showed a homogeneous distribution of Al and Mg, indicating that the LDH nanosheets covered almost the entire surface of the TiO_2 spheres.

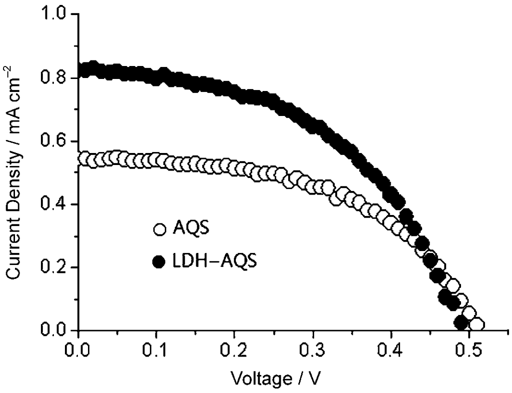

Figure 3. Current density/voltage (J/V) curves of each cell under standard AM 1.5 (100 mW cm^{-2}) illumination. The pixel area of the devices was 0.15 cm^2, and the thickness of the TiO_2 film was 10 µm. The J/V curves were obtained after 3 h of light soaking.

Current density/voltage (J/V) characteristics for the cells based on the AQS and the LDH–AQS nanosheet sensitizers are presented in Figure 3 a. The LDH–AQS-sensitized cell showed a short-circuit photocurrent (J_{SC}) of 0.82 mA cm^{-2}, an open-circuit voltage (V_{OC}) of 490 mV, and a fill factor (ff) of 0.50, corresponding to the overall solar-to-electric power conversion efficiency (η) of 0.20 %. Under the same condition, the AQS-sensitized cell gave values of J_{SC} = 0.52 mA cm^{-2}, V_{OC} = 520 mV, and ff = 0.51, corresponding to η = 0.14 %. The 0.30 mA cm^{-2} increase in the J_{SC} of the hybrid sensitized cell, which also gave a higher η than that of the AQS sensitized cell, was of particular importance although the hybrid cell had a lower number of adsorbed dye molecules (Table 1) on the TiO_2 electrodes. This result indicated that the tightly adsorbed LDH nanosheets on the TiO_2 spheres may allow electrons to transfer from the AQS

Table 1. Photovoltaic characteristics and adsorbed-dye amounts of the hybrid sensitized cells.

Dye	V_{OC} [mV]	J_{SC} [mA cm^{-2}]	*ff*	η [%]	Adsorbed dye [µmol cm^{-2}]
LDH–AQS	490	0.82	0.50	0.20	0.04
AQS	520	0.52	0.51	0.14	0.18

sensitizer to the TiO_2 electrodes, and the electrolyte can diffuse through the interconnected nanoporous TiO_2 spheres.[18]

To investigate the photochromic function of the LDH–AQS nanosheet sensitizer, the light-conversion efficiencies were plotted versus the irradiation time function (Figure 4). The J_{SC}, V_{OC}, and η were recorded over a period of 3 h. Surprisingly, both the J_{SC} and the η of the hybrid sensitized cell increased as the irradiation time increased. The overall J_{SC} and the η of the hybrid cell improved up to 144 and 160% of their initial values, respectively. This increment clearly indicated that the cell performance was strongly governed by the photochromic function of the LDH–AQS nanosheets. Clearly, this result was ascribed to the hybridization effect of the LDH nanosheets, which function as the inorganic stabilizer for the AQS^{2-} species. The overall low-energy conversion efficiencies were caused by poor electron injection of anthraquinone dyes into the conduction band of TiO_2.[19] Further studies are ongoing with the research focused on the mechanism of the interfacial electron transfer and on extending to other anions which are capable of higher conversion efficiency.

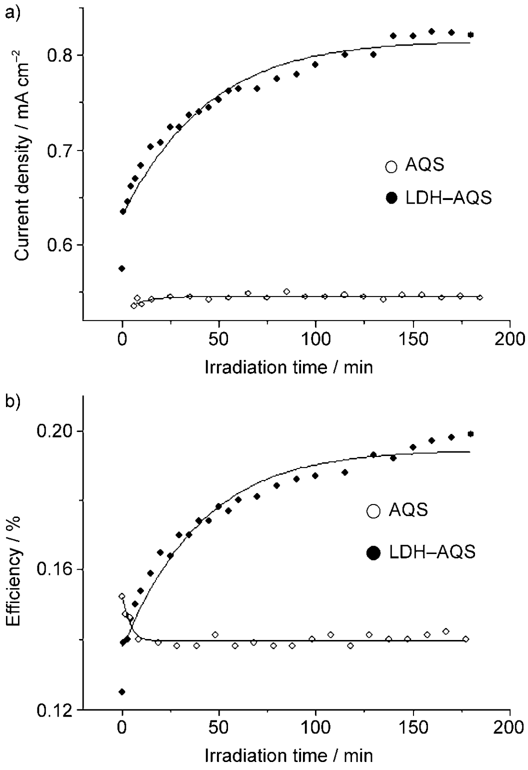

Figure 4. a) J_{SC} versus *t* and b) η versus *t* plot of each cell under standard AM 1.5 (100 mW cm^{-2}) illumination. The pixel area of the devices was 0.15 cm^2, and the thickness of the TiO_2 film was 10 µm.

In conclusion, a new hybrid light sensitizer was investigated based on employing the LDH nanosheets as an inorganic matrix to stabilize the AQS organic sensitizer in the DSCs. The LDH–AQS nanosheets showed a conspicuous photochromic property under irradiation. This hybrid sensitized cell showed improved conversion efficiency up to 160% of the initial value compared with the AQS-sensitized cell. Adopting diverse inorganic nanosheets is expected to improve the cell performance because of variable compositions of the LDHs. This functional LDH-based sensitizer provides a new platform for the development of light-harvesting sensitizers.

Experimental Section

Synthesis of LDH–AQS powder: For the synthesis of MgAl–LDH–AQS, $MgCl_2·6H_2O$ (0.20 mol, 1.22 g), $AlCl_3·9H_2O$ (0.10 mol, 0.89 g), the sodium salt of anthraquinone-2-sulfonic acid (0.15 mol, 1.40g), and hexamethylenetetramine (0.35 mol, 1.47 g) were dissolved in deionized water (30 mL). The mixture was put into a Teflon-leaned stainless steel autoclave with a capacity of 50 mL, and then maintained at 180 °C for 48 h. After the reaction was complete, the solid product was collected by filtration, washed with deionized water and acetone several times, and then dried at 70 °C.

Exfoliation of LDH–AQS: The LDH–AQS (10 mg) was mixed with formamide (10 mL) in a vial. The mixture was ultrasonically treated for 10 min, yielding a transparent suspension. To remove possible unexfoliated particles, the resulting suspension was treated by centrifugation at 5000 rpm for 10 min. No sedimentation was observed when the suspension was left standing for a month at 4 °C.

Fabrication of DSCs: Nanoporous TiO_2 spheres with a BET surface area of 81 m^{2}g and a diameter of 250 nm were synthesized by following a method described in previous report.[20] Hydroxypropyl cellulose (0.2 g), ethlylene glycol (5.0 g), and the TiO_2 spheres (1.0 g) were mixed to form a viscous paste. Prior to the coating of the viscous TiO_2 paste, a compact TiO_2 layer was coated on FTO glass (Asahi Techno Glass) by spin-coating with a commercial nanocrystalline TiO_2 paste (Advanced Nano Products, Korea). The TiO_2 photoelectrodes were fabricated by doctor-blading, followed by sintering at 450 °C. These photoelectrodes had a thickness of 10 µm and an area of 0.15 cm^2. For the AQS-based cell, the sodium salt of anthraquinone sulfonic acid (5 mM) in formamide (10 mL) was used. For the hybrid cell, the LDH–AQS nanosheets were deposited on the TiO_2 surfaces by using a self-organization process with the solution of the exfoliated LDH–AQS (1 mg/1 mL) in formamide. The substrates were rinsed with ethanol after soaking in the dye solutions and dried at 70 °C. The photovoltaic cells were constructed by combining the pretreated TiO_2 electrodes and Pt-coated FTO glass as a counter electrode with a 50 µm thick separator. A 100 µL portion of the electrolyte mixture (DMPImI (0.6 M), iodine (0.05 M), LiI (0.1 M), and *tert*-butylpyridine (0.5 M) in acetonitrile) was filled into the gap between the electrodes.

Characterizations: The powder XRD pattern was measured with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, in the θ–2θ scanning mode at 40 kV and 30 mA by using $Cu_{K\alpha}$ radiation ($\lambda = 1.5405$ Å). The fourier-transform infrared spectroscopy (FTIR) spectrum was recorded on a Biorad FTS 6000 FTIR spectrometer equipped with a high-performance DuraSamplIR II diamond accessory with an attenuated total reflectance (ATR) mode in the range of 500–4000 cm^{-1} with 100 scans at 4 cm^{-1} resolution. The UV/Vis absorption measurements were carried out with a S3100 (Sinco, Korea). Thermogravimetric analysis (TGA) was conducted on a TA instruments SDT 2960 in a nitrogen atmosphere by using a heating rate of 10 °C min^{-1} from room temperature to 800 °C. The chemical analysis for Mg and Al was carried out by using an inductively coupled plasma optical emission spectrometer (JY 38Plus, Jovin Yvon). The nitrogen adsorption–desorption isotherms were obtained with a Micromeritics TriStar at a liquid N_2 temperature. Cyclic voltammograms were obtained by using a potentiostat/galvanostat (Zahner, IM6) on a conventional three-electrode cell with a Pt plate counter electrode, a saturated Ag/AgCl reference electrode, and a Pt wire as the working electrode. The specific BET (Brunauer–Emmett–Teller) surface areas were calculated from the adsorption branches in the relative pressure (p/p_0) range of 0.05 to 0.20. The C, H, and S contents were measured by using an elemental analyzer (EA 1000, CE Instruments). The FESEM images were obtained on a JEOL 7401F (JEOL, Japan) operating at 30 kV. Before imaging, the samples were coated on carbon by sputtering with Pt to a thickness of about 3 nm. The HRTEM images were taken on a JEOL 300 KV (JEOL, Japan). The photovoltaic behavior was characterized when the cell devices were irradiated by simulated AM 1.5 sunlight with an output power of 100 mW cm^{-2} by using a Solar Simulator (Solsim, Luzchem Research) with a 300 W Xenon Lamp Power Supply (XE300BF, Luzchem Research) as the light source.

Acknowledgements

This work was supported by a National Research Foundation of Korea Grant funded by the Korean Government (NRF-2009-353-C00053), by the National Research Laboratory (NRL, ROA-2007-000-10020-0), by a Korea Research Foundation Grant funded by MOEHRD (KRF-2008-005-J00702), and by the Technology Development for New and Renewable Energies Program of Korea Institute of Energy Technology Evaluation and Planning (KETEP) (20093021010030).

Keywords: dyes/pigments • hybrid sensitizers • layered double hydroxides • nanostructures • photochromism • solar cells

---

[1] a) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737–740; b) E. A. Gibson, A. L. Smeigh, L. L. Pleux, J. Fortage, G. Boschloo, E. Blart, Y. Pellegrin, F. Odobel, A. Hagfeldt, L. Hammarström, *Angew. Chem.* **2009**, *121*, 4466–4469; *Angew. Chem. Int. Ed.* **2009**, *48*, 4402–4405.

[2] J. H. Yum, D. P. Hagberg, S. J. Moon, K. M. Karlsson, T. Marinado, L. Sun, A. Hagfeldt, M. K. Nazeeruddin, M. Grätzel, *Angew. Chem.* **2009**, *121*, 1604–1608; *Angew. Chem. Int. Ed.* **2009**, *48*, 1576–1580, and references therein.

[3] I. Robel, V. Subramanian, M. Kuno, P. V. Kamat, *J. Am. Chem. Soc.* **2006**, *128*, 2385–2393.

[4] C. H. Chang, Y. L. Lee, *Appl. Phys. Lett.* **2007**, *91*, 053503/1–3.

[5] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051.

[6] A. I. Khan, D. O'Hare, *J. Mater. Chem.* **2002**, *12*, 3191–3198.

[7] a) J. H. Choy, S. Y. Kwak, Y. J. Jung, J. S. Park, *Angew. Chem.* **2000**, *112*, 4207–4211; *Angew. Chem. Int. Ed.* **2000**, *39*, 4041–4045; b) A. I. Khan, L. Lei, A. J. Norquist, D. O'Hare, *Chem. Commun.* **2001**, 2342–2343.

[8] L. Li, Y. Feng, Y. Li, W. Zhao, J. Shi, *Angew. Chem.* **2009**, *121*, 6002–6006; *Angew. Chem. Int. Ed.* **2009**, *48*, 5888–5892.

[9] a) J. H. Lee, S. W. Rhee, H. J. Nam, D. Y. Jung, *Adv. Mater.* **2009**, *21*, 546–549; b) J. H. Lee, H. J. Nam, S. W. Rhee, D. Y. Jung, *Eur. J. Inorg. Chem.* **2008**, 5573–5578; c) J. H. Lee, S. W. Rhee, D. Y. Jung, *J. Am. Chem. Soc.* **2007**, *129*, 3522–3523; d) J. H. Lee, S. W. Rhee, D. Y. Jung, *Chem. Mater.* **2006**, *18*, 4740–4746; e) J. H. Lee, S. W. Rhee, D. Y. Jung, *Chem. Commun.* **2003**, 2740–2741.

[10] D. Yan, J. Lu, M. Wei, J. Han, J. Ma, F. Li, D. G. Evans, X. Duan, *Angew. Chem.* **2009**, *121*, 3119–3122; *Angew. Chem. Int. Ed.* **2009**, *48*, 3073–3076.

[11] R. Ma, K. Takada, K. Fukuda, N. Iyi, Y. Bando, T. Sasaki, *Angew. Chem.* **2008**, *120*, 92–95; *Angew. Chem. Int. Ed.* **2008**, *47*, 86–89.

[12] a) H. Tagaya, S. Sato, T. Kuwahara, J. Kadokawa, M. Karasu, K. Chiba, *J. Mater. Chem.* **1994**, *4*, 1907–1912; b) T. Kuwahara, H. Tagaya, K. Chiba, *Microporous Mater.* **1995**, *4*, 247–250; c) U. Costantino, M. Nocchetti in *Layered Double Hydroxides: Present and Future* (Ed.: V. Rives), Nova Science, New York, **2001**, pp. 435–468.

[13] V. A. Barachevsky, *Photochromic Quinones; Organic Photochromic and Thermochromic Compounds*, Springer, Heidelberg, **2002**, pp. 267–314.

[14] a) J. H. Lee, Y. Du, D. O'Hare, *Chem. Mater.* **2009**, *21*, 963–968; b) F. Leroux, C. Taviot-Guého, *J. Mater. Chem.* **2005**, *15*, 3628–3642.

[15] R. S. K. A. Gamage, A. J. McQuillan, B. M. Peake, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 3653–3660.

[16] a) T. Bechtold, R. Gutmann, E. Burtscher, O. Bobleter, *Electrochem. Acta* **1997**, *42*, 3483–3487; b) T. Bechtold, E. Burtscher, A. Turcanu, *J. Electroanal. Chem.* **1999**, *465*, 80–87.

[17] a) N. S. Allen, G. Pullen, M. Shah, M. Edge, D. Holdsworth, I. Weddell, R. Swart, F. Catalina, *J. Photochem. Photobiol. A* **1995**, *91*, 73–79; b) H. Görner, *Photochem. Photobiol.* **2003**, *78*, 440–448.

[18] Y. J. Kim, M. H. Lee, H. J. Kim, G. Lim, Y. S. Choi, N. G. Park, K. Kim, W. I. Lee, *Adv. Mater.* **2009**, *21*, 3668–3673.

[19] a) C. Li, X. Yang, R. Chen, J. Pan, H. Tian, H. Zhu, X. Wang, A. Hagfeldt, L. Sun, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1863–1871; b) L. M. Gonçalves, V. Z. Bermudez, H. A. Ribeiro, A. M Mendes, *Energy Environ. Sci.* **2008**, *1*, 655–667.

[20] L. S. Zhong, J. S. Hu, L. J. Wan, W. G. Song, *Chem. Commun.* **2008**, 1184–1186.

Received: March 19, 2010