Bulgarian Chemical Communications, Volume 47, Number 2 (pp. 547 – 551) 2015

Application of mechanochemical method as a new route for synthesis of β-phase AgI nanoparticles

M. Malekshahi Byranvand[1*], S. Shahbazi[2], A. Nemati Kharat[1], S. Afshar[2]

[1]*School of Chemistry, University College of Science, University of Tehran, Tehran, Iran*
[2]*Department of Chemistry, Iran University of Science and Technology, 16846-13114 Tehran, Iran*

Received March 7, 2014, revised May 12, 2014

In this contribution, we introduce a one-pot, rapid solvent-free method for preparation of silver iodide nanoparticles (AgI NPs). The AgI NPs were characterized by X-ray powder diffraction patterns (XRD), energy dispersive X-ray spectroscopy (EDX), diffuse reflectance spectra (DRS), scanning electron microscopy (SEM) and dynamic light scattering (DLS). The XRD data indicated a wurtzite structure of the β-phase of AgI in the synthesized NPs. The EDX analysis confirmed the formation of a 100% pure AgI compound. The SEM images and the DLS data confirmed the nanosized spherical morphology of 25-70 nm. The DRS of the AgI nanoparticles showed a band gap about 2.7 eV.

Keywords: Nanoparticles; Semiconductors; Silver iodide; Solvent free synthesis.

INTRODUCTION

Silver iodide (AgI) is frequently used in photography and in cloud-seeding to promote rainfalls [1]. Also, the application of AgI-based superionic conducting glasses [2] has attracted much attention. The conductivity of the solid AgI is comparable to that of liquid sulfuric acid, and is even higher than that of liquid AgI [3]. At ambient temperature and pressure, AgI usually exists as a mixture of two phases, β-AgI and γ-AgI. The β-phase has a hexagonal wurtzite structure and the γ-phase has a cubic zinc blende structure [4]. Amongst the various types of nanomaterials, semiconductor nanoparticles attract special interest because they are expected to exhibit excellent properties compared to the corresponding bulk material [5]. Recently, there has been increasing interest in AgI in form of nanoparticles (NPs) which have different optical, electrical and superionic properties compared to the bulk compound [6].

We have recently reported the facile synthesis of CuI NPs by a mechanochemical method [7]. This method involves the mechanical activation of solid-state displacement reactions at low temperatures in a ball mill [8, 9]. When comparing the mechanochemical process with the hydrothermal [10], thermal decomposition [11], microemulsion and reverse micelles [6], laser-based synthesis [12], electrospinning [13] and sonochemical [14, 15] methods for the preparation of AgI NPs, it obvious that the mechanochemical reaction has many advantages such as: one-pot synthesis, rapid reaction, solvent -free and safe reaction conditions. To the best of our knowledge, no reports for the preparation of AgI NPs under these conditions have been reported. Nevertheless, recently Hawari et al. synthesized AgI NPs using the mechanochemical method in the liquid-state over a long period of time (40–70 h) [16]. This study, for the first time, introduces a solid-state mechanochemical method for the synthesis of spherical β-AgI NPs. The proposed method is solvent-free and facile which would result in a lower cost and environmental safety.

MATERIALS AND METHODS

$AgNO_3$ (99%) and KI (99.5%) were purchased from Merck Company and were used without further purification. In a 10 ml stainless steel vial a mixture of $AgNO_3$ and KI solids with a molar ratio of 1:1 were milled using a Mixer Mill (Retsch MM-400) apparatus at 1800 rpm (30 Hz) for 40 min at room temperature. The resulting mixture was washed with deionized water to remove the potassium nitrate salt. The precipitate was then dried in a vacuum oven at 100 °C for 2 h to obtain the final yellow product.

X-ray powder diffraction patterns (XRD) were recorded on a SIEFERT XRD 3003 PTS diffractometer using Cu Kα irradiation (λ¼1.5418 Å). Diffuse reflectance spectra (DRS) were measured on a TU-1901 spectrophotometer. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed with a Hitachi S-4160 microscope with

* To whom all correspondence should be sent:
E-mail: mahdi.malekshahi@gmail.com

attached camera operating at 30 kV to determine the morphology, particle size and purity of the prepared synthesized salt. Dynamic light scattering (DLS) analysis was performed on a Zetasizer Nano-Z model apparatus to determine the size distribution of AgI NPs. All measurements were done at room temperature.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern was used to investigate crystallinity and phase structure of the product before and after the washing process (Fig. 1a, b). As shown in Fig. 1a, peaks related to KNO_3 phases were indexed and before washing the peak intensity of the products was relatively high. Due to overlapping of AgI and KNO_3 peaks in a certain region, after washing the sharpness of AgI peaks decreased (Fig. 1b). So it was concluded that AgI NPs were completely formed by the solid-state method. The β-AgI phase can be characterized by the peaks located at 2Θ value of 22.32°, 23.71°, 25.35°, 32.76°, 39.20°, 42.63° and 45.57°, which are assigned to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) planes of β-AgI crystal, respectively (Fig. 1 b)[17].

All diffraction peaks can be indexed to the hexagonal phase for the β-AgI with a wurtzite structure (space group P63mc, JCPDS card no. 3-0940). As we expected, all products generated from these simple mechanochemical reaction systems are pure AgI crystals, no diffraction signal from other byproducts such as Ag_2O was detected.

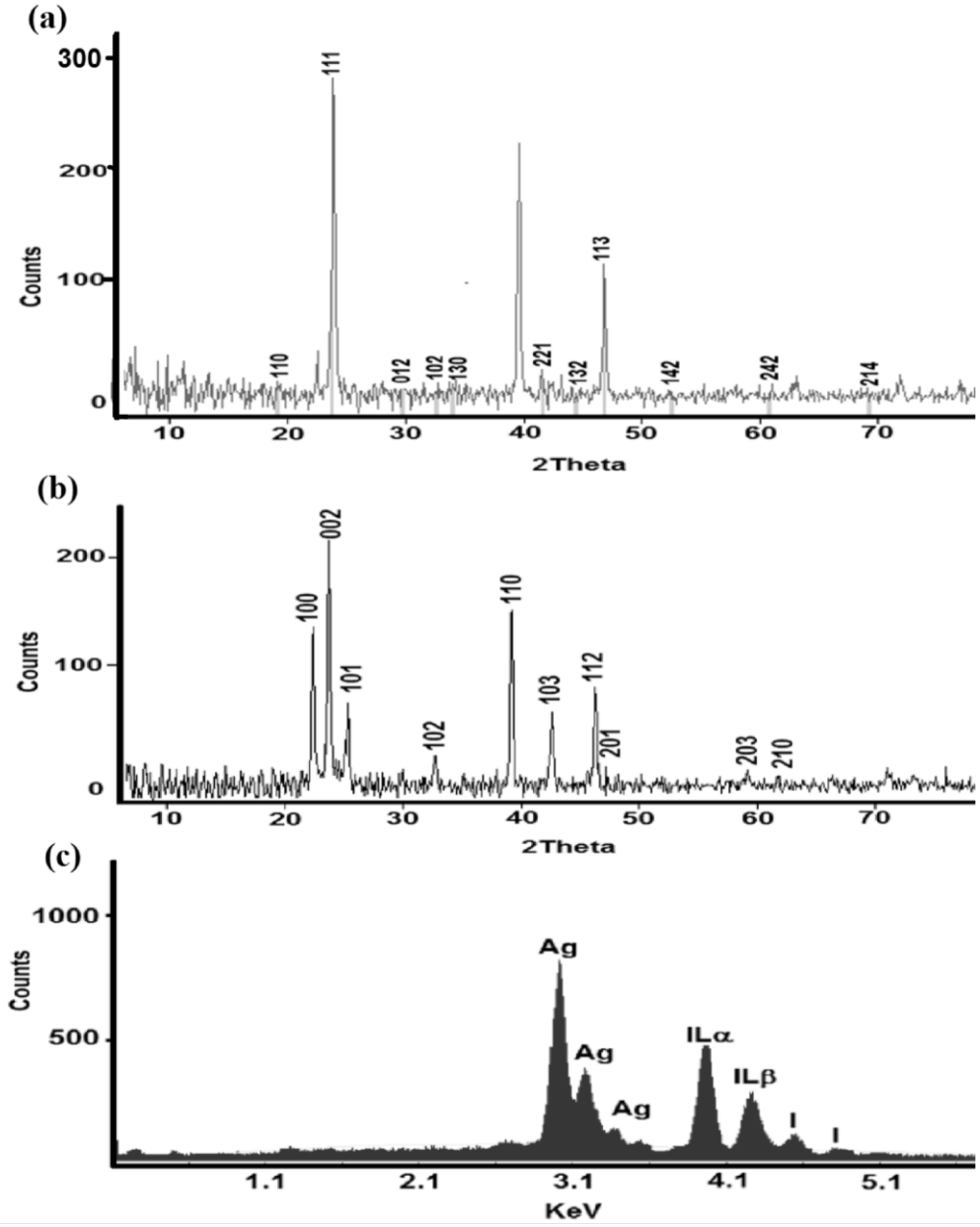

Fig. 1. (a) XRD pattern of the mixture of AgI NPs and KNO_3 salt (b) AgI NPs after the washing process; (c) EDX pattern of the synthesized product.

In the long history of investigation of AgI, one main difficulty was to obtain pure single phase crystals [18, 19]. According to our studies, AgI single phase crystals were obtained during mechanochemical reaction for 40 min at room temperature without any solvent. The estimated grain size of the AgI powder using Debye-Scherrer's formula [20] was found to be about 32 nm. The purity of the prepared AgI NPs was evidenced by the EDX pattern shown in Fig. 1c. The EDX analysis verified the existence of silver and iodide atoms in the final product. This analysis showed 100% purity of the synthesized compound which is in good agreement with the XRD data.

The morphology of the obtained product was investigated by SEM. As can be seen in Fig. 2a and b, the SEM images show that the AgI NPs powder consists of 25-50 nm spherical nanoparticles.

The DLS analysis was also used to estimate the particle size and size distribution. The particle size histogram in Fig. 2 c shows that size distribution is 25-70 nm and nanoparticles are uniformly aggregated, which is very close to the results obtained by SEM analysis. Optical absorption measurements were used extensively, because they are some of the most important methods to investigate the energy structures and optical properties of semiconductor nanocrystals [21, 22]. Based on the theory of optical absorption, the relation between the absorption coefficient and photon energy is as follows:

$$\alpha h\nu = A(h\nu - Eg)^{n/2} \qquad (1)$$

where α is the absorption coefficient, ν is the frequency of photons, A is a constant, Eg is the band gap energy and n depends on the nature of the transition (n=1 for direct transitions) [23].

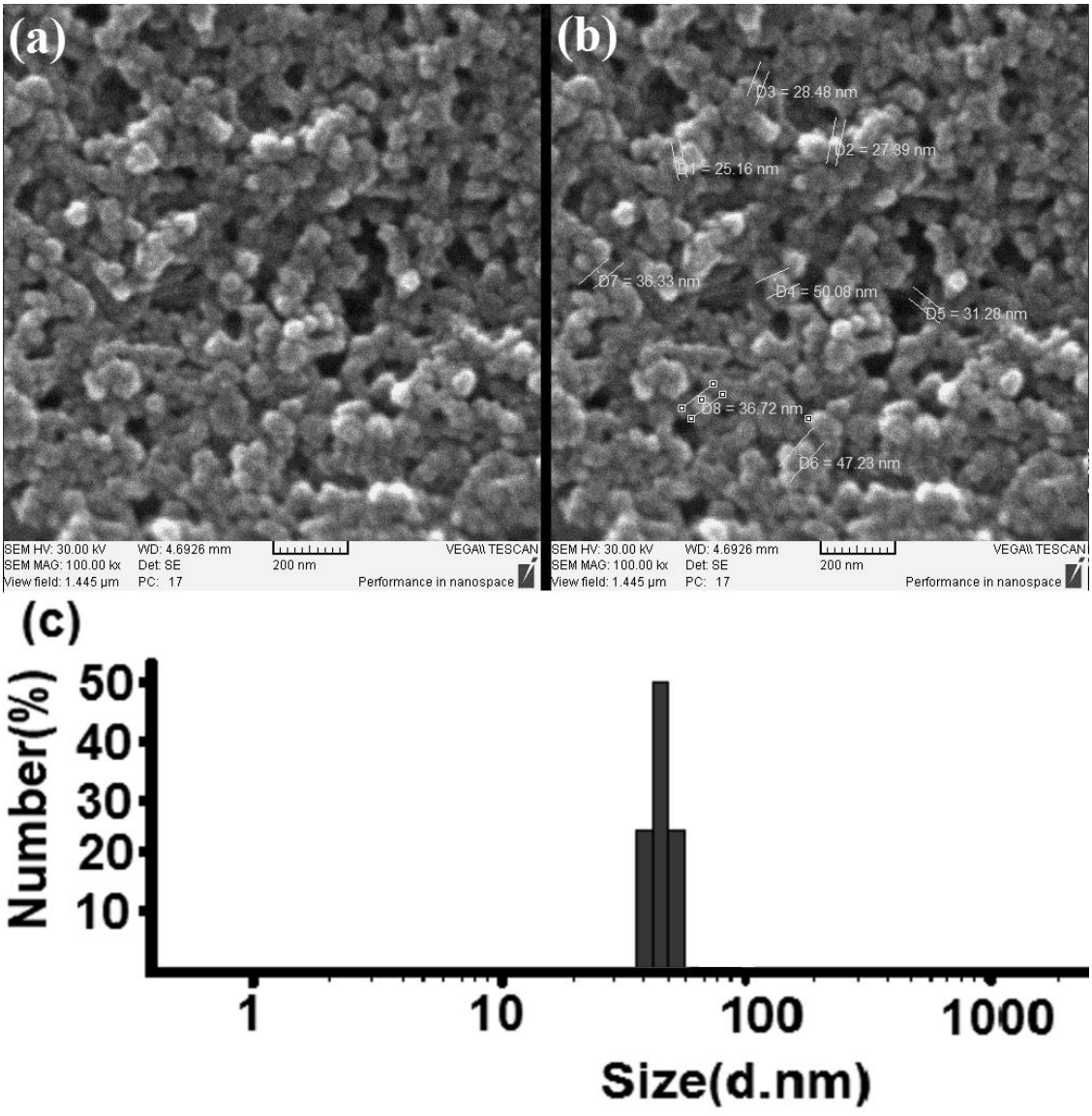

Fig. 2. (a, b) SEM images of AgI NPs; (c) Size distribution histogram extracted from DLS analysis data.

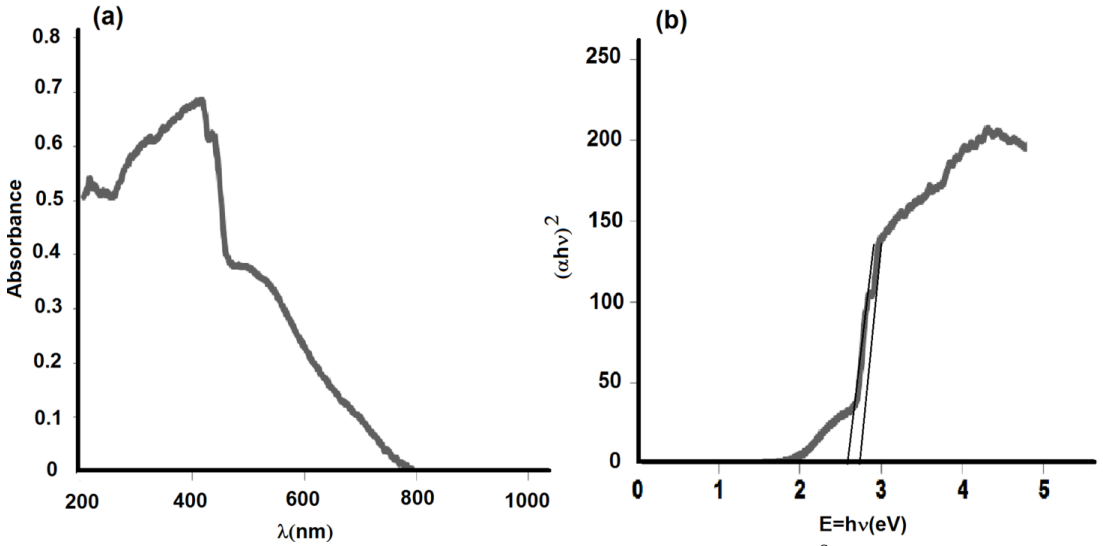

Fig. 3. (a) Optical absorption spectrum of obtained AgI NPs; (b) the plot of $(\alpha h\nu)^2$ vs.h*ν*.

Figs. 3a and b show the optical absorption spectrum and the plot of $(ahν)^2$ *vs.* hν for the prepared AgI nanoparticles, respectively. There is a broad absorption peak with broader shoulders at about 495 nm and weak absorption peak at about 505 nm. According to the extrapolated values of the linear section, the band gap Eg is estimated to be 2.7 eV and 2.8 eV.

CONCLUSION

In this work, β-phase of AgI with spherical morphology of NPs was successfully synthesized using the mechanochemical method. The XRD and EDX analyses of these NPs revealed a pure β-phase. According to our studies, AgI NPs were obtained during mechanochemical reaction for 40 min without any solvent. This facile, solvent-free, short-time and one-pot method for the synthesis of AgI compound is reported for the very first time. The method proposed in this work has many advantages, such as solvent free characteristics which result in lower costs, environmental safety and a very easy procedure of synthesis. We believe that this simple method will be adopted in realizing other forms of nano-sized silver compounds on industrial scale.

REFERENCES

1. Z. Zheng, A. R. Liu, S. M. Wang, B. J. Huang, X. M. Ma, H. X. Zhao, D. P. Li , L. Z. Zhang, *Materials Research Bulletin*, **43**:2491(2008).
2. T. Usuki, S. Saito, K. Nakajima, O. Uemura, Y. Kameda, T. Kamiyama, M. Sakurai, *Journal of Non-Crystalline Solids*, **312–314**, 570 (2002) T. Usuki, S. Saito, K. Nakajima, O. Uemura, Y. Kameda, T. Kamiyama,
3. J. Non-Cryst. Solids, (2002), p.
4. S. Yamasaki, T. Yamada, H. Kobayashi, H. Kitagawa, *Chemistry – An Asian Journal*, ***8***, 73 (2013).
5. C. Liang, K. Terabe, T. Tsuruoka, M. Osada, T. Hasegawa, M. Aono, *Advanced Functional Materials*, **17**, 1466 (2007).
6. M. Bangal, S. Ashtaputre, S. Marathe, A. Ethiraj, N. Hebalkar, S. W. Gosavi, J. Urban, and S. K. Kulkarni, *Hyperfine Interact*, **160**, 81 (2005).
7. I. L. Validžić, I. A. Janković, M. Mitrić, N. Bibić, J. M. Nedeljković, *Materials Letters*, **61**, 3522 (2007).
8. S. Shahbazi, S. Afshar, *Materials Letters,* **115**, 190 (2014).
9. A. Tadjarodi, M. Izadi, M. Imani, *Materials Letters*, **92,** 108 (2013).
10. J. Huot, D. B. Ravnsbæk, J. Zhang, F. Cuevas, M. Latroche, T. R. Jensen, *Progress in Materials Science*, **58**, 30 (2013).
11. L. Chen, J. Ma, Q. Chen, R. Feng, F. Jiang, M. Hong, *Inorganic Chemistry Communications*, **15**, 208 (2012).
12. L. Yang, J. ,Lu Z. Wang, L. Li, *Kuei Suan Jen Hsueh Pao/Journal of the Chinese Ceramic Society*, **39**, 929 (2011).
13. H. Tan, W. Y. Fan, *Chem Phys Lett.*, **406**, 289 (2005).
14. H. Liang, C. Li, J. Bai, L. Zhang, L. Guo, Y. Huang, *Applied Surface Science*, **270**, 617 (2013).
15. F. Mohandes, M. Salavati-Niasari, *Materials Research Bulletin*, **48,** 3773 (2013).
16. A. R. Abbasi, A. Morsali, *Ultrason Sonochem.*, **17**, 704 (2010).
17. N. L. Hawari, M. R. Johan, *Journal of Alloys and Compounds*, **509**, 2001 (2011).
18. S. Feng, H. Xu, L. Liu, Y. Song, H. Li, Y. Xu, J. Xia, S. Yin, J. Yan, *Colloids and surfaces A: Physicochemical and engineering aspects*, **410**, 23 (2012).
19. Y. Wang, J. Mo, W. Cai, L. Yao, L. Zhang, *Materials Letters*, **56**, 502 (2002).
20. H. He, Y. Wang, H. Chen, *Solid State Ionics*, **175**, 651 (2004).

21. M. Song, Z. Zhang, *Materials Research Bulletin*, **39**,2273 (2004)
22. K.H. Schmidt, R. Patel, D.Meisel, *Journal of the American Chemical Society*, **110**, 4882 (1988).
23. J. Liu, X. Huang, Y. Li, K .M. Sulieman, X. He, F. Sun, *Crystal Growth & Design*, **6**, 1690 (2006).
24. B. Sharma, M. K. Rabinal, *Journal of Alloys and Compounds*, **556**, 198 (2013).

ПРИЛОЖЕНИЕ НА МЕХАНОХИМИЧНИ МЕТОДИ КАТО НОВ ПЪТ ЗА СИНТЕЗАТА НА β-ФАЗОВИ НАНОЧАСТИЦИ ОТ AgI

М. Малекшани Биранванд[1*], С. Шахбази[2], А. Н. Кхарат[1], С. Афшар[2]

[1] *Училище по химия, Колеж за наука, Университет в Техеран, Иран*
[2]*Департамент по химия, Ирански университет по наука и технология 6846-13114 Техеран, Иран*

Постъпила на 7 март, 2014 г., коригирана на 12 май, 2014 г.

(Резюме)

В настоящата работа се предлага едно-стадийна, бърза синтеза, без разтворител, за приготвянето на наночастици от сребърен йодид (AgI NPs). Наночастиците са охарактеризирани чрез прахова рентгенова дифракция (EDX), дифузионни отражателни спектри (DRS), сканираща електронна спектроскопия (SEM) и динамично светоразсейване (DLS). XRD-данните показват, че синтезираните наночастици имат структурата на вюрцит на β-фаза от сребърен йодид. В допълнение EDX-анализът потвърждава образуването на сребърен йодид със 100% чистота. Освен това SEM-образите и DLS-анализът потвърждават сферичната морфология на частиците с размери 25-70 nm. DRS-спектрите на продукта показват, че наночастиците от AgI имат забранена зона около 2.7 eV.