

## Magnetodielectric effect of CuO grown within highly ordered two dimensional mesoporous silica template SBA 15

Amrita Mandal, Shilpi Banerjee, Sourish Banerjee, and Dipankar Chakravorty

Citation: *Journal of Applied Physics* **112**, 074310 (2012); doi: 10.1063/1.4757421

View online: <http://dx.doi.org/10.1063/1.4757421>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/112/7?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Observations on size confinement effect in B-C-N nanoparticles embedded in mesoporous silica channels](#)  
*Appl. Phys. Lett.* **105**, 014106 (2014); 10.1063/1.4890000

[Nanoindentation studies of nickel zinc ferrite embedded mesoporous silica template](#)  
*AIP Conf. Proc.* **1512**, 198 (2013); 10.1063/1.4790979

[Synthesis and optical properties of nickel zinc ferrite nanoparticles grown within mesoporous silica template](#)  
*AIP Conf. Proc.* **1447**, 233 (2012); 10.1063/1.4709965

[Magnetic properties and microstructures of iron oxide@mesoporous silica core-shell composite for applications in magnetic dye separation](#)  
*J. Appl. Phys.* **111**, 07B301 (2012); 10.1063/1.3670049

[Effects of anisotropic strain on perovskite LaMnO<sub>3</sub>+δ nanoparticles embedded in mesoporous silica](#)  
*J. Appl. Phys.* **110**, 044307 (2011); 10.1063/1.3624741

---

The advertisement features a dark blue background with a film strip graphic on the left. The text is in white and orange. The main headline reads 'Not all AFMs are created equal' in orange, followed by 'Asylum Research Cypher™ AFMs' in white, and 'There's no other AFM like Cypher' in orange. At the bottom, the website 'www.AsylumResearch.com/NoOtherAFMLikeIt' is listed in white, and the Oxford Instruments logo is in the bottom right corner with the tagline 'The Business of Science®'.

# Magnetodielectric effect of CuO grown within highly ordered two dimensional mesoporous silica template SBA 15

Amrita Mandal,<sup>1,2</sup> Shilpi Banerjee,<sup>1,3</sup> Sourish Banerjee,<sup>2</sup> and Dipankar Chakravorty<sup>1,a)</sup><sup>1</sup>MLS Professor's Unit, Indian Association for the Cultivation of Science, Kolkata 700032, India<sup>2</sup>Department of Physics, University of Calcutta, Kolkata, India<sup>3</sup>Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata 700032, India

(Received 6 June 2012; accepted 5 September 2012; published online 4 October 2012)

A two component, inhomogeneous medium can produce magnetodielectric (MD) effect without any magnetoelectric coupling. Here, we have prepared an inhomogeneous material by growing CuO within two dimensional mesostructures of silica template SBA-15 by a single step method. The  $(\text{CuO})_x\text{-(SBA-15)}_{1-x}$  nanocomposites with different weight percentages ( $x = 0.2, 0.35,$  and  $0.5$ ) were characterized by small angle x-ray diffraction study and transmission electron microscopy. Both studies confirmed the highly ordered hexagonal mesostructure for CuO(20) where 20 is the weight percentage of CuO in nanocomposite (i.e.,  $x = 0.2$ ). The mesostructure was destroyed on increasing the percentage of CuO incorporated. The nanocomposites exhibited magnetodielectric effect with dielectric constant change of 4.4% and 3% for CuO(20) and CuO(35), respectively, at 1.8 T magnetic field. This effect was explained on the basis of a two dimensional inhomogeneous two component composite model. No such effect occurs in CuO(50) due to total disappearance of the ordered mesostructure. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4757421>]

## I. INTRODUCTION

The magnetodielectric (MD) (or magnetocapacitance) effect involving a change in dielectric permittivity with applied magnetic field has been a topic of great research interest in recent years because of basic physics as well as possible applications.<sup>1–5</sup> Dielectric response under a magnetic field is often used to characterize the multiferroic systems where ferroelectric and ferromagnetic orders coexist and are coupled.<sup>6,7</sup> However, a combination of Maxwell-Wagner polarization and magnetoresistance can produce MD effect without any magnetoelectric coupling.<sup>8,9</sup> There is another possibility which does not require magnetoresistance to produce magnetodielectric effect in an inhomogeneous system because of space charge polarization coupled with Hall effect at the interface.<sup>4</sup> Composite structures, therefore, should provide a wonderful opportunity to tailor make materials with useful magnetodielectric property. This should be specially so in nanostructured systems, which could be exploited for use in nanodevices and nanosensors. We have explored the possibility of preparing nanocomposites of a semiconducting metal oxide and mesoporous silica with the above objective in view.

Mesoporous materials (pore size 2–50 nm) have attracted considerable attention in recent years due to their unique characteristics (large surface area, high pore volume, and uniform pore distribution)<sup>10,11</sup> and potential applications in catalysis<sup>12–14</sup> and sensors.<sup>15–17</sup> Highly ordered mesoporous silica materials, such as MCM-41, KIT-6, and SBA-15 are widely used as templates for preparation of nanomaterials with controlled size and shape. Various metal<sup>18,19</sup> and metal oxides such as CuO, NiO,  $\text{Co}_3\text{O}_4$ ,<sup>20</sup>  $\text{TiO}_2$ ,<sup>21</sup>  $\text{In}_2\text{O}_3$ ,<sup>22</sup>  $\text{Fe}_3\text{O}_4$ ,<sup>13</sup>

$\text{MgO}$ ,<sup>17</sup> and  $\text{ZnO}$ <sup>23,24</sup> have been synthesized within the mesoporous templates. Recently, mesoporous transition metal oxides have been studied extensively due to their novel sensing, photocatalytic and optical properties.<sup>17,21,25</sup> Among the transition metal oxides, CuO is a promising material for catalysis<sup>26</sup> and gas sensing.<sup>27</sup> It is also used as lithium ion electrode material<sup>28</sup> field emission emitter<sup>29</sup> and so on. There are several reports on mesoporous CuO mainly focusing on the different routes for its synthesis.<sup>20,30–32</sup> In the present work, we have synthesized highly ordered CuO-SBA-15 nanocomposite in one pot method and investigate its magnetodielectric property at room temperature. SBA-15 was chosen because of its two-dimensional configuration. Reasonably, high values of magnetodielectric coefficient have been found. The results have been satisfactorily explained using an inhomogeneous conductor model.<sup>4</sup> The details are reported in this paper.

## II. EXPERIMENTAL

### A. Preparation of SBA-15 and CuO-SBA-15

Mesoporous silica SBA-15 was prepared according to the method reported by Zhao *et al.*<sup>11,33</sup> At first, block



FIG. 1. Schematic representation of preparation of the CuO-SBA-15 nanocomposite.

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: [mlsdc@iacs.res.in](mailto:mlsdc@iacs.res.in).

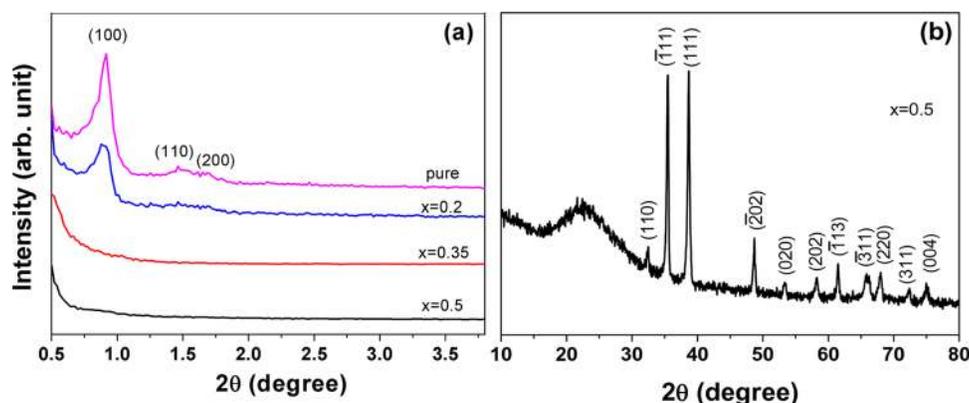


FIG. 2. (a) Small angle x-ray diffraction patterns of the pure SBA-15 and CuO-SBA-15 nanocomposites. (b) Wide angle x-ray diffraction pattern of CuO(50).

co-polymer P123 taken as a soft template was dissolved in 2M HCl solution. Tetraethylorthosilicate (TEOS) was added into that solution with stirring at 308 K for 24 h. For hydrothermal treatment, the resulting solution was transferred into a Teflon-lined stainless steel autoclave at 373 K for 24 h. After hydrothermal reaction, the resulting solid product was recovered through filtration, washed with deionized water and dried at room temperature. To remove the template, the sample was calcined at 823 K for 6 h. Pure mesoporous silica SBA-15 was obtained.

To prepare CuO-SBA-15, Copper nitrate salt was added in different weight percentages to the 2M HCl solution of P123 and stirred for 1 h before addition of TEOS. The next steps were the same as those mentioned above. The  $(\text{CuO})_x(\text{SBA-15})_{1-x}$  samples are designated as CuO(20), CuO(35), and CuO(50) for the nanocomposites with  $x = 0.2$ , 0.35, and 0.5, respectively. The preparation of CuO-SBA-15 nanocomposite starting from P123 micelle is shown schematically in Fig. 1.

Small and wide angle x-ray diffraction patterns of different samples were recorded in BRUKER D8 XRD SWAX diffractometer (manufactured by Bruker, Karlsruhe, Germany) using  $\text{CuK}_\alpha$  radiation. The microstructures of the samples were studied by a JEOL Model JEM 2010 CX transmission electron microscope (TEM) manufactured by JEOL from Tokyo, Japan operated at 200 kV. The change of dielectric constant as a function of magnetic field was measured using an electromagnet supplied by M/S Control Systems & Devices, Mumbai, India and an Agilent E4980A precision LCR meter (manufactured by Agilent Technologies, Santa Clara, USA).

### III. RESULTS AND DISCUSSION

Figure 2(a) shows the small angle x-ray diffraction (SAXRD) patterns of the three CuO-SBA-15 nanocomposites with different CuO percentages along with pure SBA-15. The XRD patterns of pure SBA-15 and CuO(20) exhibit three well-resolved peaks attributed to (100), (110), and (200) of SBA-15. These are characteristic of a 2D-hexagonal mesoporous material. But in the case of CuO(35) and CuO(50), the peaks almost disappear which indicate that with an increase in CuO the ordered mesoporous structure is destroyed. This is also confirmed by transmission electron microscopy. No reflections of the crystalline CuO phase were found in the wide angle x-ray diffraction patterns for CuO(20) and

CuO(35). Only CuO(50) showed prominent peaks corresponding to monoclinic CuO phase (JCPDS file no: 80-1916) as shown in Fig. 2(b). The amount of CuO phase was too small for  $x = 0.2$  and 0.35 compositions to cause any x-ray diffraction peaks in the wide angle x-ray diffraction pattern. Such observations were also reported earlier in similar systems involving the mesoporous material SBA-15.<sup>17,30</sup>

Figures 3(a) and 3(b) show the transmission electron micrographs of pure SBA-15 taken along and perpendicular to the channel direction, respectively. It is evident from the images that SBA-15 has highly ordered 2D hexagonal

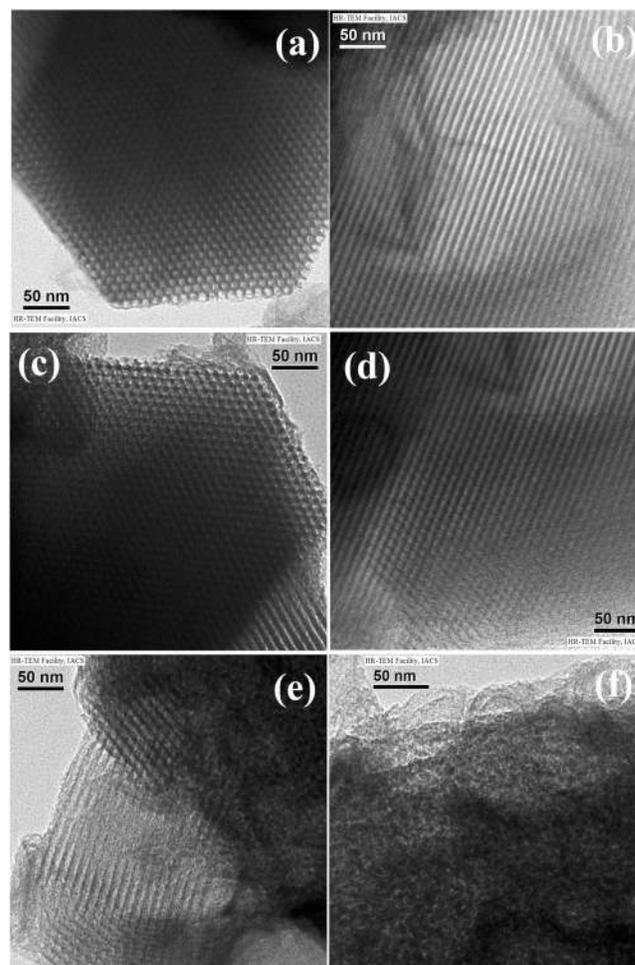


FIG. 3. Transmission electron micrographs of (a) and (b) pure SBA-15, (c) and (d) CuO(20), (e) CuO(35), and (f) CuO(50).

(p6mm) mesoporous structure. The pore width of the hexagonal pores estimated from the TEM images is found to be  $\sim 5$  nm. Figures 3(c) and 3(d) show the TEM images of the nanocomposite CuO (20), which confirm that the ordered mesoporous structure remains unaffected in this nanocomposite. Figures 3(e) and 3(f) show the morphologies of CuO (35) and CuO (50), respectively. Although the SAXRD results show no peaks for both CuO(35) and CuO(50), TEM image indicates that CuO(35) has a partially destroyed ordered mesostructures whereas in CuO(50) the structure has totally disappeared.

Figures 4(a) and 4(b) show the variation of dielectric constant  $\epsilon'$  with magnetic field ( $H$ ) measured at frequency 200 kHz for CuO(20) and CuO(35), respectively. It is evident that  $\epsilon'$  decreases with the increasing magnetic field. This can be explained on the basis of an inhomogeneous, two-dimensional, two component composite model proposed by Parish and Littlewood.<sup>4</sup> They have shown theoretically that magnetocapacitance can be produced in an inhomogeneous composite medium without any magnetic order. When an electric field is applied to a system consisting of conducting and non-conducting layers, there will be an accumulation of space charges at the boundary. An effective dipole moment results in the process. On applying a magnetic field, the

charges are moved perpendicular to both the electric and magnetic field directions due to Hall effect. The electric charge concentration at the boundary is hereby reduced. As a consequence, the dielectric constant goes down. Magnetic field dependent dielectric relaxation has been found experimentally in case of NiFe nanowires in nanoporous silicon.<sup>34</sup> Recently, we have reported the magnetodielectric effect in Ni nanosheets within Na-4 mica, which also support the above mentioned model.<sup>35</sup> In the present work, CuO phase was grown within the two-dimensional mesoporous silica template SBA-15. Here, conducting CuO and insulating silica template make an ideal inhomogeneous, two-dimensional, two component composite system. The dielectric permittivity  $\epsilon_c(\omega)$  of such a composite system consisting of a purely resistive and a purely capacitive region connected in series is given by<sup>4</sup>

$$\epsilon_c(\omega) = \epsilon \frac{(1 + i\omega\tau)}{\sqrt{i\omega\tau[(1 + i\omega\tau)^2 - (\omega\tau\beta)^2]}} \quad (1)$$

where,  $\omega$  is the angular frequency of the electric field applied,  $\epsilon$  the dielectric constant of the insulating part of SBA-15,  $\tau = \epsilon\rho$ ,  $\rho$  being the resistivity of the CuO phase

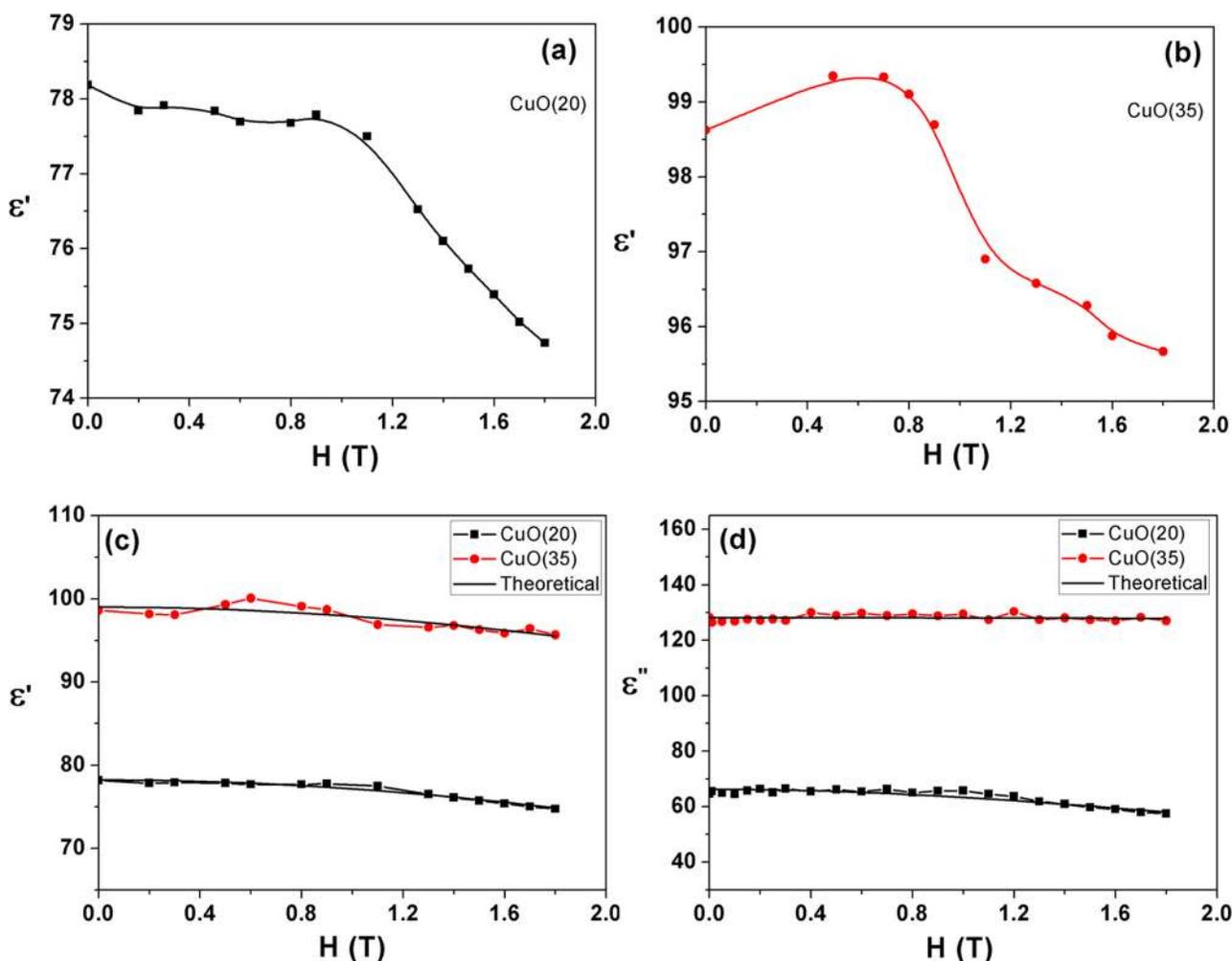


FIG. 4. Variation of dielectric constant with magnetic field for (a) CuO(20) and (b) CuO(35) at room temperature. (c) Real and (d) imaginary part of dielectric permittivity fitted with theoretical values for CuO(20) and CuO(35). Solid line represents the theoretically fitted curve.

and  $\beta = \mu H$ ,  $\mu$  being the carrier mobility, and  $H$  the applied magnetic field. It should be mentioned here that the above equation was derived by assuming that the proportions of each phase in the material were equal. Though in the present system as a whole, the volumes of the two phases are not equal, it has to be kept in mind that the regions contributing to the Maxwell-Wagner and Hall effect consist of silica with a wall thickness approximately equal to the thickness of CuO within its pore. Hence, it is justified to use Eq. (1) for the nanocomposite studied here. The experimental results for real and imaginary part of dielectric permittivity  $\epsilon_c(\omega)$  shown in Figs. 4(c) and 4(d), respectively, were fitted with the above equation using  $\mu$  and  $\omega\tau$  as parameters. The theoretical results are shown by solid lines. It can be seen that the theoretical model gives results in satisfactory agreement with the experimental data. The fitting was carried out to substantiate the model of space charge polarization modified by Hall effect as invoked earlier. The MD parameter is defined as  $MD = [\epsilon(H) - \epsilon(0)]/\epsilon(0)$ , where  $\epsilon(H)$  and  $\epsilon(0)$  are dielectric constants at magnetic field  $H$  and zero, respectively. The percentage change in real part of dielectric permittivity is found to be 4.4% and 3% for CuO (20) and CuO (35) nanocomposites, respectively, for 1.8 T applied magnetic field. It must be noted that percentage change of dielectric constant decreases with increasing CuO content in the nanocomposite. As CuO content increases in the nanocomposite the ordered mesoporous structure of SBA-15 starts getting destroyed and eventually disappear in case of 50% CuO. Through this disordered structure, CuO phase makes a percolating path. Therefore, CuO (50) does not show any magnetodielectric effect as the two component, inhomogeneous model does not apply any more to the system.

#### IV. SUMMARY AND CONCLUSIONS

In summary, CuO-SBA-15 nanocomposites were synthesized by growing CuO phase (with 20, 35, and 50 weight percentage) within 2D ordered mesoporous structures of SBA-15. CuO(20) and CuO(35) showed magnetodielectric effect with dielectric constant change of 4.4% and 3%, respectively, for 1.8 T magnetic field. CuO(50) did not exhibit such effect because of the destruction of ordered mesoporous structure with increasing percentage of CuO in the nanocomposite. This magnetodielectric effect has been explained on the basis of an inhomogeneous, two-dimensional, two component composite model. These mesoporous nanocomposites can be used in nanodevices and nanosensors. Also the present approach will open up the possibility of synthesizing tailor-made nanocomposites with required values of magnetodielectric parameter.

#### ACKNOWLEDGMENTS

Support for this work was derived from a grant by the Department of Science and Technology under an Indo-Australian Project on nanocomposites. A. Mandal and S. Banerjee thank University Grants Commission and Council for Scientific and Industrial Research, respectively, for

Senior Research Fellowships. D. Chakravorty thanks Indian National Science Academy, New Delhi for the award of an Honorary Scientist's position.

- <sup>1</sup>J. Cao, R. C. Rai, S. Brown, S. Brown, J. L. Musfeldt, R. Tackett, G. Lawes, Y. J. Wang, X. Wei, M. Apostu, R. Suryanarayanan, and A. Revcolevschi, *Appl. Phys. Lett.* **91**, 021913 (2007).
- <sup>2</sup>Y. Guo, Y. Liu, J. Wang, J. Wang, R. L. Withers, H. Chen, L. Jin, and P. Smith, *J. Phys. Chem. C* **114**, 13861 (2010).
- <sup>3</sup>J. Rivas, J. Mira, B. Rivas-Murias, B. Rivas-Murias, A. Fondado, J. Dec, W. Kleemann, and M. A. Senaris-Rodríguez, *Appl. Phys. Lett.* **88**, 242906 (2006).
- <sup>4</sup>M. M. Parish and P. B. Littlewood, *Phys. Rev. Lett.* **101**, 166602 (2008).
- <sup>5</sup>P. Mandal, V. S. Bhadram, Y. Sundarayya, C. Narayana, A. Sundaresan, and C. N. R. Rao, *Phys. Rev. Lett.* **107**, 137202 (2011).
- <sup>6</sup>N. Hur, S. Park, P. A. Sharma, S. Guha, and S.-W. Cheong, *Phys. Rev. Lett.* **93**, 107207 (2004).
- <sup>7</sup>P. Hajra, M. Pal, A. Datta, D. Chakravorty, V. Meriakri, and M. Parkhomenko, *J. Appl. Phys.* **108**, 114306 (2010).
- <sup>8</sup>G. Catalan, *Appl. Phys. Lett.* **88**, 102902 (2006).
- <sup>9</sup>A. Mandal, S. Mitra, A. Datta, S. Banerjee, and D. Chakravorty, *J. Appl. Phys.* **111**, 074303 (2012).
- <sup>10</sup>N. Nishiyama, J. Kaihara, Y. Nishiyama, Y. Egashira, and K. Ueyama, *Langmuir* **23**, 4746 (2007).
- <sup>11</sup>D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.* **120**, 6024 (1998).
- <sup>12</sup>Y. Huang, S. Xu, and V. S.-Y. Lin, *Angew. Chem. Int. Ed.* **50**, 661 (2011).
- <sup>13</sup>T. A. Crowley, K. J. Ziegler, D. M. Lyons, D. Ertz, H. Olin, M. A. Morris, and J. D. Holmes, *Chem. Mater.* **15**, 3518 (2003).
- <sup>14</sup>A. Taguchi and F. Schüth, *Microporous Mesoporous Mater.* **77**, 1 (2005).
- <sup>15</sup>J. Yang, K. Hidajat, and S. Kawi, *Mater. Lett.* **62**, 1441 (2008).
- <sup>16</sup>T. Yamada, H. Zhou, H. Uchida, I. Honma, and T. Katsube, *J. Phys. Chem. B* **108**, 13341 (2004).
- <sup>17</sup>R. Wang, X. Liu, Y. He, Q. Yuan, X. Li, G. Lu, and T. Zhang, *Sens. Actuators B* **145**, 386 (2010).
- <sup>18</sup>Z. Liu, O. Terasaki, T. Ohsuna, K. Hiraga, H. J. Shin, and R. Ryoo, *Chem. Phys. Chem.* **2**, 229 (2001).
- <sup>19</sup>A. Carrero, J. A. Calles, and A. J. Vizcaino, *Appl. Catal. A-Gen.* **327**, 82 (2007).
- <sup>20</sup>J. Zong, Y. Zhu, X. Yang, and C. Li, *J. Alloys Compd.* **509**, 2970 (2011).
- <sup>21</sup>Z. Zhang, F. Zuo, and P. Feng, *J. Mater. Chem.* **20**, 2206 (2010).
- <sup>22</sup>T. Waitz, T. Wagner, T. Sauerwald, C.-D. Kohl, and M. Tiemann, *Adv. Funct. Mater.* **19**, 653 (2009).
- <sup>23</sup>O. P. Tkachenko, K. V. Klementiev, E. Löffler, I. Ritzkopf, F. Schüth, M. Bandyopadhyay, S. Grabowski, H. Gies, V. Hagen, M. Muhler, L. Lu, R. A. Fischer, and W. Grünert, *Phys. Chem. Chem. Phys.* **5**, 4325 (2003).
- <sup>24</sup>T. Wagner, T. Waitz, J. Roggenbuck, M. Fröba, C.-D. Kohl, and M. Tiemann, *Thin Solid Films* **515**, 8360 (2007).
- <sup>25</sup>B. J. Scott, G. Wirnsberger, and G. D. Stucky, *Chem. Mater.* **13**, 3140 (2001).
- <sup>26</sup>J. A. Switzer, H. M. Kothari, P. Poizot, S. Nakanishi, and E. W. Bohannon, *Nature* **425**, 490 (2003).
- <sup>27</sup>C. Wang, X. Q. Fu, X. Y. Xue, Y. G. Wang, and T. H. Wang, *Nanotechnology* **18**, 145506 (2007).
- <sup>28</sup>X. P. Gao, J. L. Bao, G. L. Pan, H. Y. Zhu, P. X. Huang, F. Wu, and D. Y. Song, *J. Phys. Chem. B* **108**, 5547 (2004).
- <sup>29</sup>C.-T. Hsieh, J.-M. Chen, H.-H. Lin, and H.-C. Shih, *Appl. Phys. Lett.* **83**, 3383 (2003).
- <sup>30</sup>Y. M. Wang, Z. Y. Wu, L. Y. Shi, and J. H. Zhu, *Adv. Mater.* **17**, 323 (2005).
- <sup>31</sup>X. Lai, X. Li, W. Geng, J. Tu, J. Li, and S. Qiu, *Angew. Chem. Int. Ed.* **46**, 738 (2007).
- <sup>32</sup>S. K. Maji, N. Mukherjee, A. Mondal, B. Adhikary, and B. Karmakar, *J. Solid State Chem.* **183**, 1900 (2010).
- <sup>33</sup>D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science* **279**, 548 (1998).
- <sup>34</sup>R. Vasic, J. S. Brooks, E. Jobiliong, S. Aravamudan, K. Luongo, and S. Bhansali, *Curr. Appl. Phys.* **7**, 34 (2007).
- <sup>35</sup>S. Mitra, A. Mandal, A. Datta, S. Banerjee, and D. Chakravorty, *Euro. Phys. Lett.* **92**, 26003 (2010).