



## Research article

## Self-assembly of silver nanoparticles through functionalization with coumarin-thiazole fused-ring thiol

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## ABSTRACT

Self-assembly of nanoscale building blocks plays a critical role for the edifice of functional nanomaterials. In this work coumarin based fused-ring heterocyclic thiol functionalized silver nanoparticle exhibiting large self-assembly is reported. The particles spontaneously self-organise towards the formation of larger superstructures, yet still retaining their individual particle morphology (~10nm). The  $\pi$ -stacking behaviour of coumarin based fused ring aromatic skeleton seems to play the key role for the induction of dense assembly in this hybrid nanoparticles. In the present work the anchoring group (thiol) is directly attached to the aromatic framework of the Coumarin-thiazole fused-ring, for easier electron flow between the metal and the aromatic ligand. The synthesized materials have been characterized by UV-Vis, Fluorescence, XRD, TEM, SAED, IR, <sup>1</sup>H and <sup>13</sup>C NMR. The synthesis of the ligand and process of functionalization is simple and easily reproducible.

## 1. Introduction

Self-assembly of nanoparticles is a field of great research expectation due to their unusual collective properties. Controlled self-assembly based on selective control of non-covalent interactions in various classes of nanomaterials provide a great possibility of exploitation of these functional properties in tailor-made device applications [1, 2, 3]. The crucial component to realize self-assembly is the proper balance of attractive forces (covalent, H-bond etc.) and repulsive forces (electrostatic, steric etc.) [4,5]. Various approaches have been reported to organize nanoparticles in assembly like, anisotropy in ligand attachment [6], phase separation [7], grafting complementary DNA [8, 9], charge transport [10], electroless deposition [11] etc. Apart from that, various microbes, like Spirulina algae [3], M13 virus aerogel [12], Tobacco Mosaic Virus [13, 14], genetically engineered viruses [15, 16] etc. Diverse driving methods like, light [17], heat [18], electric field [19], magnetic field [20], evaporation induced [21] etc. have been reported by many researchers. Because of the strong electronic interactions the self-assembled hybrid materials are being explored intensively in optoelectronics [22] and related fields. Recently Raghuvanshi and his colleagues, using sputtering in deep eutectic solvent reported the formation of small self-assembled clusters of Au nanoparticles without undergoing agglomeration [23, 24].

Self-assembly of hybrid nanoparticles through surface modification with small functional molecules, mostly possess a spacer unit [25] like, alkyl (1) [26], H-bonded spacer (2) [27], silyl [28], polymeric linker (3) [29] between the functional unit and nanoparticle. Mainly, H-Bonding and Co-valent bonding are explored for such assembly. To enhance the interaction between the surface electronic cloud of the central nano-particle and the conjugated pi-electrons of the organic moiety grafted on its surface, the present design focuses on pi stacking mediated organization of nanoparticles (Figure 1). Very few works have been reported on self-assembly originating from pi-pi interactions, and it remained intangible yet, what actually controls such pi-pi stacking mode [30].

In this work, a coumarin skeletal framework have been extended with fused thiazole-ring with an -SH anchoring group. Silver is taken for the formation of the metal nanoparticle core due to its well-documented applications [31]. Such design is having two major benefits, firstly, the pi-electrons of the organic fuse-ring system will be in direct interaction with the metal surface electrons, and secondly, the  $\pi$ -stacking (and associated interactions) of the surface organic moieties would effectively mediate self-assembly of metallic nano-particles, as coumarin derivatives are reportedly known to exhibits  $\pi$ -stacking [32].

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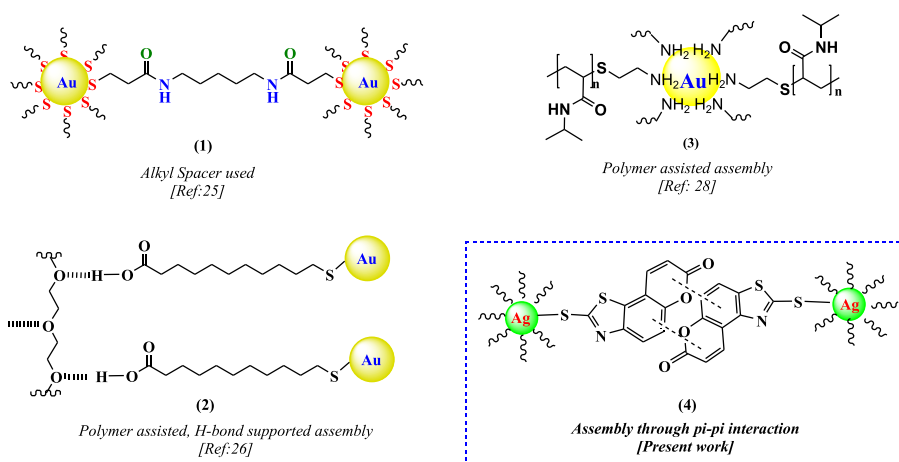


Figure 1. Previous reports of nanoparticle self-assembly (1–3) and the present design (4).

## 2. Materials and methods

### 2.1. Equipments and materials

The UV-Visible and the Fluorescence spectra of the synthesized compounds were recorded on Shimadzu UV 1601 PC and on PerkinElmer LS45 spectrofluorimeter respectively. The TEM was done with JEOL JEM-100-CX-II and the XRD on Phillips X'Pert Pro.  $^{13}\text{C}$  and  $^1\text{H}$ -NMR spectra were obtained using Bruker Avance III 400 MHz NMR in  $\text{CDCl}_3$  with tetramethylsilane as internal standard. Coumarin, potassium thioacetate, KOH, silver nitrate were from Sigma Aldrich. All solvents were purchased from Merck. All chemicals were used as received.

### 2.2. Synthesis of the target material

#### 2.2.1. Synthesis of 6-nitrocoumarin (1)

Nitration mixture (16mL) was slowly added to the solution of Coumarin (8g, in conc.  $\text{H}_2\text{SO}_4$ ) at  $0^\circ\text{C}$  and then stirred at room temperature for an hour before pouring into crushed ice. The solid product separated out and recrystallized from glacial acetic acid (82% yield).

#### 2.2.2. Synthesis of 6-aminocoumarin (2)

6-nitro coumarin (6.5g) was slowly added into a suspension of Fe-dust in distilled water, containing  $\text{NH}_4\text{Cl}$  at  $80^\circ\text{C}$ – $90^\circ\text{C}$ . The mixture was heated on water bath for 2 h. Then reaction mixture was cooled, filtered and residue extracted with acetone. The extract was distilled off the solvent and product recrystallized from ethanol (65% yield).

#### 2.2.3. Synthesis of 6-amino-5-bromo-2H-chromen-2-one (3)

6-amino coumarin (1eq) was dissolved in minimum volume of acetonitrile and vigorously stirred while N-Bromosuccinamide (1.2eq) was added. Stirring continued for 2hours at room temperature. Then solvent was removed and the crude product was purified by column chromatography (silica gel) using ethyl acetate and petroleum ether (1:9) as eluent (73% yield).

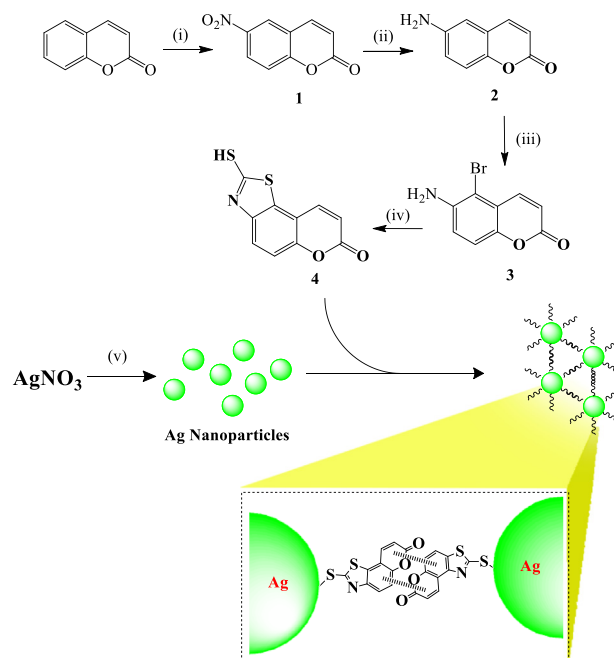
#### 2.2.4. Synthesis of 2-mercapto-7H-chromeno [6,5-d]thiazol-7-one (4, the thiol ligand)

$\text{CS}_2$  and DBU was added to toluene solution of 6-amino-5-bromo-2H-chromen-2-one in a sealable tube and stirred at room temperature under  $\text{N}_2$  atm. After 1hour the tube was sealed and the mixture was stirred at  $80^\circ\text{C}$ – $100^\circ\text{C}$  for 36 h. After completion of reaction (by TLC) the mixture was cooled to room temperature. The crude product obtained was washed repeatedly with dichloromethane to afford the target ligand (95% yield) [Modified process of Ref. [33]].

Pale yellow, MP:  $110^\circ\text{C}$ , IR:  $2750\text{cm}^{-1}$ ,  $3072\text{cm}^{-1}$ ,  $1747\text{cm}^{-1}$ ,  $1602\text{cm}^{-1}$ ,  $628\text{cm}^{-1}$ ,  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ , TMS): 6.651 (d,  $J = 10$ , 1H), 7.494(d,  $J = 8.8$ , 1H), 7.782 (d,  $J = 9.2$ , 1H), 8.216 (d,  $J = 10$ , 1H), 9.783 (singlet, 1SH),  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ , TMS): 30.64, 116.04, 117.75, 118.80, 121.96, 133.37, 134.89, 142.64, 152.55, 159.12, 182.02.

#### 2.2.5. Synthesis of silver nanoparticles functionalized with the thiol ligand 4

The preparation and functionalization of Silver nanoparticle was performed by modified Turkevich method [34]. A water-alcohol-acetone solution of the thiol ligand (100 mM in 25ml solution) was added to silver nitrate solution (10 mM in 10ml aqueous solution), followed by drop-wise addition of sodium citrate solution (15 mM in 25ml solution) keeping the mixture stirred at about  $60^\circ\text{C}$ . After addition the stirring was continued at  $60^\circ\text{C}$  for one more hour (or till a dark solution is



i) Nitration mixture,  $0^\circ\text{C}$ ; ii) Fe dust /  $\text{NH}_4\text{Cl}$ ,  $80$ – $90^\circ\text{C}$ , 2Hrs; iii) NBS,  $\text{CH}_3\text{CN}$ ; iv)  $\text{CS}_2$ , DBU; v)  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $60^\circ\text{C}$

Figure 2. The scheme of synthesis (number of ligands shown over the surface of Ag NP are arbitrary and for illustration purpose only).

formed), and then kept on stirring in room temperature overnight. The suspension so obtained after the removal of larger particles by centrifugation, was used for further studies. The synthetic scheme of the work is elaborated in Figure 2.

### 3. Results and discussion

#### 3.1. Absorption and fluorescence studies

The thiol, absorbed at 289nm (Red markers in Figure 3), attributed to  $\pi \rightarrow \pi^*$  transition for (C=O). The fluorescence spectrum of the thiol (Green markers in Figure 3) exhibits emission at 520nm on excitation by light of wavelength 289nm. The fluorescence got quenched upon functionalization of Ag nanoparticle with this compound (the quenching was observed through UV-chamber and confirmed by Fluorescence spectroscopy). The UV-visible spectrum of the functionalized particles exhibited a wide absorption band at  $\lambda_{\text{max}} = 650\text{nm}$  characteristics of assemblage of silver nanoparticles [[35], for special remarks refer [36]]. The interaction between the thiol molecules and AgNPs is presented schematically in Figure 2. The thiol molecule mainly binds with the Ag-NP mainly through the -SH group. The nearby heterocyclic S and N also enhances the binding affinity of the ligand for the metal surface. Due to the strong affinity of the thiol ligand to AgNPs, and the direct attachment of the -SH

group to the aromatic framework of the fused-ring structure, electron transfer occurs easily causing significant spectral overlap between the emission profile of the ligand with the absorption spectrum of AgNPs [37]. This is probably responsible for the nonradiative energy transfer between the thiol ligand and AgNPs, in accordance with Forster's theory [37, 38], thereby causing the quenching of fluorescence (see Figure 3b).

#### 3.2. Transmission electron microscopy (TEM) and powder XRD

TEM image of the thiol-functionalized Ag-nanomaterials demonstrated the self-assembly and superior regularity of size. At wide-view, the material appeared rod-like (Figure 4a), but at closer view the self-assembly of almost spherical nanoparticles of  $\sim 10\text{nm}$  diameter was clearly noticeable (Figure 4b-d). This was supported by the XRD pattern of functionalized material (Figure 4e). The crystallite size of functionalized material calculated to be 17 nm using Scherrer's equation [39] from (111) preferred orientation, indicating that the particulate nature has been retained in this assembly. The material exhibited diffraction peaks corresponds to (111), (200), (220) and (311) planes assigned to face centered cubic (fcc) structure [40].

In an earlier report, García-Báez and group [30] demonstrated through single crystal XRD, the fused polar rings of coumarins can associate through  $\pi$ -stacking interactions along with C-H...O and

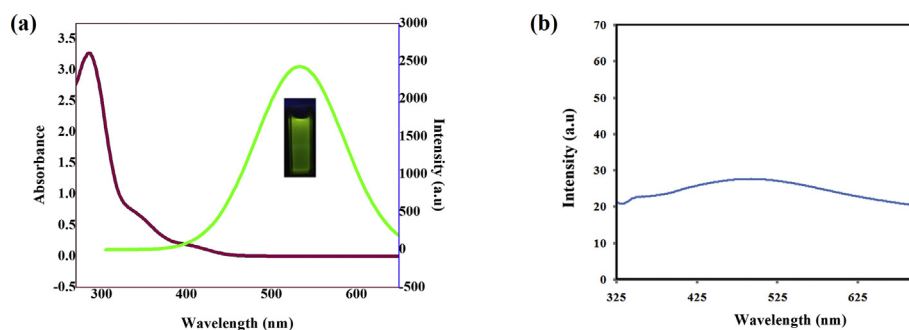


Figure 3. (a) Absorption (red) and Fluorescence (green) spectrum of 2-mercapto-7H-chromeno [5,6-d]thiazole-7-one; (b) Fluorescence spectrum of the thiol functionalised Ag nanoparticle.

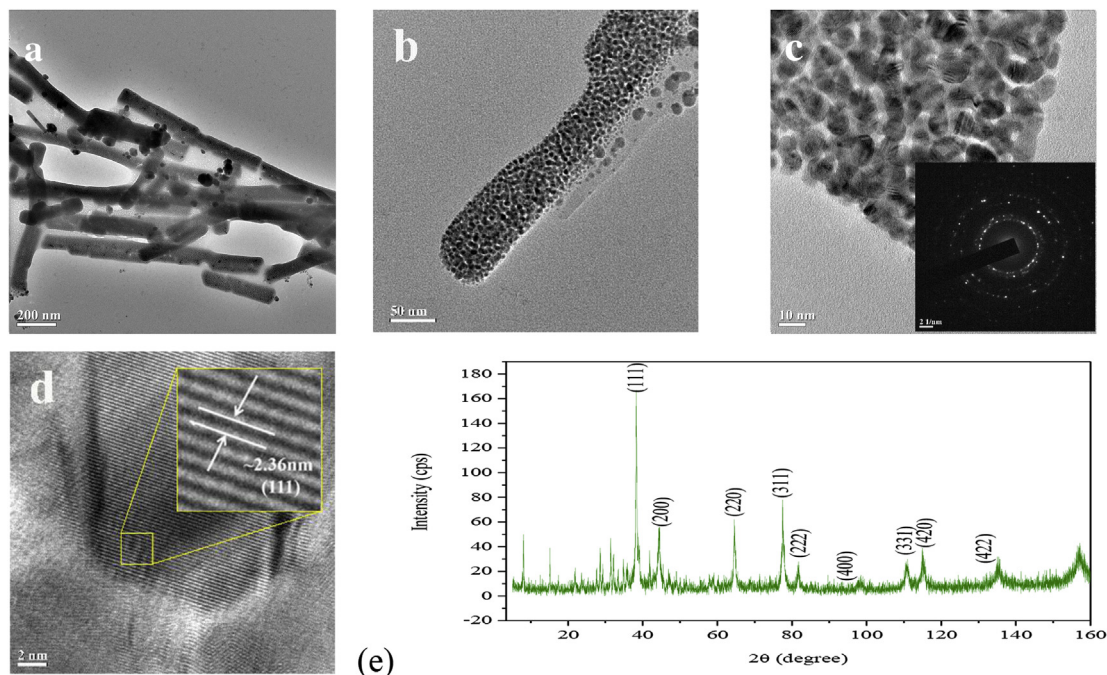


Figure 4. (a-d) TEM image of thiol-functionalised Ag-nanoparticles, (e) XRD of the same material.

C–H $\cdots\pi$  interactions. Similar  $\pi$ -stacking interactions between the aromatic ring centroids was reported in substituted coumarin based compound by Estrada-Soto [41]. In a similar fashion, a network of such interaction between the coumarin based fused-ring thiol ligands in the present material, seems to play the vital role in bringing the surface-anchored Ag nanoparticles close enough for an assembly formation (as depicted in the schematic presentation in Figure 2) leading to a closely packed ensemble of particles. A control synthesis of Ag nanoparticles without adding this thiol-ligand yielded mixture of unassembled spherical, hexagonal and pyramidal silver nanoparticles. Keeping the issue of resistance of citrate anions on desorption from silver nanoparticles in view, the thiol (in excess) was kept in the reaction from the beginning (before the addition of citrate) and citrate was added in near stoichiometric amount corresponding to silver ion concentration. However, it is possible to have coadsorption of thiols with some preadsorbed citrates on the surface of the nanoparticles, but that does not seem to prevent the formation of the observed self-assembly [for a related case Ref. [42] may be cited].

### 3.3. Selected area electron diffraction (SAED)

The selected area electron diffraction (SAED) pattern of functionalized Ag-nanoparticles (Figure 4c inset), was of particular interest here. In spite of several attempts at different regions of the sample, it was not possible to obtain a spot pattern with SAED, rather ended up with ring pattern or spotty ring pattern. The unavailability of spot pattern articulately supported the fact that, the functionalised particles stayed 'small' i.e., had remained as nanoparticles after such a large self-assembly and did not get converted in larger rods or agglomerates. Otherwise, a single silver nano-rod (spanning about 100nm here), the electron diffraction would have resulted in exhibition of the characteristic spot pattern of Ag nanorod [43]. Earlier works of Raghuvanshi and groups cited earlier [23, 24] reported similar clusterisation of nanoparticles retaining their particle-nature using special deep eutectic solvents. In our work, larger uniform clusterisation has occurred without the requirement of any special treatment.

The circular fringes in the SAED pattern of functionalized Ag-NP corresponds to (111), (200), (220) and (311), characteristic of face centred cubic crystalline structure, which is also supported by XRD.

## 4. Conclusion

Self-assembly of silver nanoparticles has been observed upon functionalization with the coumarin based organic thiol, *2-mercapto-7H-chromeno [5, 6-d] thiozole-7-one*. Formation of large arrangement of nanoparticles has been achieved by the simple method discussed, without the requirement of any special treatment or equipment. The fluorescence of the thiol got quenched when conjunct with Ag-NP. The particles though organized very closely in a larger secondary structure, were capable to sustain their individual particle nature which is evidenced from the TEM/SAED and further supported by the size of particles from XRD. The work portrays the practicability of no-bond interaction like  $\pi$ -stacking, in the construction of organized functional nanomaterials.

## Declarations

### Author contribution statement

Sudip Choudhury: Conceived and designed the experiments; Wrote the paper.

Saurav Paul, Siddique Anwar: Analyzed and interpreted the data.

Bimal B. Chakraborty: Performed the experiments; Analyzed and interpreted the data.

Satya B. Paul: Contributed reagents, materials, analysis tools or data.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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### References

- [1] A.K. Boal, F. Ilhan, J.E. DeRouchey, T. Thurn-Albrecht, T.P. Russell, V.M. Rotello, *Nature* 404 (2000) 746.
- [2] Z. Nie, A. Petukhova, E. Kumacheva, *Nat. Nanotechnol.* 5 (2010) 15.
- [3] X. Wang, J. Cai, L. Sun, S. Zhang, D. Gong, X. Li, S. Yue, L. Feng, D. Zhang, *ACS Appl. Mater. Interfaces* 11 (2019) 4745.
- [4] K.J.M. Bishop, C.E. Wilmer, S. Soh, B.A. Grzybowski, *Small* 5 (2009) 1600.
- [5] B.B. Chakraborty, S. Anwar, S. Das, S.B. Paul, G. Mohiuddin, J. De, S. Choudhury, *Liq. Cryst.* 45 (2018) 1644.
- [6] Z. Nie, D. Fava, E. Kumacheva, S. Zou, G.C. Walker, M. Rubinstein, *Nat. Mater.* 6 (2007) 609.
- [7] B.K. Nakata, Y. Hu, O. Uzun, O. Bakr, F. Stellacci, *Adv. Mater.* 20 (2008) 4294.
- [8] D. Nykypanchuk, M.M. Maye, D. van der Lelie, O. Gang, *Nature* 451 (2008) 549.
- [9] F.A. Aldaye, A.L. Palmer, H.F. Sleiman, *Science* 321 (2008) 1795.
- [10] A. Zabet-Khosousi, A.-A. Dhirani, *Chem. Rev.* 108 (2008) 4072.
- [11] L. Sun, D. Zhang, Y. Sun, S. Wang, J. Cai, *Adv. Funct. Mater.* 28 (2018) 1707231.
- [12] S.M. Jung, J. Qi, D. Oh, A. Belcher, J. Kong, *Adv. Funct. Mater.* 27 (2017) 1603203.
- [13] K. Zhou, J. Zhang, Q. Wang, *Small* 11 (2015) 2505.
- [14] E. Dujardin, C. Peet, G. Stubbs, J.N. Culver, S. Mann, *Nano Lett.* 3 (2003) 413.
- [15] Y. Huang, C.-Y. Chiang, S.K. Lee, Y. Gao, E.L. Hu, J.D. Yoreo, A.M. Belcher, *Nano Lett.* 5 (2005) 1429.
- [16] A. Blum, C. Soto, C. Wilson, T. Brower, S. Pollack, T. Schull, A. Chatterji, T. Lin, J. Johnson, C. Amsinck, P. Franzone, R. Shashidhar, B. Ratna, *Small* 1 (2005) 702.
- [17] R. Klajn, K.J.M. Bishop, B.A. Grzybowski, *Proc. Natl. Acad. Sci.* 104 (2007) 10305.
- [18] M.Q. Zhu, L.Q. Wang, G.J. Exarhos, A.D.Q. Li, *J. Am. Chem. Soc.* 126 (2004) 2656.
- [19] S. Gupta, Q. Zhang, T. Emrick, T.P. Russell, *Nano Lett.* 6 (2006) 2066.
- [20] A. Ahniyaz, Y. Sakamoto, L. Bergstrom, *Proc. Natl. Acad. Sci.* 104 (2007) 17570.
- [21] X.B. Zhao, F. Chen, J. You, X.Z. Li, X.W. Lu, Z.G. Chen, *J. Mater. Sci.* (2010) 3563.
- [22] X. Wang, F. He, X. Zhu, F. Tang, L. Li, *Sci. Rep.* (2015) 4406.
- [23] V.S. Raghuvanshi, M. Ochmann, A. Hoell, F. Polzer, K. Rademann, *Langmuir* 30 (2014) 6038.
- [24] V.S. Raghuvanshi, M. Ochmann, F. Polzer, A. Hoell, K. Rademann, *Chem. Commun.* 50 (2014) 8693.
- [25] H.W. Cheng, S.I. Lim, W. Fang, H. Yan, Z. Skeete, Q.M. Ngo, J. Luo, C.J. Zhong, *J. Phys. Chem. C* 119 (2015) 27786.
- [26] J.G. Worden, A.W. Shaffer, Q. Huo, *Chem. Commun.* 518 (2004).
- [27] R.R. Bhattacharjee, T.K. Mandal, *J. Colloid Interface Sci.* 307 (2007) 288.
- [28] H.H. Kyaw, S.H. Al-Harathi, A. Sellai, J. Dutta, *Beilstein J. Nanotechnol.* 6 (2015) 2345.
- [29] T. Ding, A.W. Rudrum, L.O. Herrmann, V. Turek, J.J. Baumberg, *Nanoscale* 8 (2016) 15864.
- [30] E.V. García-Báez, F.J. Martínez-Martínez, H. Höpfl, I.I. Padilla-Martínez, *Cryst. Growth Des* 3 (2003) 35.
- [31] S. Perni, V. Hakala, P. Prokopovich, *Colloids Surf. A Physicochem. Eng. Asp.* 460 (2014) 219.
- [32] A. Ananthi, K.L. Phani, *J. Electro. Anal. Chem.* 764 (2016) 7.

- [33] F. Wang, S. Cai, Z. Wang, C. Xi, *Org. Lett.* 13 (2011) 3202.
- [34] G.A. Valencia, L.C. de Oliveira Vercik, R. Ferrari, A. Vercik, *Starch – Stärke* 65 (2013) 931.
- [35] A. Atta, H. Al-Lohedan, A. Ezzat, *Molecules* 19 (2014) 6737.
- [36] G. Nichols, S. Byard, M.J. Bloxham, J. Botterill, N.J. Dawson, A. Dennis, V. Diart, N.C. North, J.D. Sherwood, *J. Pharmacol. Sci.* 91 (2002) 2103.
- [37] A.M. Asiri, O.I. Osman, S.H. Al-Thaqafy, S.A. Khan, *RSC Adv.* 7 (2017) 8402.
- [38] S.R. Kavitha, M. Umadevi, S.R. Janani, T. Balakrishnan, R. Ramanibai, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 127 (2014) 115.
- [39] M. Faried, K. Shamel, M. Miyake, A. Hajalilou, K. Kalantari, Z. Zakaria, H. Hara, N.B.A. Khairudin, *Res. Chem. Intermed.* 42 (2016) 7991.
- [40] A.L. Patterson, *Phys. Rev.* 56 (1939) 978.
- [41] S. Estrada-Soto, A. Sánchez-Recillas, G. Navarrete-Vázquez, H. Tlahuext, *Struct. Rep. E70* (2014) 451.
- [42] A. Mocanu, I. Cernica, G. Tomoaia, L.-D. Bobos, O. Horovitz, M. Tomoaia-Cotisel, *Colloid. Surface. Physicochem. Eng. Aspect.* 338 (2009) 93.
- [43] S. Navaladian, B. Viswanathan, T.K. Varadarajan, R.P. Viswanath, *Nanoscale Res. Lett.* 4 (2009) 471.