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MICROWAVE-ASSISTED NON-AQUEOUS SYNTHESIS OF ZnO NANOPARTICLES

SINTEZA NANODELCEV ZnO V NEVODNEM MEDIJU POD VPLIVOM MIKROVALOV

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In this work, the microwave-assisted non-aqueous synthesis of ZnO nanoparticles is reviewed. In comparison with the "classical" (conductive) heating, the microwave method provides for a better control over experimental parameters and, therefore, opens exciting opportunities for a better understanding of the influence of the reaction conditions on the reaction and growth mechanisms of ZnO particles. As the morphology and size determine the physicochemical behavior of ZnO, a variety of polymer-ZnO nanomaterials with tunable optoelectrical and mechanical properties can be *in-situ* or *ex-situ* prepared by the microwave-assisted synthesis.

In the article, a special attention is devoted to investigations performed in our laboratory on the systems of zinc acetylacetonate as a precursor and 1-butanol as media as well as oxygen supplier. Contrary to analogous syntheses performed under reflux conditions, we showed that under microwave conditions the precursor's initial amount exerts a tremendous effect on the morphology and size of ZnO particles.

Keywords: ZnO nanoparticles, microwave chemistry, non-aqueous synthesis, crystal growth

V delu podajamo pregled sinteze nanodelcev ZnO v nevodnem mediju pod vplivom mikrovalov. V primerjavi s segrevanjem s konvekcijo mikrovalovno segrevanje omogoča boljši nadzor nad eksperimentalnimi parametri in tako ponuja zanimive priložnosti za boljše razumevanje vpliva reakcijskih pogojev na mehanizem in rast delcev ZnO. Ker pa velikost in oblika delcev določata fizikalno-kemijske lastnosti ZnO-nanomateriala, bo mikrovalovna sinteza v prihodnosti omogočila *in-situ* ali *ex-situ* pripravo širokega spektra nanokompozitov ZnO/polimer z nastavljivimi optoelektronskimi in mehanskim lastnostmi.

V članku je posebna pozornost namenjena raziskavam, ki smo jih opravili v našem laboratoriju na sistemu cinkovega acetilacetonata kot prekurzorja in 1-butanola kot medija in donorja kisika. V nasprotju s prejšnjimi študijami na analognem sistemu pod pogoji refluksa smo pokazali, da pod mikrovalovnimi vplivi začetna količina prekurzorja ključno vpliva na morfologijo in velikost delcev ZnO.

Ključne besede: ZnO-nanodelci, mikrovalovna kemija, brezvodna sinteza, rast kristalov

1 INTRODUCTION

The unique and fascinating properties of nanostructured materials have triggered tremendous motivation among scientists to explore and understand their formation and growth processes as well as their subsequent implementation in the steady and fast growing research on the preparation of new polymer composite nanomaterials, which can exhibit new functionalities based on nanoparticle's optical and electrical properties.[1] Due to the fact that morphologies and sizes of inorganic particles determine the properties and applications of the polymer nanocomposites, the possibility to tune the physical and chemical properties of nanoscale materials through varying the crystal size and shape is a major driving force in nanoparticle research.

In general, three types of processes are applied for the synthesis of metal oxide particles in solution: the "classical" synthesis under reflux conditions, the autoclave synthesis and, the most recent microwave-assisted synthesis.[2]

In the oil bath synthesis, where the walls of the reactor are heated by convection or conduction, the core of the sample needs longer time to achieve the target temperature and this may result in inhomogeneous temperature profiles within the reaction flask.

One possibility to overcome this problem is the use of microwave or dielectric heating, which is becoming an increasingly popular synthetic method for organic[3, 4] as well as inorganic materials.[5] Microwave process enables the rapid and homogeneous heating of the reaction mixture to the desired temperature without heating the entire furnace or oil bath, which saves time and energy.

The microwave heating is based on two mechanism of the conversion of the electromagnetic radiation into heat energy, namely dipolar rotation and ionic conduction (**Figure 1**). The dipolar rotation (**Figure 1a**) occurs when polar molecules having an electrical dipole moment align with the oscillating electromagnetic field. In this process, energy is lost as heat due to the molecular friction and dielectric loss.

The ionic conduction heating mechanism (**Figure 1b**) results from the dissolved (dissociated) charged particles (ions). In dependence from the charge, the ions oscillate back and forth under the influence of the electric component of microwave radiation. In comparison with the

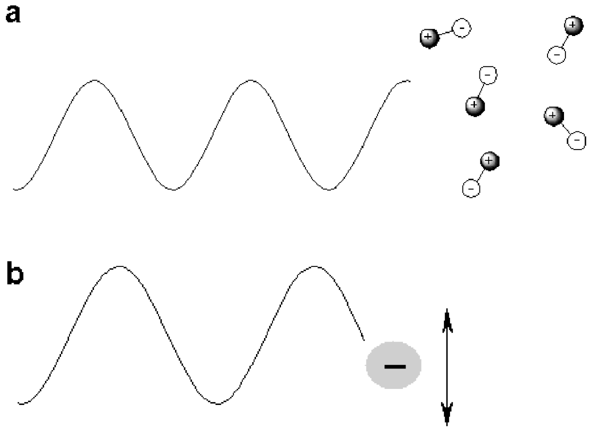

Figure 1: Microwave-mediated heating process: a) dipolar rotation and b) ionic conduction

Slika 1: Proces segrevanja pod vplivom mikrovalov: a) dipolarna rotacija in b) ionska prevodnost

former mechanism, the absorption of microwave irradiation by this mechanism is more efficient and the energy transfer is faster.

Due to the fact that different compounds convert microwave radiation to heat to different extents, i.e., they have different microwave absorbing properties, microwave radiation allows a selective heating of compounds in the reaction mixture.

Therefore, the general advantages of microwave-mediated synthesis over conventional heating are (**Figure 2**): a) reaction rate acceleration as a consequence of high heating rates, b) versatility of applied reaction conditions, i.e. mild conditions (low-power/low-temperature synthesis) or autoclave conditions (high temperatures and pressures), c) higher chemical yields with less by-products, d) different reaction selectivity due to different microwave absorbing properties, e) better reproducibility (excellent control over reaction conditions), f) easy handling, which allows fast and easy optimization of the experimental parameters.

However, there are few disadvantages of microwave over the conventional heating. The monitoring of the reaction course or, in the case of inorganic species, the time-dependent monitoring of the particles growth can not be performed. Furthermore, the microwave synthesis reactor is expensive in comparison with glassware equipment used for conventional (oil-bath) synthesis

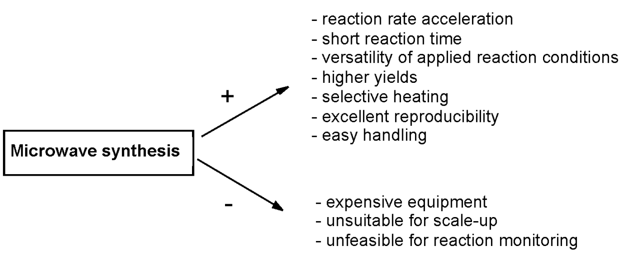

Figure 2: Pros (+) and cons (-) of the microwave-assisted synthesis.

Slika 2: Prednosti (+) in pomanjkljivosti (–) sintez pod vplivom mikrovalov

and, up-to-now, the microwave-mediated scale-up production has not yet reached the production quantities of the "classical" reactors.

Nevertheless, the microwave synthesis promise to offer many new benefits in the field of inorganic nanoparticle precipitations, and, particularly in gaining an insight into the dynamics of the formation of inorganic nanoparticles under defined experimental conditions. Given that microwave-mediated synthesis of inorganic materials offer even better control over reaction parameters that conventional approach, methodological investigations are indispensable to explore the full potential of this synthetic method.

The purpose of this article is first a brief review of the state-of-the art of the ZnO microwave synthesis using organic solvents, particularly alcohols, and second, to report on our own results of the non-aqueous microwave-mediated synthesis of ZnO nanoparticles from zinc acetylacetonate hydrate ($Zn(acac)_2xH_2O$) in 1-butanol.

2 MICROWAVE HEATING IN THE SYNTHESIS OF ZNO NANOPARTICLES

As a wide band gap II–VI semiconductor (3.37 eV), zinc oxide (ZnO) is promising material for numerous applications, such as gas sensors, transparent electrodes, pH sensors, biosensors, acoustic wave devices, and UV photodiodes.[6] Its extraordinary properties makes it one of the most intensively studied materials and, as so, there is a rapid growth in number of recent publications concerning the synthesis performed under microwave conditions (**Figure 3**).

The investigations on the solution-based microwave-assisted growth of ZnO were mainly performed in the water systems.[7–10]

In nonaqueous routes, the organic reaction mechanisms play a dominant role in ZnO formation. The organic species (i.e., the solvent and the organic ligands in the precursor) undergo chemical reactions that are responsible for supplying the monomers for nucleation

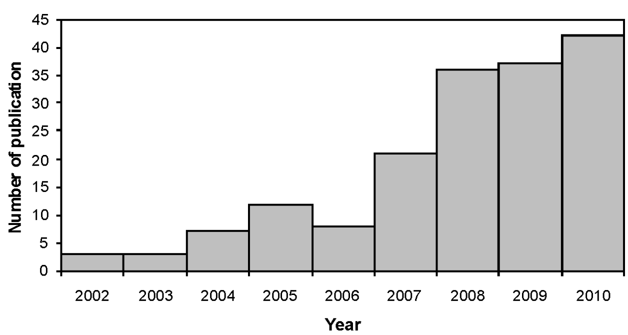

Figure 3: Number of publication per year on the solution-phase (aqueous and non-aqueous) microwave-assisted synthesis of ZnO particles (source ISI Web of Knowledge).

Slika 3: Število objav na leto o sintezi ZnO-delcev v vodnem ali nevodnem mediju pod vplivom mikrovalov (vir ISI Web of Knowledge) and growth of ZnO nanoparticles. Therefore, in these systems, a high sensitivity of both the organic reactions and the crystal growth towards microwave irradiation can be expected. Because of the fact that species differ in their microwave absorption behavior, a selective heating in a homogeneous or heterogeneous system might lead to diverse morphology and size of the ZnO particles.

The wide parameter window for controlling the microwave-assisted synthesis of ZnO has been investigated in numerous of alcohol reaction systems. Hu et al.[11] reported on the rapid microwave-polyol process that leads to the formation to monodisperse spherical ZnO clusters, which average size can be tuned by the amount of the precursor (zinc acetate). The striking effects of the microwave heating parameters and the solvent composition on morphology hierarchical ZnO nanostructures were demonstrated in ethylene glycol-water systems.[12,13] Straw-bundle-like, wide chrysanthemum-like and oat-arista-like morphologies and microspheres were prepared on the basis of the applied cycling mode, which determine the growth of the particles in the nucleation stage, whereas T-like, X-like and cross-like linked hexagonal prisms were observed by changing the volume ratio of ethylene glycol to water.

Bilecka et al [14,15] studied in details the kinetic and thermodynamic aspects of microwave-assisted synthesis of ZnO nanoparticles from zinc acetate and benzyl alcohol. It was concluded that microwave radiation drastically accelerated the particle formation by enhancing the dissolution of the precursor in alcohol as well as increasing the rate constants of the esterification reaction and the crystal growth.

3 SYNTHESIS OF ZnO BY MICROWAVE HEATING USING ZINC ACETYLACETONATE

The syntheses were carried out in a Milestone MEGA 1200 laboratory microwave oven. The precursor (2.3, 4.6 and 6.9) mmol was initially dispersed in 17 mL of 1-butanol and heated in 2 min to 120 °C. Samples were irradiated for 30 min with 250 W pulsed microwave irradiation power. After irradiation, the samples were cooled to room temperature, centrifuged and vacuum dried at 40 °C.

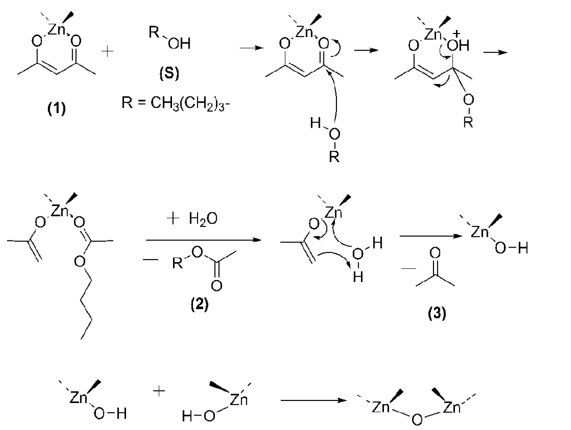

Figure 4: Reaction mechanism of ZnO formation from zinc acetylacetonate and 1-butanol.[16]

Slika 4: Mehanizem nastanka ZnO iz cinkovega acetilacetonata in 1-butanola [16]

The mechanism of the zinc acetylacetonate conversion into ZnO[16] relies on the nucleophilic attack of the alcohol to the carbonyl group of the acetylacetonate ligand and subsequent hydrolytic formation of the reactive Zn-OH intermediates, which polycondensate forming repeating -Zn-O-Zn- bonds. (**Figure 4**).

For the microwave-assisted synthesis, besides the alcohol reactivity, the crucial property of the alcohol as a medium is its ability to convert effectively the electromagnetic energy into heat energy. Based on the experimental data[17], 1-butanol is efficient microwave absorbing solvent so under the microwave conditions the transformation of zinc acetylacetonate into ZnO occurs in an excellent yield (up to 85 %).

FTIR spectra (Perkin Elmer's Spectrum One spectrometer) and XRD diffractograms (Bruker AXS D4 Endeavor diffractometer with Cu Kα radiation and a Sol-X energy-dispersive detector) of the precipitates obtained from 2.3 mmol and 6.9 mmol of initial amount of zinc acetylacetonate are shown in **Figure 5**. Both of the FTIR spectra (**Figures 5a and 5b**) consist of bands

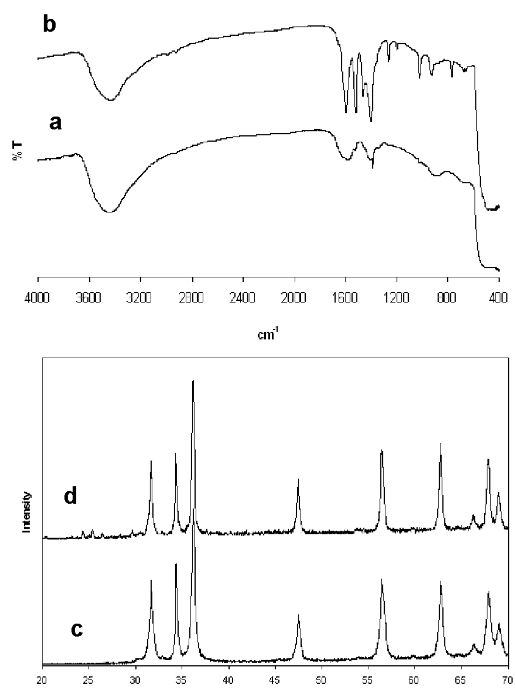

Figure 5: FTIR spectra and XRD diffractograms of the as-prepared ZnO particles obtained from 2.3 (curves a and c) and 6.9 mmol (curves b and d) of initial amount of zinc acetylacetonate in 17 mL of 1-butanol. The samples were exposed for 30 min with 250 W pulsed microwave irradiation at 120 °C.

Slika 5: FTIR-spektra in XRD-difraktograma ZnO-delcev, pripravljenih iz 2.3 mmol (krivulji a in c) in 6.9 mmol (krivulji b and d) cink acetilacetonata v 17 mL 1-butanola. Vzorci so bili 30 min izpostavljeni pulznemu mikrovalovnemu sevanju z močjo 250 W pri 120 °C.

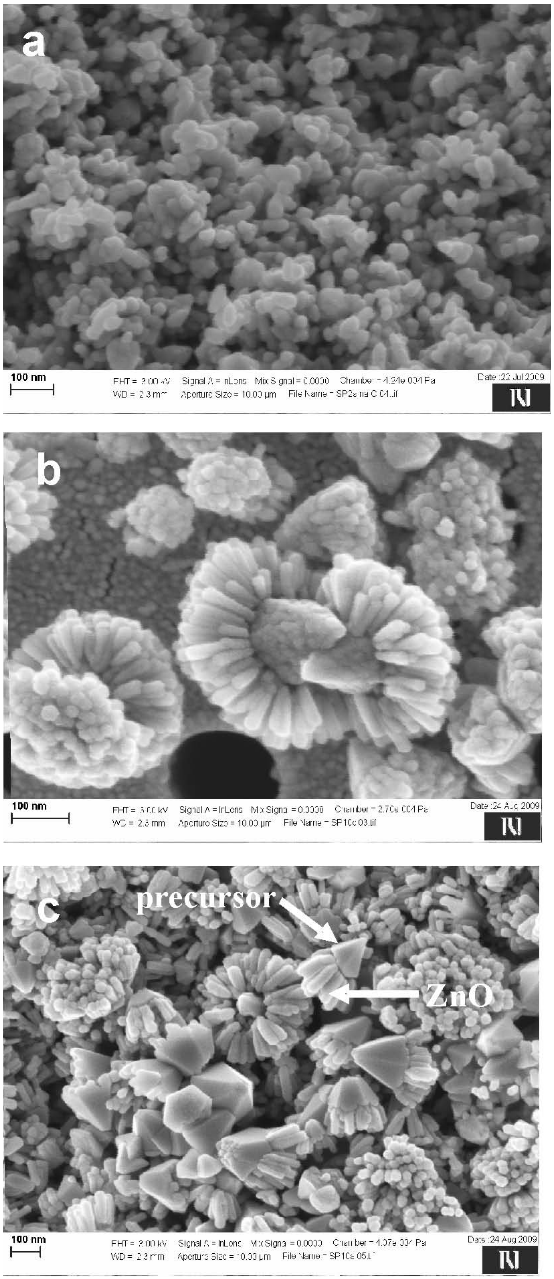

Figure 6: FE-SEM images of as-prepared ZnO particles synthesized from a) 2.3, b) 4.6 and c) 6.9 mmol of zinc acetylacetonate in 17 ml of 1-butanol. The samples were exposed for 30 min with 250 W pulsed microwave irradiation at 120 °C.

Slika 6: FE-SEM-mikrografije ZnO-delcev pripravljenih iz a) 2.3 mmol, b), 4.6 mmol in c) 6.9 mmol cink acetilacetonata v 17 mL 1-butanola. Vzorci so bili 30 min izpostavljeni pulznemu mikrovalovnemu sevanju z močjo 250 W pri 120 °C.

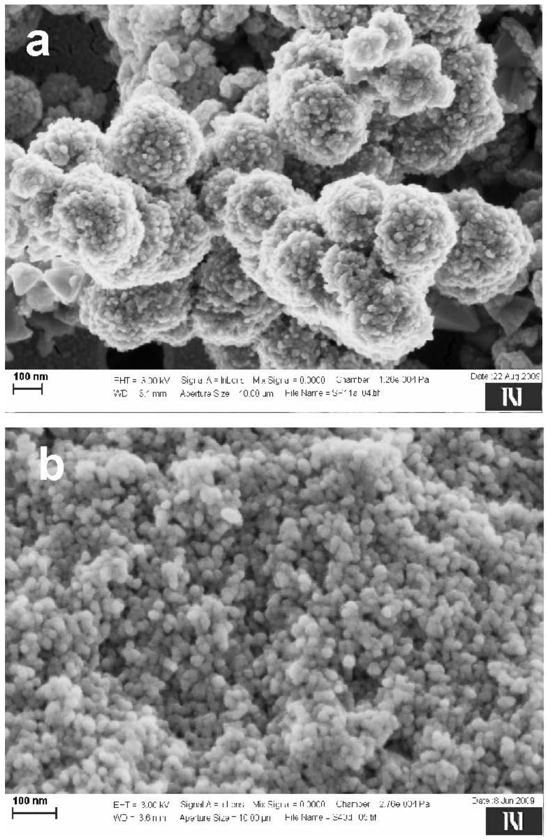

Figure 7: FE-SEM images of as-prepared ZnO nanoparticles synthesized from 2.3 mmol of zinc acetylacetonate and 1.16 mmol of 1-hexadecyl-3-methyl imidazole chloride monohydrate in 17 ml of 1-butanol under a) 250 W pulsed microwave irradiation microwave conditions (30 min, 120 °C) and b) reflux conditions after 3 h.

Slika 7: FE-SEM-mikrografije ZnO-nanodelcev, pripravljenih iz 2.3 mmol cink acetilacetonata in 1.16 mmol 1-heksadecil-3-metil imidazol klorid monohidrata v 17 mL 1-butanola. Vzorci so bili 30 min izpostavljeni pulznemu mikrovalovnemu sevanju z močjo 250 W pri 120 °C.

representing Zn-O stretching vibration at approximately 450 cm^{-1} and diffuse signals at cca. 3400 cm^{-1} attributed to water molecules adsorbed on the ZnO surface. The FTIR spectrum of as-prepared precipitate obtained from higher amount of zinc acetylacetonate (**Figure 5b**) shows also numerous signals of unreacted precursor. Correspondingly, besides the intensive zincite reflections, the XRD pattern in **Figure 5d** shows additional low intensity signals in the low-angle region representing the crystalline phase of the precursor.

Figure 6 shows FE-SEM images (FE-SEM SUPRA 35VP (Carl Zeiss) equipped with an energy-dispersive spectrometer (EDXS, Inca 400, Oxford Instruments)) of as-prepared ZnO nanoparticles synthesized from different amounts of zinc acetylacetonate (2.3, 4.6 and 6.9) mmol in 17 mL of 1-butanol. It was observed that the initial quantity of the precursor exerts a tremendous effect on the morphology of the particles, similarly to the reported ethylene-glycol-water systems.[12,13] Contrary to the mentioned microwave-assisted ZnO preparation, in the syntheses performed under reflux conditions by using analogous concentration of the precursor in 1-butanol, the rod-shaped ZnO particles were formed from all of the investigated solution meaning that in this case the product shape is concentration-independent.[16]

The particles in **Figure 6a** are approximately 10 nm to 60 nm in size, while the complex ZnO architectures in **Figure 6b** consist of a few-nanometers-large ZnO crystallites, which form approximately 100-nm-long nanorods growing on one side of the agglomerated, densely packed, quasi-spherical ZnO particles. In accordance with FTIR and XRD data (**Figures 5b and 5d**), in the case of 6.9 mmol of precursor, the micrograph in Figure 6c shows that after 30 min of microwave exposure approximately 100 nm long ZnO nanorods formed close to the surface of the undissolved pyramidal precursor. The similar phenomenon was observed during the monitoring of the ZnO growth from the oversaturated solution of zinc acetylacetonate in 1-butanol under the reflux conditions, where, due to the local supersaturation of the reactive monomer species, the initial formation of ZnO occurs around the solid precursor.[16]

Ionic liquids are particularly interesting species in microwave chemistry not only as they can act as template to control the particle shape and assembly behaviour, but also their ionic properties can drastically enhance the microwave absorbance of the system. For that mean, we have performed the microwave assisted synthesis of ZnO from the 1-butanol solution of zinc acetylacetonate in the presence of 1-hexadecyl-3-methyl imidazole chloride monohydrate. Contrary to the reactions carried out under "classical" reflux conditions (**Figure 7a**), under microwave radiation the product precipitates in form of round-shape architectures, which are formed by the aggregation of ZnO nanocrystals (**Figure 7b**). The similar effect of ionic liquid on the aggregation of primary ZnO nanoparticles was already reported in the microwave irradiated system of tetrabutylammonium hydroxide hydrate and zinc acetate dehydrate.[18] The formation of thermodinamically favorable spherical shape was attributed to the electrostatic interactions of polar charges in small ZnO particles, which uncontrolled growth is prevented by the absorption of charged species of the ionic liquid. This shows that microwaves can be used to influence and control the oriented attachment process, so new exciting opportunities for the assembly of ZnO nanoparticles could be opened.

4 CONCLUSIONS

The application of microwave radiation for the preparation of metal oxides under aqueous and non-aqueous conditions, especially relevant for the preparations of polymer/ZnO nanocomposites, has been shown to be a versatile approach to the design on novel nanoparticles' morphologies. Particularly the fast reaction rates (short reaction times), better product yields and the possibility to automatically combine different experimental parameters makes microwave-assisted synthesis suitable for the studies of the influences of the reaction conditions on the morphology and sizes of ZnO particles, which determine its properties and applications.

The different examples of the microwave-assisted synthesis of ZnO described in this article show that the general rules of the influence of the reaction parameters on the mechanism of the particle growth in microwave processes are not yet fully understand. This opens new research challenges in designing the nanoparticles with defined sizes, morphologies and complex architectures by using different experimental conditions.

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