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A new method for synthesis of a new class reducing agent with expected application in nanotechnology

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Abstract: It is of great importance for the monodispersion of nanomaterials to limit the nucleation in the initial stages of the synthesis, which is then followed by growth without new nucleation. A reducing agent, corresponding to these conditions, is the hydrazine bishypophosphite $N_2H_6(H_2PO_2)_2$. There is no data about this compound, but related substances have long since been studied.

In this article a new synthesizing method of $N_2H_6(H_2PO_2)_2$ using $N_2H_4.2HCl$ and $Na_2H_2PO_2.H_2O$ is proposed. The lateral sodium chloride NaCl serves to later determine the degree of conversion and the yield of the target product.

Keywords: synthesis; new reducing agent; monodispersed particles; hydrazine (bis) hypophosphite

1. INTRODUCTION

It is of great importance to obtain monodispersed nanomaterials in nanotechnology. One way to achieve this goal is to limit the nucleation in the initial stages of the synthesis, which is followed by growth without new nucleation. A reducing agent, which is expected to fulfill these requirements, is the hydrazine (bis) hypophosphite $N_2H_6(H_2PO_2)_2$. Hydrazine (bis) hypophosphite is assumed to be able to act as reducer by both of its parts – anion and cation:

$N_2H_4 + 4OH^- \rightarrow 4H_2O + N_2 + 4e^-$, E_0=1.16 V

$H_2PO_2^- + 3OH^- \rightarrow 2H_2O + HPO_3^{2-} + 2e^-$, E_0=1.57 V

$H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H^+ + 2e^-$, E_0=0.28 V.

This means that a higher reduction potential in the beginning and an average reduction potential in the end of a process, based on the degree of reduction, can be achieved. That is a good prerequisite for controlling the supersaturation and the speed of separate stages during the process. Moreover, consumption of reducing agent in the course of time of nucleation, significantly decreases its concentration, reduction potential and supersaturation - Figure 1[1].

As the reducing agent is being consumed during the process of nucleation the supersaturation also decreases in areas I and II. Therefore, time of nucleation process is very short, and practically finishes. Afterwards a process of growth prevails and nucleation is suppressed. As a result, monodispersed material can be obtained. This could happen if two-stage reducer is used which has significant difference of reduction potentials in both stages.

However, to the best of our knowledge there is not a study dealing with synthesis and properties of such a compound, even though the existence of this composite is predictable. We are aware of the existence of common compounds with similar anion parts, such as $NH_4H_2PO_2$, $(NH_3OH^+)(H_2PO_2^-)_2$, and a similar cation part– $N_2H_5H_2PO_4$ and $N_2H_6(H_2PO_4)_2$[2, 3], but information on the synthesis and properties of $N_2H_6(H_2PO_2)_2$ is not available.

Currently known method of synthesis, developed by us [4] in the past and we have encountered some difficulties. The precursor compounds are difficult to access and are dangerous. The interaction between them releases a lot of heat and toxic fumes. In this work we propose a new method for synthesis of $N_2H_6(H_2PO_2)_2$ by using $N_2H_4.2HCl$ and $Na_2H_2PO_2.H_2O$. The quantity of the co-product sodium chloride NaCl serves to determine the degree of conversion and the yield of the target product. Potential applications of hydrazine (bis) hypophosphite for preparation of silver micro- and nano-particles will be examined according to aforementioned premises.

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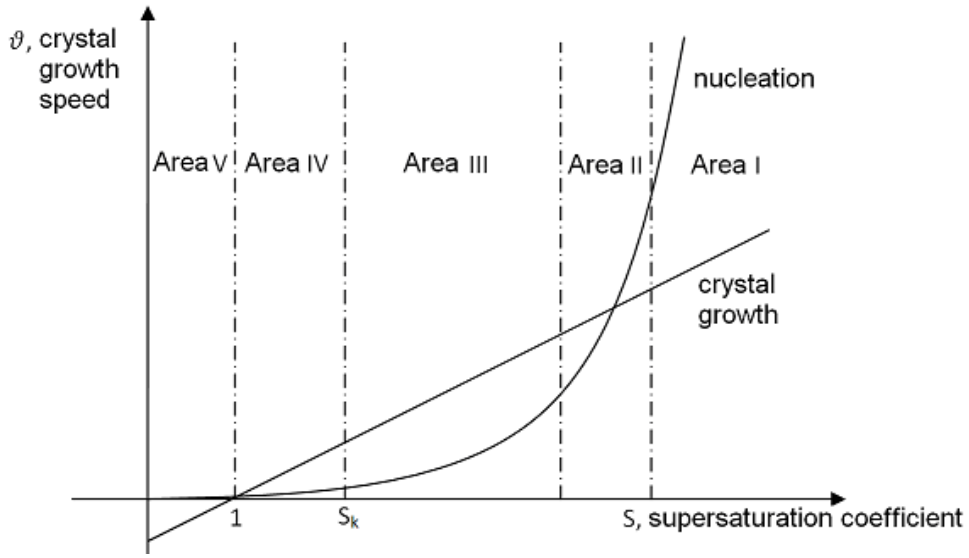


Figure 1. Speed of nucleation and crystal growth depending on supersaturation.

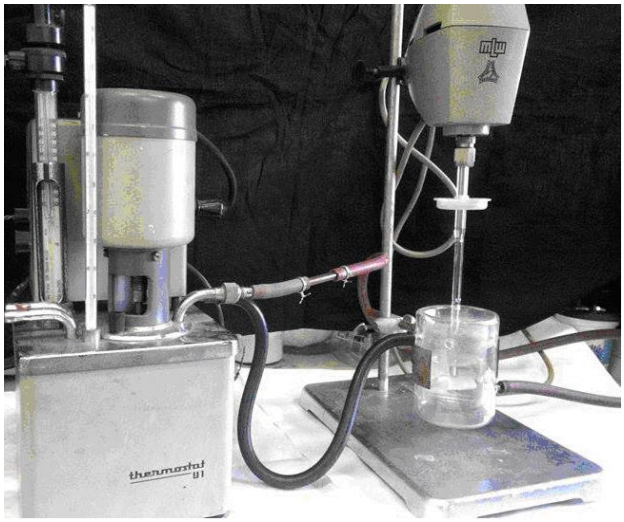


Figure 2. Cooling apparatus during synthesis.

2. EXPERIMENTAL

2.1. Materials, reagents and technical equipment

Hydrazine dihydrochloride $N_2H_4.2HCl$ (CAS Number: 5341-61-7) and sodium hypophosphite monohydrate $NaH_2PO_2.H_2O$ (CAS Number: 10039-56-2) are the compounds used for synthesis of the new reducing agent.

2.2. Synthesis procedure

$N_2H_4.2HCl + 2NaH_2PO_2.H_2O \rightarrow$

$\rightarrow (N_2H_6^{2+})(H_2PO_2^-)_2 + 2NaCl + 2H_2O$

Hydrazine dihydrochloride $N_2H_4.2HCl$ and sodium hypophosphite monohydrate $NaH_2PO_2.H_2O$ are weighed in a stoichiometric proportion and crushed to a very fine grade in a mortar. The received mixture is poured in a beaker and hypophosphorous acid (50% water solution) is added, in order to acidify the solution. Meanwhile the water, contained in the acid, the solution becomes undersaturated for $(N_2H_6)(H_2PO_2)_2$ and oversaturated for NaCl, so the latter can crystallize from the solution. The mixture is stirred and heated until the complete dissolution of the solid phase. The crystallization of white NaCl can be observed immediately, whose crystals are difficult to be distinguished from the starting material. The suspension is dried in a vacuum desiccator dish, so highest possible quantity of NaCl could crystallize. After that the suspension is filtrated in a fritted filter and the sediment is washed in distilled water and ethyl alcohol, as NaCl's solubility in a water-alcohol solution sharply decreases. The filtrate is continuously stirred for about 12 hours under cooling (Figure 2), in order to get small and similarly-sized crystals of $(N_2H_6)(H_2PO_2)_2$, and not large crystals of it. The solution along with the crystals is filtered with a frilled filter and the

experimental yield is determined. The lateral NaCl is checked for chloride ions with $AgNO_3$. White photosensitive sediment of AgCl is observed, which proves that the separated crystals are NaCl. This, on its own, proves that in the solution remains the target product.

Based on the described method we calculated the necessary quantities of starting materials for the synthesis of 100 g product as follows: 64.00 g $N_2H_4.2HCl$ and 124.29 g $NaH_2PO_2.H_2O$. For the acidification of the solution and the supersaturation by the target product were needed 157.2 ml H_3PO_2, which is calculated based on the solubility of $N_2H_6(H_2PO_2)_2$. As a result of the synthesis we gained 58.13 g NaCl and 56.7 g $N_2H_6(H_2PO_2)_2$. That shows that this method of synthesis leads to approximate yield of about 56.7%.

The previously known method of synthesis does not show exact quantitative data for the degree of conversion of the starting materials. They are difficult to determine, as hydrazine hydrate is a volatile liquid, and the vacuum-vaporization is not always complete. During vaccum-vaporization the temperature must not exceed 40-50 ^oC, because this may destroy the product and the initial compounds as well. On the other hand, the lack of byproducts is a prerequisite for higher purity of the target product.

By using the new method, dry starting materials, following vacuum-vaporization is not necessary and the reaction takes place without a noticeable enthalpy of formation. The extraction of lateral NaCl allows the potential determination of the yield of the products. Also, this synthesis method is safer. The difficult separation of the byproduct may cause impurity in the target product.

The choice of one of these methods may be determined by the pursued purity of the target product and the availability of initial compounds. This way it will be possible to make an easier assessment which of the two methods would be preferred for a primary method of synthesis based on the concrete abilities of the laboratory and the team.

2.3. Methods used to identify new compound

The elemental analysis was carried out by using an elemental analyzer VARIO EL III "Elementer" Germany; pH measurements were done by using a precise digital pH-meter OP208-1 "Radelkis"-Budapest, Hungary with combined electrode HA 405-60/S7 WTW GmbH -Weilheim, Germany. The elemental analysis of crystals, give composition values very close to expected for $(N_2H_6)^{2+}(H_2PO_2^-)_2$. Opposite to our expectations, we could not obtain specimen which shows elemental composition values comparable with $(N_2H_5)^+H_2PO_2^-$ at any change in acidity.

3. RESULTS AND DISCUSSION

The advantages and disadvantages of both methods developed by us could be compared as follows (Table 1).

3.1. Efficiency of the new reducing agent

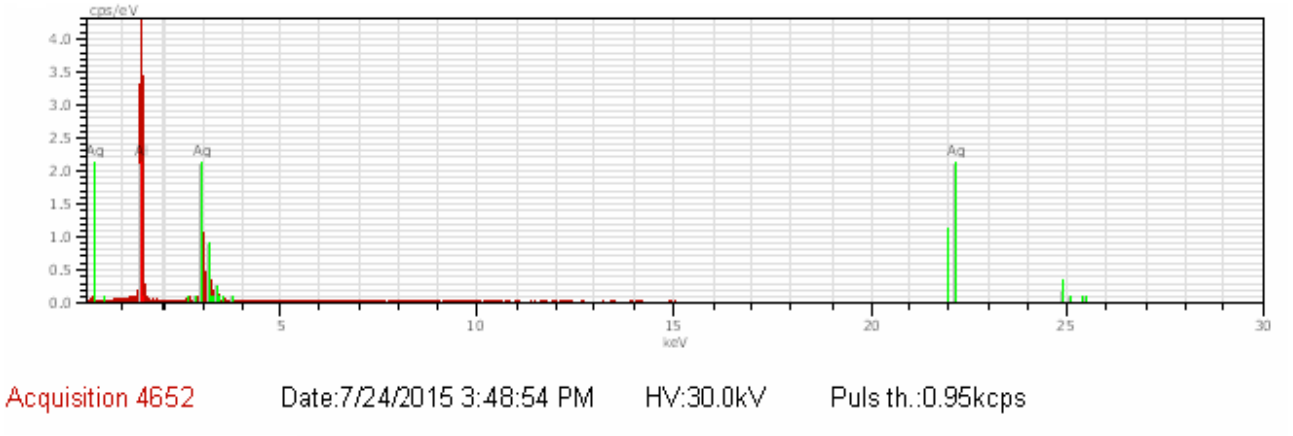
Reducing efficiency of hydrazine (bis) hypophosphite is extremely high: Reducing power of one mole of substance is 12 equivalents. (One mole of compound gives 12 N_A electrons!)

3.2. Application of the new reducing agent for synthesis of Ag nanoparticles

3.2.1. Methods used to characterize Ag nano-particles. The received reducing agent was used for the synthesis of silver particles from $AgNO_3$ solution by the following procedure: polycrystalline material of the product was dissolved in distilled water and was mixed with a solution of silver nitrate under constant stirring. The obtained silver particles were washed thoroughly three times with bi-distilled water and centrifuged in-between. Dual beam scanning electron/focused ion beam system (SEM/FIB LYRA I XMU, TESCAN), equipped

Table 1. Comparison between the two methods.

	Earlier method [4]	Method in the present study
Safety measures	It is required to outlet the toxic vapors of hydrazine and to monitor temperature	Safe; the enthalpy of formation is insignificant
Determination of yield	Difficult	Relatively easy
Accessibility of compounds	Limited	High
Purity	High	Average



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Al	13	K-series	42.32	47.47	78.32	2.2
Ag	47	L-series	46.83	52.53	21.68	1.7
		Total:	89.15	100.00	100.00	

Figure 4. Elemental analysis data.

with EDX detector (Quantax 200, Bruker) is used to determine the size, shape and composition of the obtained Ag nano-particles.

SEM analysis was done in order to determine the qualitave composition and the approximate size of the particles. The EDX analysis (Figures 3 and 4) shows that the material which they were made of is silver.

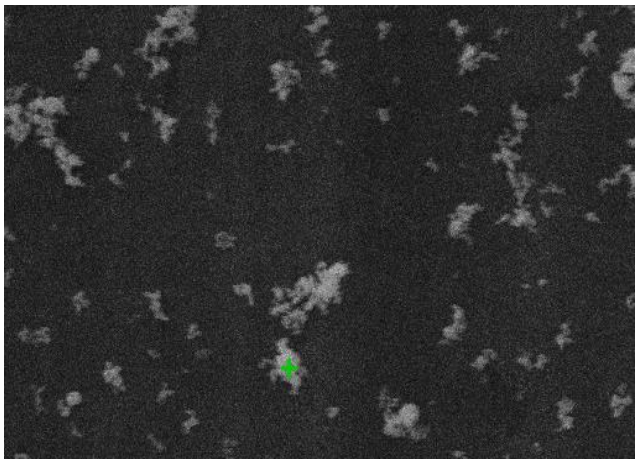


Figure 3. SEM map; the green point relates to the area of the EDX analysis.

The presence of Al is due to the fact that the signal of EDX cannot be received from a very small area. The resolution of the EDX analysis is approximately 1 μm. Since the pad is aluminum foil, we observe Al presence in the result.

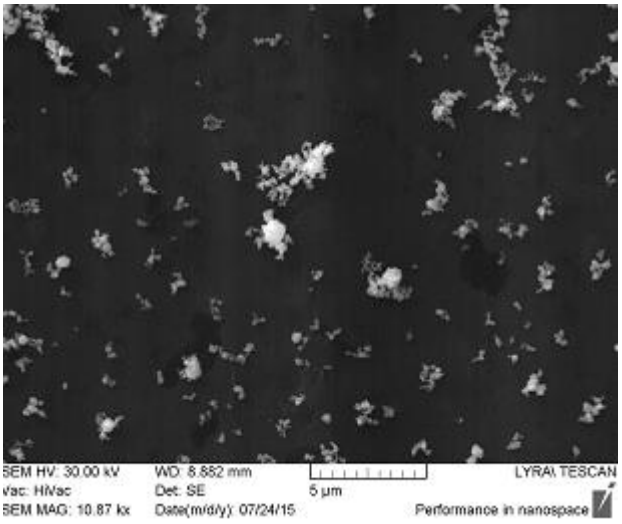
Figure 5 shows approximately the monodispersed size of the particles. This trend remains, even with a different particle concentration. A large portion of particle conglomerates have probably formed during the evaporation of the suspension, which is part of preparing the sample for analysis.

The monodisperse characteristics of the particles confirm the proposed theoretical formulation. The goal of the current study was precisely that – to support the given propositions and conclude upon the application of the new material based on the results. This opens up a new opportunity for conducting additional research on the synthesis of particles with a target size, by optimizing the process and the conditions of the experiment. With a series of further experiments it would be possible to find suitable concentrations of the reducing agent in solution and appropriate pH for obtaining monodispersed particles with the target size.

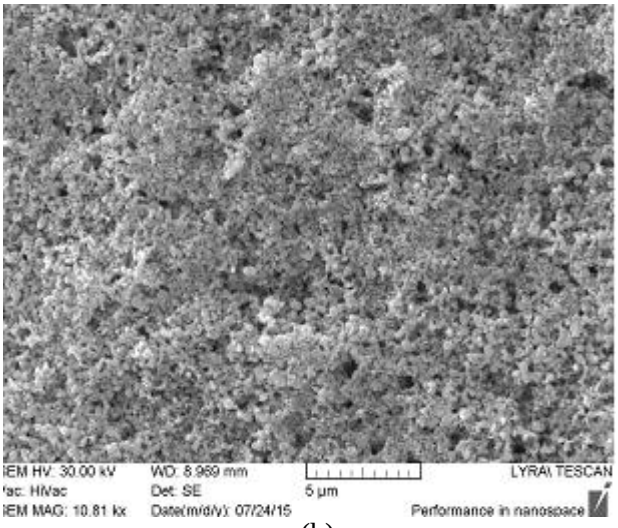
4. CONCLUSIONS

In the present study was submitted a new method of synthesis of a new reducing agent with specific hypothetic properties and a method for its application was proposed.

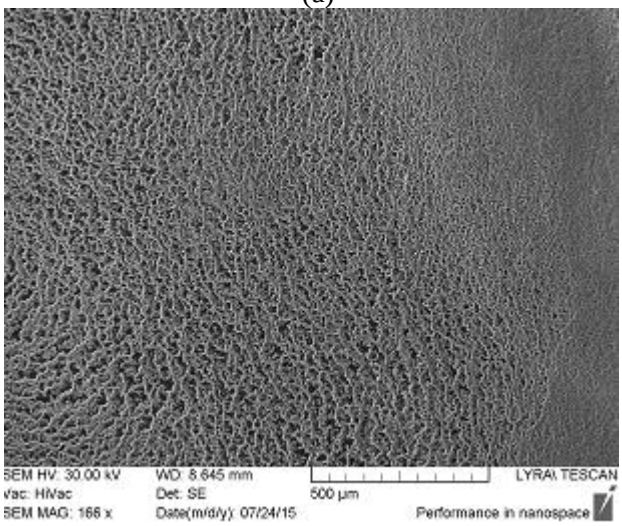
SEM analysis confirmed the correctness of the theoretical prerequisites for obtaining relatively monodispersed metal particles.



(a)



(b)



(c)

Figure 5. a) SEM image on a small particle population; b) SEM image on a large particle population; c) SEM image on lower magnification and ultra large particle population.

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НОВ МЕТОД ЗА СИНТЕЗА НА НОВ КЛАС РЕДУКТОРИ С ОЧАКВАНИ ПРИЛОЖЕНИЯ В НАНОТЕХНОЛОГИИТЕ

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(Резюме)

Идеята на настоящото изследване е да се получи монодисперсен Ag-зол като силно се ограничи времето през което е възможно зародишообразуване, а след това да се извършва само кристален растеж. Това се постига чрез 2 предпоставки: двустъпален редуктор със значителна разлика в редукционните потенциали на стъпалата и бързото изразходване на редуктора по стъпалото с по-висок редукционнен потенциал по време на зародишообразуването.

Целта на изследването е да се провери експериментално тази идея и дали е възможно да се синтезира редукторът по процедура, не свързана с бурна реакция, а също така с по-малко опасни и лесно достъпни реактиви.

Предложената методика на синтез чрез двойно заместване между $N_2H_4.2HCl$ и $Na_2H_2PO_2.H_2O$ дава по-ниски добиви (56.7%) и по-ниска чистота на продукта (% съдържание на Cl^-), но протича плавно без бурни реакции и без отделяне на токсични емисии.

Чрез провеждане на пилотен експеримент е показана приложимостта на $N_2H_6(H_2PO_2)_2$ като редуктор за получаване на Ag-зол. SEM-микрофотографии при различни популации показват, че разпределението по размери е в тесни граници, независимо от популацията. EDX- анализът показа, че материалът на частиците е Ag.