Chemical Engineering Journal 288 (2016) 432–440

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Gold nanocubes – Direct comparison of synthesis approaches reveals the need for a microfluidic synthesis setup for a high reproducibility

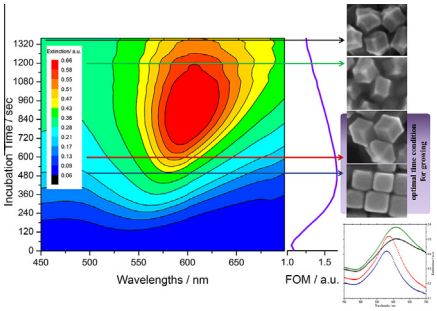
Matthias Thiele [a,*], Joanne Zi En Soh [b], Andrea Knauer [c], Daniell Malsch [a], Ondrej Stranik [a], Robert Müller [a], Andrea Csáki [a], Thomas Henkel [a], J. Michael Köhler [c], Wolfgang Fritzsche [a]

[a] Leibniz Institute of Photonic Technology (IPHT), Dept. of Nano Biophotonics, Albert-Einstein-Straße 9, 07745 Jena, Germany
[b] Universiti Teknologi Malaysia, Advanced Diagnostics and Progressive Human Care Research, Skudai, 81310 Johor, Malaysia
[c] Technische Universität Ilmenau, Institute for Chemistry and Biotechnology, Dept. of Physical Chemistry and Micro Reaction Technology, Gustav-Kirchhoff-Str. 1, D-98693 Ilmenau, Germany

HIGHLIGHTS

- Pointing out the need of four steps-synthesis (different incubation times) of Au-cubes.
- Investigates kinetic study and highlights the variations for different growth steps.
- We create a FOM (TEM, UV–VIS) for easy quantifications of the critical parameters.
- Discusses the need of reactor types (batch, microfluidics) for different parameters.
- Show automation ways, raise in yield/shape & reduced material usage by microfluidics.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 September 2015
Received in revised form 25 November 2015
Accepted 3 December 2015
Available online 12 December 2015

Keywords:
Plasmonic nanoparticles
Gold nanoparticles
Gold nanocubes
Microfluidics
Continuous high-throughput synthesis
Segmented flow synthesis

ABSTRACT

The production of non-spherical gold nanoparticles is a rather complex process and requires a multistep synthesis including surface blocking detergents such as CTAC and CTAB (cetyltrimethylammonium chloride; -bromide). Especially gold nanocubes are difficult to realize since they have six close packed 100-planes and they need at least three separate, highly controlled production steps: the synthesis step, where the seed particles will be formed, followed by two independent growing steps. One main challenge is to find the optimal conditions for the different steps, since the incubation times differs in several magnitudes for each step (seeds: ms, growing solution 1: sec, growing solution 2: min). Based on this discrepancy we present a study and comparison of different synthetic methods for each step. Starting with a classical batch approach we also transferred the synthesis into microfluidics and therefore compare continuous (one-phase) as well as segmented flow techniques, and discusses the benefits of each method. We present the additional advantage of CTAC in microfluidics since it passivates the channel surfaces and thereby inhibits clogging. A further detailed kinetic study of the two growing steps identifies the incubation time as critical parameter for a defined (cubed-like) geometry and facilitates the use of microfluidic methods for the first growing step, since it eliminates subjective decisions. Due to the kinetic study in combination with electron-microscopic characterization we propose a Figure Of Merit (FOM) for the second growth step that simplifies the evaluation of the point in time when to terminate the reaction to obtain perfectly shaped Au nanocubes. We also demonstrate the sensitivity (comparison of Au

Abbreviations: meNP, metal nanoparticle; SPR, surface plasmon resonance; LSPR, localized surface plasmon resonance; GS 1, growth solution 1; GS 2, growth solution 2; DCS, differential centrifugal sedimentation; SF, segmented flow; FOM, Figure Of Merit; RI, refractive index; RIU, refractive index unit; FWHM, full wide at half maximum.

* Corresponding author. Tel.: +49 3641 206 360.
E-mail address: matthias.thiele@ipht-jena.de (M. Thiele).

http://dx.doi.org/10.1016/j.cej.2015.12.020

nanocube and Au nanosphere) and the possibility of tuning the cube edge length (and so the plasmon peak position) and highlight their correlation as a fundament for an automated microfluidic synthesis and versatile applications, like biosensing.

1. Introduction

Noble metal – such as gold (Au) and silver (Ag) – nanoparticles (meNP) exhibit unique physical and chemical properties attributed to their intermediate sizes between bulk and molecular compounds. Especially the optical behavior is characteristic, since the conductive electrons of nano scaled noble metals behave like an oscillate dipole while exciting with coherent light and resulting in a surface plasmon. In the case of planar metal (layers) this process is known as surface plasmon resonances (SPR), for meNP it is termed localized surface plasmon resonance (LSPR). The plasmon resonance is the base for different kinds of optical labels and sensors in biology, chemistry and medicine [1–5]. Changes in the surrounding medium – in detail the change of the refractive index (RI) around the particle – such as induced by the binding of molecular layers result in a shift of the LSPR signal and can be measured without any previous labeling [6]. Indeed the meNP acts as a mediator, known as optical transducer [3]. Based on this principle, it is possible to realize different arrangements of LSPR-sensors like meNP solutions or immobilized meNP (ensembles or single particles) [7] to detect various kinds of analytes like small molecules, DNA, proteins, or even whole cells [2,8–14]. Depending on composition, size, and shape, different resonance regimes and sensitivities can be realized [15,16]. Furthermore, the use of anisotropic meNPs like cubes, prisms, bipyramids and rods enables amplified signals based on the local field enhancement at tips and corners [16,17]. Especially surface enhanced Raman spectroscopy (SERS) benefits from these features. However, based on the different aim and the need of defined meNP, a lot of effort was done in new NP-designs [18–21], whereas for many applications a fine tuning is still needed regarding yield, quality, reproducibility and simplicity. One example is the synthesis of gold nanocubes [17,22,23] which is widely considered as difficult since the cubes are confined by six closed 100-planes, requiring for their formation exact growth conditions. Xia et al. [24] also described how small changes in temperature, mixing conditions, precursor composition, impurity and reaction-time can lead to different results and further discusses microfluidic platforms as a strategy to fulfill these requirements [25]. In this work we describe a reproducible protocol that is based on the micro fluid technique and leads to the generation of homogeneous gold nanocubes with adjustable geometrical dimensions, high yields of the desired shape, and narrow particle size distributions. The synthesis method is based on a protocol published in 2010 by Wu et al. [26] in conventional flask based laboratory batch-type (discontinuous, Fig. 1a) reaction. The synthesis consists of three steps (depicted in Fig. 2) and is transferred into microfluidic techniques, whereat continuously (the mixed fluid streams and therefore also the resulting solution have the same phase Fig. 1b) and segmented flow (a fluid stream consisting of two phases, that creates in-line small separated droplets as single reactors Fig. 1c) approaches will be used and compared directly. Compared to the poor mixing qualities of conventional batch methods, we show that with microfluidic approaches a precise control and mass transfer for the nucleation and the grow processes is possible. That allows us to control the different requirements for the several synthesis steps (Fig. 2) and yields ideal homogeneity of Au seed particles based on the good mixing opportunities. We will further show that the success of the protocol depends on a strict schedule of time-critical process steps. This again will be supported by using microfluidics with well-defined residence times that enables a significantly increased reproducibility of optimal shaped Au nanocubes and a simple tuning of particle sizes, since the micro flow-through based protocol is much less prone to random errors during the synthesis. The segmented flow technique also realizes a decreased reactor volume down to segment volumes of some pl and nl by keeping the mixing conditions and therefore minimizes material consumption [27]. Regarding this, we will discuss the benefit of microfluidics at each step. At the end we will shortly compare the sensitivity (shift of the plasmon peak by changing the RI) of classical spherical and cubed Au nanoparticles, to highlight the potential of Au nanocubes for sensor applications.

2. Experiments

The synthesis of Au cubes is based on the procedure of Wu et al. [26] that includes three steps. Fig. 2 provides the chronology of the three synthetic steps and lists the appropriate method, that is used for this step. At the beginning of synthesis, Au seeds are produced by reduction of gold ions with sodium borohydride in the presence of CTAC. The formation of gold cubes is achieved by growing the Au seeds through a metal-catalyzed deposition of gold atoms upon the reduction of gold salt solution with ascorbic acid. For all steps, the conventional synthesis procedure (batch) is done by following

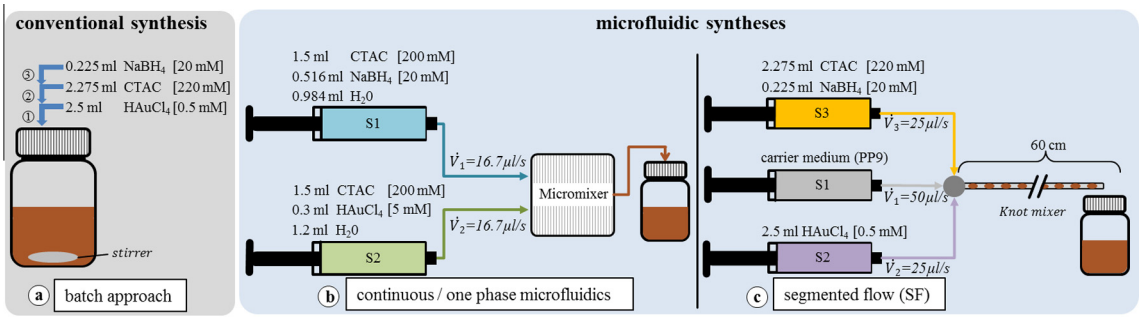


Fig. 1. Comparison of different synthesis methods for Au seed particles and experimental arrangement, including the used chemical and fluidic parameters. For the conventional synthesis a discontinuous batch approach (a) is used whereas two microfluidic approaches based on continuous (b) and segmented flow (c) technique are used.