Self-Assembled Sr₃Al₂O₆-CuPc Nanocomposites: A Potential Electrochemical Hydrogen Storage Material

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Abstract: Self-assembled strontium aluminum oxide $(Sr_3Al_2O_6)/copper$ phthalocyanine (CuPc) nanocomposites were successfully synthesized *via* an in-situ preparation technique. Prior to nanocomposites preparation, nonscale $Sr_3Al_2O_6$ was synthesized by a facial solution combustion method using glucose as a reductant (fuel). The lattice structure of $Sr_3Al_2O_6$ was identified in its XRD patterns. Electrochemical hydrogen storage property of the samples (host, sensitizer, nanocomposites) was recorded to be around 3100, 2500 and 4000 mAh/g after 15 cycles, respectively.

Keywords: Nanostructures; Sr₃Al₂O₆; copper phthalocyanine; hydrogen storage.

1. Introduction

The world's need for energy is expected to carry on growing for the immediate future [1], [2]. Hydrogen storage technologies are significant and critical hydrogen economy[3], [4]. Hydrogen gas is a clean, highly abundant and non toxic renewable fuel. Their burned exhaust is only water and dissipates quickly into the atmosphere. Moreover, hydrogen contains larger amount of chemical energy per mass (142 MJ) than any other hydrocarbons [5].

Hydrogen can absorbed on various materials; metal hydrides [4], alloys [6]–[10], binary metal oxides [11], [12], MOFs [13]–[15], graphene [16]–[20] and carbon [21]–[23] are the most abundant materials in hydrogen absorption technology. Among various materials, nanoscaled binary metal oxides with unique structures and properties can be considered as a most promising hydrogen storage materials.

Oxygen deficient structure with $A_3B_2O_6$ formula has not yet reported as an individual group of materials, like $Sr_3Al_2O_6$. In the literature, such a material is considered as a composite of two metal oxides by fitting the potential parameters to all available $SrO-Al_2O_3$ crystalline system [24] or in general a polycrystalline materials [25]. Chakoumakos and coworkers [26] reported that $Sr_3Al_2O_6$ has a cubic crystal unit containing puckered six-membered AlO_4 tetrahedral ring. The rare earth elements-doped $Sr_3Al_2O_6$ prepared *via* microwave or sol-gel synthesis methods have been reported [27]–[31]. To the best of our knowledge, this is the first report which deals with the combustion synthesis of $Sr_3Al_2O_6$ nanomaterials and its application in energy storage.

In order to harvest the hydrogen storage more efficiently, organic dye sensitizer like Copper phthalocyanine (CuPc) can be used. It is an organic pigment which can improve the photo-response and conductivity of the host materials [32]–[36]. In a typical example, CuPc/Bi₂WO₆ nanocomposites have been reported for improvement of photo-response with enhanced photocatalytic activity [37]. They reported that

large amounts of hydroxyl groups on the surface of Bi_2WO_6 can form hydrogen bonds with CuPc. The nitrogen in the structure of CuPc governs this reaction.

In current study, a novel synthesis routes for preparation of $Sr_3Al_2O_6$ nanoparticles were performed. Rational fraction of glucose was used in a solution combustion process. Here, for the first time, a sensitizer *i.e.* CuPc were used as a modifier into $Sr_3Al_2O_6$ to prepare a self-assembled material with enhanced hydrogen storage capacity.

2. Experimental

2.1. Materials

 $Sr_3Al_2O_6$ was synthesized *via* a combustion method. All starting materials were supplied in analytical grade from Sigma-Aldroch. Moreover, the sensitizer *i.e.* copper phthalocyanine (Blue 15, M_w=576.07 g.mol⁻¹) were supplied from Sigma-Aldrich.

2.2. Synthesis of Sr₃Al₂O₆

Appropriate amount of $Sr(NO_3)_2$ and $Al(NO_3)_3 \cdot 9H_2O$ were separately dissolved in distilled water by simultaneous addition of reductant (glucose). The ratio of Sr^{3+} : glucose was chosen to be 1:3. The solution was stirred vigorously at 70 °C for 45 minutes to obtain a clear solution. The reaction was started by sudden increase in temperature to around 200 °C. By continuous heating, NO_2 and O_2 gases were evolved and a yellowish fluffy like materials growth. The final product was grinded and calcined at 850 °C for 4 hours. The schematic preparation process is presented in Fig. 1.



Fig. 1. Synthesis of Sr₃Al₂O₆ nanoparticles and Sr₃Al₂O₆/CuPc nanocomposites.

2.3. Preparation of Sr₃Al₂O₆/CuPc Nanocomposites

To impregnate $Sr_3Al_2O_6$ host with CuPc, 10 µmol of CuPc was dissolved in 100 ml of propylene glycol (PG) to form a dark blue solution. Subsequently, 1 mmol of $Sr_3Al_2O_6$ nanoparticles was dispersed in 20 ml of PG to form a suspension followed by continuous stirring, heating and ultra-sonicataion. 1 ml of CuPc solution was added into the dispersed $Sr_3Al_2O_6$. The amixture was stirred at 50 °C for 6 h, centrifuged, and decanted to remove propylene glycol. The products were collected by filtration, washed with distilled water for several times, and dried at 70 °C to obtained light blue powder. Fig.1 also shows the impregnation process.

2.4. Characterization

The phase compositions and structures of the samples were determined by X-ray diffraction analyzer with Cu-K_{α} radiation (λ = 0.15418 nm) over the 2 θ range of 10-80° using Rigaku D-max C III, X-ray diffractometer (XRD). The morphology of the sample was determined using Field Emission Scanning Electron Microscopy (FE-SEM, TESCAN-Brno-Czech Republic, 30VP) operated at an acceleration voltage of 5 kV and transmission electron microscope (TEM, Philips *CM30 TEM* instrument). In order to investigate the electrochemical hydrogen storage performance of the samples, the discharge capacities were measured in a three electrodes setup (SAMA 500 potentiostat-Isfahan, Iran). The electrochemical cell was thermostated at room temperature in 6 M KOH electrolyte. The potential of the copper coated materials (working) electrode was measured with respect to Ag/AgCl reference electrode and Pt counter electrode.

3. Results and Discussion

3.1. Structural Analysis

X-ray diffraction analysis was performed in order to study the phase composition, and the structural feature of $Sr_3Al_2O_6$ and its respective nanocomposites. Fig. 2 compares the XRD patterns of as mentioned materials. It was observed that the $Sr_3Al_2O_6$ nanoparticles (JCPDS 01-081-0506) formed purely in glucose. Several intense peaks at 20.11°(020), 27.17°(021), 28.51°(-211), 29.35°(220), 35.11°(031) and 32.04°(440), 45.88°(800), 56.97°(844) confirmed the formation of pure structure. Sr3Al2O6 nanostructures were grown in a cubic crystal system in a Pa-3 space group. The crystallite size of the host calculated from Scherrer equation (1); D=0.9\lambda/\betacos\theta (1); were obtained to be around 26.5 nm.



Fig. 2. XRD patterns of (a) Sr₃Al₂O₆ nanoparticles and (b) Sr₃Al₂O₆/CuPc nanocomposites.

CuPc is a type of metal organic framework with copper (II) central metal. The most of the diffraction peaks are in the range of $2\theta = 5$ to 20° . The main diffractograms of CuPc is reported at 2θ equal to 6.38° , 7.04° , 8.62° , 9.15° , 12.63° , 14.09° , 15.65° [38].

On the basis of XRD pattern of impregnated $Sr_3Al_2O_6$ nanoparticles with CuPc, there is no distinct difference compared with the XRD pattern of $Sr_3Al_2O_6$ due to a low molar ratio of CuPc, however, the position and the intensity of the peaks are slightly influenced.

3.2. Morphology

TEM images of $Sr_3Al_2O_6$ nanoparticles and $Sr_3Al_2O_6$ -CuPc show in Fig. 3. $Sr_3Al_2O_6$ nanoparticles are mostely spherical and distributed homogenousely (Fig. 3a). The particles diameters are in the range of 20-34 nm with the major probability of 26-28 nm (Fig. 3b). In the nanocomposites containing CuPc, the

host textures are covered homogeneousely (Fig. 3c-d). However, some of the host materials (texture) can be observed.



Fig. 3. TEM micrographs of (a) Sr₃Al₂O₆ nanoparticles, (b) its respective histograms and (c,d) Sr₃Al₂O₆/CuPc nanocomposites (mag. 80-200 nm)

3.3. Electrochemical Hydrogen Storage Properties

The Hydrogen discharge capacity of the samples ($Sr_3Al_2O_6$ and $Sr_3Al_2O_6/CuPc$) was obtained electrochemically under 1 mA current in 6M KOH using a three electrodes galvanistatic charge-discharge cycle (Fig. 4). In the alkaline solution, water can dissociate to form OH⁻ and H after electron transfer as Eq. 2; $H_2O + e^- \rightarrow H + OH^-$ (2). The process of surface hydrogen sorption can be explained on the basis of Eq. 3; $Sr_3Al_2O_6 + xH_2O + xe^- \leftrightarrow Sr_3Al_2O_6-H_x + xOH^-$ (3).

During the charging process of working electrode, the electrolyte dissociates and the sample adsorbs hydrogen. The maximum discharge capacity of $Sr_3Al_2O_6$ nanoparticles after 15 cycles obtained to be around ~3500 mAh/g (Fig. 4a). We have already reported that the maximum discharge curves of CuPc are located at 2500 mAh/g (~8.8%) after 15 cycles [38].

Impregnation of host nanoparticles by CuPc clearly enhanced the discharge capacity of the obtaining nanocomposites to ~4500 mAh/g (Fig. 4b). The hydrogen sorption mechanism of the nanocomposites involves reduction of central metal of sensitizers as following equation (Eq. 4); $Sr_3Al_2O_6$ -Cu^(II)Pc²⁻ + xH₂O \leftrightarrow Sr₃Al₂O₆-Cu^(II)Pc²⁻H_x + xOH⁻(4). Moreover, a part of hydrogen absorbed by host materials, therefore, dual discharge capacities can be observed.

In the KOH electrolyte, due to the high value of polarization, the CuPc demonstrates a noticeable hydrogen capacity with a well defined discharge plateau [39]. Hence, the electroreduction of water in the basic medium allows higher hydrogen pressure to be reached.

The NiAl₂O₄/NiO and CoAl₂O₄ are reported as the appropriate nanomaterials for hydrogen storage 800 mAh/g (after 15 cycles) and 1200 (after 20 cycles) discharge capacities, respectively [40], [41]. Our results show that the $Sr_3Al_2O_6$ and CuPc have an excellent storage efficiency rarely reported elsewhere. It is obvious that the impregnation of pigment (CuPc) into the $Sr_3Al_2O_6$ texture can highly affect the hydrogen storage





Fig.4. The discharge capacity sequences of (a) Sr₃Al₂O₆, and (b) Sr₃Al₂O₆-CuPc nanocomposites.

4. Conclusion

In current study, $Sr_3Al_2O_6$ nanoparticles were successfully synthesized *via* a solution combustion method using glucose. The crystal structure and the average crystallite size confirm the formation of nanoscale particles. Impregnation of $Sr_3Al_2O_6$ nanoparticles with CuPc showed that the hydrogen storage efficiencies of host enhanced. Taking into account of this process for future work need further investigation of electrochemical hydrogen storage in CuPc, $Sr_3Al_2O_6$ and respective nanocomposites. Moreover, the detailed elaboration of the electrochemical reactions during the discharging process needs further investigation.

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References

[1] Eftekhari, A., & Fang, B. (2017). Electrochemical hydrogen storage: Opportunities for fuel storage, batteries, fuel cells, and supercapacitors. *International Journal of Hydrogen Energy*, *42(40)*, 25143-25165.

- [2] Coutanceau, C., Baranton, S., Audichon, T., Coutanceau, C., Baranton, S., & Audichon, T. (2018). Hydrogen Electrochemical Production. In *Hydrogen Electrochemical Production* (pp. 1-6). Elsevier. http://doi.org/10.1016/B978-0-12-811250-2.00001-7
- [3] Sun, Y., Shen, C., Lai, Q., Liu, W., Wang, D.-W., & Aguey-Zinsou, K. F. (2018). Tailoring magnesium based materials for hydrogen storage through synthesis: Current state of the art. *Energy Storage Materials, 10*, 168-198.
- [4] Millet, P. (2014). Hydrogen storage in hydride-forming materials. In A. Basile, & A. Iulianelli (Eds.), *Advances in Hydrogen Production, Storage and Distribution* (pp. 368-409). Elsevier Ltd.
- [5] Niaz, S., Manzoor, T., & Pandith, A. H. (2015). Hydrogen storage: Materials, methods and perspectives. *Renewable and Sustainable Energy Reviews*, *50*, 457-469.
- [6] Yao, Q. R., Zhou, H. Y., Wang, Z. M., Pan, S. K., & Rao, G. H. (2014). Electrochemical properties of the LaNi4.5Co0.25Al0.25 hydrogen storage alloy in wide temperature range. *Journal of Alloys and Compounds*, 606(5), 81-85.
- [7] Sun, L., Lin, J., Cao, Z., Liang, F., & Wang, L. (2015). Electrochemical hydrogen storage properties of Ti1.4V0.6Ni alloy comprising quasicrystal coating with Cu. *Journal of Alloys and Compounds*, *650*, 15-21.
- [8] Belgacem, Y. Ben, Khaldi, C., Lamloumi, J., & Takenouti, H. (2015). Effect of the discharge rate on the electrochemical properties of LaY2Ni9 hydrogen storage alloy. *Journal of Alloys and Compounds, 631*, 7-14.
- [9] CAO, D., CHEN, D., LIU, Y., MA, L., LÜ, M., & YANG, K. (2011). Structure and hydrogen storage performance of LaNi4.25Al0.75 alloy. *Transactions of Nonferrous Metals Society of China*, 21(3), 517-522.
- [10] Liang, F., Lin, J., Wu, Y., & Wang, L. (2017). Enhanced electrochemical hydrogen storage performance of TiVNi composite employing NaAlH4. *International Journal of Hydrogen Energy*, *42(21)*, 14633-14640.
- [11] Salehabadi, A., Salavati-Niasari, M., Sarrami, F., & Karton, A. (2017). Sol-Gel auto-combustion synthesis and physicochemical properties of BaAl₂O₄ nanoparticles; electrochemical hydrogen storage performance and density functional theory. *Renewable Energy*, 114, 1419-1426.
- [12] Gholami, T., Salavati-Niasari, M., Salehabadi, A., Amiri, M., Sabani, M., & Rezaei, M. (2018). Electrochemical hydrogen storage properties of NiAl₂O₄/NiO nanostructures using TiO₂, SiO₂ and graphene by auto-combustion method using green tea extract. *Renewable Energy*, 115, 199-207.
- [13] Hou, X. X., Sulic, M., Ortmann, J. P., Cai, M., & Chakraborty, A. (2016). Experimental and numerical investigation of the cryogenic hydrogen storage processes over MOF-5. *International Journal of Hydrogen Energy*, 41(6), 4026-4038.
- [14] Kaye, S. S., Dailly, A., Yaghi, O. M., & Long, J. R. (2007). Impact of preparation and handling on the hydrogen storage properties of Zn₄O(1,4-benzenedicarboxylate)₃ (MOF-5). *Journal of American Chemical Society*, 129(46), 14176-14177.
- [15] Li, J., Cheng, S., Zhao, Q., Long, P., & Dong, J. (2009). Synthesis and hydrogen-storage behavior of metal-organic framework MOF-5. *International Journal of Hydrogen Energy*, 34(3), 1377-1382.
- [16] Pumera, M. (2011). Graphene-based nanomaterials for energy storage. *Energy & Environmental Science, 4(3)*, 668-674.
- [17] Choi, M. H., Min, Y. J., Gwak, G. H., Paek, S. M., & Oh, J. M. (2014). A nanostructured Ni/graphene hybrid for enhanced electrochemical hydrogen storage. *Journal of Alloys and Compounds, 610*, 231-235.
- [18] Masjedi-Arani, M., & Salavati-Niasari, M. (2017). Novel synthesis of Zn₂GeO₄ /graphene nanocomposite for enhanced electrochemical hydrogen storage performance. *International Journal of Hydrogen Energy*, 42(27), 17184-17191.
- [19] Gohari-Bajestani, Z., Akhlaghi, O., Yürüm, Y., & Yürüm, A. (2017). Synthesis of anatase TiO₂ with

exposed (001) facets grown on N-doped reduced graphene oxide for enhanced hydrogen storage. *International Journal of Hydrogen Energy*, *42(9)*, 6096-6103.

- [20] Han, L., Qin, W., Jian, J., Liu, J., Wu, X., Gao, P., et al. (2017). Enhanced hydrogen storage in sandwich-structured rGO/Co_{1-x}S/rGO hybrid papers through hydrogen spillover. *Journal of Power Sources*, 358, 93-100.
- [21] Yang, S. J., Choi, J. Y., Chae, H. K., Cho, J. H., Nahm, K. S., & Park, C. R. (2009). Preparation and enhanced hydrostability and hydrogen storage capacity of CNT@MOF-5 hybrid composite. *Chemistry of Materials*, 21(9), 1893-1897.
- [22] Mohammadi, M., Khoshnevisan, B., & Varshoy, S. (2016). Electrochemical hydrogen storage in EPD made porous Ni-CNT electrode. *International Journal of Hydrogen Energy*, *41*(*24*), 10311-10315.
- [23] Liu, E., Wang, J., Li, J., Shi, C., He, C., Du, X., *et al.* (2011). Enhanced electrochemical hydrogen storage capacity of multi-walled carbon nanotubes by TiO₂ decoration. *International Journal of Hydrogen Energy*, 36(11), 6739-6743.
- [24] Rezende, M. V. S., Araújo, R. M., Montes, P. J. R., & Valerio, M. E. G. (2010). Optical properties of rare-earth doped Sr₃Al₂O₆. *Optical Materials*, *32(10)*, 1341-1344.
- [25] Alahraché, S., Al Saghir, K., Chenu, S., Véron, E., De Sousa Meneses, D., Becerro, A. I., et al. (2013). Perfectly transparent Sr₃Al₂O₆ polycrystalline ceramic elaborated from glass crystallization. *Chemistry* of *Materials*, 25(20), 4017-4024.
- [26] Chakoumakos, B. C., Lager, G. A., & Fernandez-Baca, J. A. (1992). Refinement of the structures of Sr₃Al₂O₆ and the hydrogarnet Sr₃Al₂(O₄D₄)₃ by rietveld analysis of neutron powder diffraction data. *Acta Crystallographica Section C Crystal Structure Communications*, 48(3), 414-419.
- [27] Zhang, P., Lingxia, L., & Yuming, T. (2009). The low temperature synthesis of Eu²⁺and Dy³⁺ activated Sr₃Al₂O₆ nanophosphors by microwave method. *Physica B: Condensed Matter, 404(21),* 4286-4289.
- [28] Zhang, P., Xu, M., Zheng, Z., Sun, B., & Zhang, Y. (2006). Microwave synthesis and characterization of new red long afterglow phosphor Sr₃Al₂O₆:Eu. *Transactions of Nonferrous Metals Society of China*, 16, 423-425.
- [29] Zhang, P., Xu, M., Zheng, Z., Liu, L., & Li, L. (2007). Synthesis and characterization of europium-doped Sr₃Al₂O₆ phosphors by sol–gel technique. *Journal of Sol-Gel Science and Technology*, *43*(*1*), 59-64.
- [30] Chen, L., Zhang, Z., Tian, Y., Fei, M., He, L., Zhang, P., et al. (2017). Origin of the red luminescence in Sr₃Al₂O₆:Eu phosphor—From the synergetic effects of Eu²⁺ and Eu³⁺. Journal of Rare Earths, 35(2), 127-134.
- [31] Huang, P., Zhang, Q., Cui, C., & Li, J. (2011). Influence of excitation wavelengths on luminescent properties of Sr₃Al₂O₆:Eu²⁺, Dy³⁺ phosphors prepared by sol–gel-combustion processing. *Optical Materials*, 33(8), 1252-1257.
- [32] Basova, T. V, Kiselev, V. G., Schuster, B. E., Peisert, H., & Chasse, T. (2009). Experimental and theoretical investigation of vibrational spectra of copper phthalocyanine : polarized single-crystal Raman spectra , isotope effect and DFT calculations. *Journal of Raman Spectroscopy*, *40*, 2080-2087.
- [33] Wojdyła, M., Derkowska, B., Bała, W., Bratkowski, A., & Korcala, A. (2006). Investigation of optical transition energy in copper phthalocyanine by transmission, reflection and photoreflectance spectroscopy. *Optical Materials*, *28(8)*, 1000-1005.
- [34] Schwieger, T., Peisert, H., Golden, M. S., Knupfer, M., & Fink, J. (2002). Electronic structure of the organic semiconductor copper phthalocyanine and K-CuPc studied using photoemission spectroscopy. *Physical Review B*, 66(15), 1552071-1552075.
- [35] Ambily, S., & Menon, C. (1999). The effect of growth parameters on the electrical, optical and structural

properties of copper phthalocyanine thin films. *Thin Solid Films*, 347(1–2), 284-288.

- [36] Downes, J. E., Mcguinness, C., Glans, A., Learmonth, T., Fu, D., Sheridan, P., et al. (2004). Electronic structure near the Fermi level of the organic semiconductor copper phthalocyanine. *Chemical Physics Letters*, 390, 203-207.
- [37] Zhang, Z., Wang, W., & Zhang, L. (2013). Large improvement of photo-response of CuPc sensitized
 Bi₂WO₆ with enhanced photocatalytic activity. *Dalton Transactions*, *42(13)*, 4579–4585.
- [38] Salehabadi, A., Salavati-Niasari, M., & Gholami, T. (2017). Effect of copper phthalocyanine (CuPc) on electrochemical hydrogen storage capacity of BaAl₂O₄/BaCO₃ nanoparticles. *International Journal of Hydrogen Energy*, 42(22), 15308-15318.
- [39] Jurewicz, K., Frackowiak, E., & Beguin, F. (2004). Towards the mechanism of electrochemical hydrogen storage in nanostructured carbon materials. *Applied Physics A, 78(2)*, 981-987.
- [40] Gholami, T., Salavati-Niasari, M., & Varshoy, S. (2017). Electrochemical hydrogen storage capacity and optical properties of NiAl₂O₄/NiO nanocomposite synthesized by green method. *International Journal* of Hydrogen Energy, 42(8), 5235-5245.
- [41] Gholami, T., Salavati-Niasari, M., & Varshoy, S. (2016). Investigation of the electrochemical hydrogen storage and photocatalytic properties of CoAl₂O₄ pigment: Green synthesis and characterization. *International Journal of Hydrogen Energy*, 41(22), 9418-9426.



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