

# Photo-induced green synthesis and antimicrobial efficacy of poly( $\epsilon$ -caprolactone)/curcumin/grape leaf extract-silver hybrid nanoparticles

Ibrahim M. El-Sherbiny<sup>a,\*</sup>, Ayman El-Shibiny<sup>b</sup>, Ehab Salih<sup>a</sup>

<sup>a</sup> Center for Materials Science, Zewail City of Science and Technology, 6th October City, 12588, Giza, Egypt

<sup>b</sup> Biomedical Science, Zewail City of Science and Technology, 6th October City, 12588, Giza, Egypt

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## ABSTRACT

This study reports the photo-induced green synthesis and antimicrobial assessment of poly( $\epsilon$ -caprolactone)/curcumin/grape leaf extract-Ag hybrid nanoparticles (PCL/Cur/GLE-Ag NPs). PCL/Cur/GLE NPs were synthesized via emulsion-solvent evaporation in the presence of PVA as a capping agent, then used as active nano-supports for the green synthesis and stabilization of AgNPs on their surfaces. Both Cur and GLE were selected and incorporated into the PCL nano-supports due to their reported promising antimicrobial activity that would further enhance that of the synthesized AgNPs. The developed PCL/Cur/GLE NPs and PCL/Cur/GLE-Ag hybrid NPs were characterized using UV-visible spectrophotometry, high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). HRTEM images showed that the PCL/Cur/GLE NPs are monodispersed and spherical with size of about 270 nm, and the AgNPs were formed mainly on their surfaces with average size in the range 10–30 nm. The synthesized AgNPs were found to be crystalline as shown by XRD patterns with fcc phase oriented along the (111), (200), (220) and (311) planes. The antimicrobial characteristics of the newly developed NPs were investigated against gram-positive and gram-negative bacteria in addition to two fungal strains. The results demonstrated that the PCL/Cur/GLE-Ag hybrid NPs have a potential antimicrobial activity against pathogenic bacterial species and could be considered as an alternative antibacterial agent.

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## 1. Introduction

Bacteria always develop resistance to different antibiotics by mutating their existing genes or through acquiring new genes from other bacterial strains [1]. According to the “Antimicrobial resistance: global report on surveillance” published by the World Health Organization (WHO) in April 2014, the high rates of antibiotics resistance have been observed in every region of the world, and more than half a million person die each year worldwide from antibiotic resistant bacterial infections [2]. Therefore, the world is heading for a post-antibiotic era, and there is a growing interest to use natural herbs and their extracts as antimicrobial agents, and as alternatives to antibiotics and chemical compounds [3]. Generally, herbal extracts contain various phytochemicals that have multiple modes of antimicrobial effect including the cell wall degradation and the destruction of RNA, DNA and protein translocation [4–6].

Grape leaf (GL) has been used to treat hypertension [7], inflammatory disorders [8], diarrhea, hemorrhage and varicose veins [9], and to reduce the blood glucose levels in diabetic patients [10]. Aqueous extract of GL (GLE) was found to contain a wide range of antimicrobial phenolic compounds, particularly kaempferol, quercetin, myricetin,

ellagic acid, and gallic acid [11,12]. On the other hand, curcumin (Cur) is a pharmacologically safe phenolic compound and it has been used for centuries as a food-coloring additive and a dietary spice [13]. Several studies have revealed good antimicrobial, anti-inflammatory and antioxidant properties of Cur [14,15]. Cur also showed a potential for inhibition of tumor genesis [16] and correction of cystic fibrosis imperfections [17].

The antimicrobial activity of herbal extracts such as GLE and Cur could be further enhanced via incorporation into polymeric nanoparticles (NPs) and/or developing them in a hybrid form with the antimicrobial AgNPs.

AgNPs have been widely used in a large number of applications such as bio-labeling, catalysts in chemical reactions and as antibacterial agents [18,19]. A number of approaches are available for the synthesis of AgNPs. For instance, Ag<sup>+</sup> can be reduced into atomic Ag by chemical [20] electrochemical [21–23], irradiation [24], photochemical [25], and biological methods [26]. Among these methods, green synthesis methods that involve using herbal extracts, nontoxic polymers and UV-irradiation are not only good ways to fabricate benign nanostructures, but also to reduce the use or generation of hazardous substances to human health and the environment [27,28].

Recently, a great deal of interest has focused on the use of biopolymers in developing nanocomposites due to their desirable properties and enormous valuable applications in bio-related fields [29–36]. For

\* Corresponding author.

E-mail address: [ielsherbiny@zewailcity.edu.eg](mailto:ielsherbiny@zewailcity.edu.eg) (I.M. El-Sherbiny).

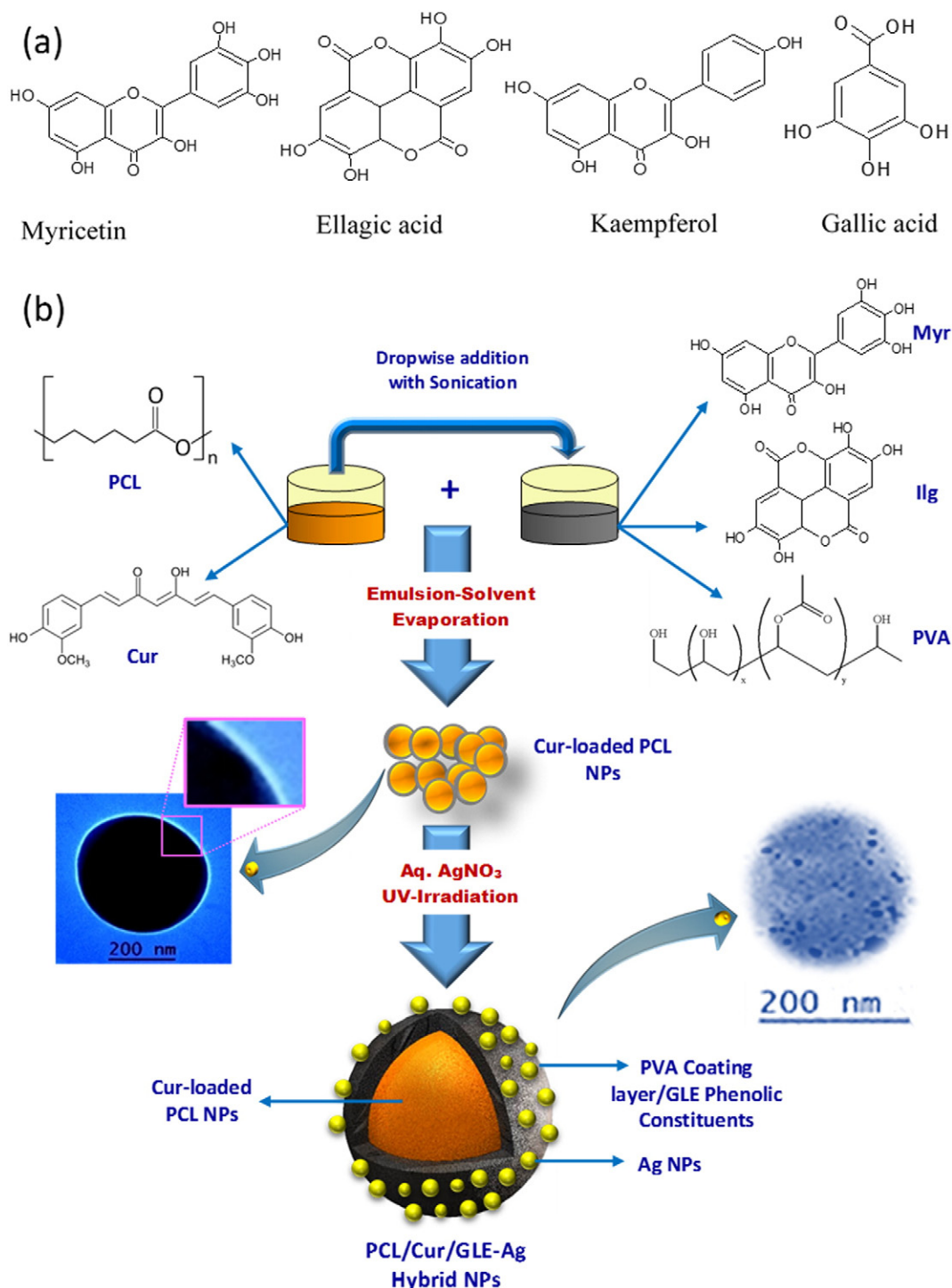
**Table 1**

The composition of all the tested samples.

Code	Sample
A1	GLE (20% w/v)
A2	GLE/AgNPs (1 mM)
A3	GLE/AgNPs (5 mM)
A4	GLE/AgNPs (10 mM)
A5	PCL/Cur NPs
A6	PCL/Cur/GLE-Ag hybrid NPs (1 mM)
A7	PCL/Cur/GLE-Ag hybrid NPs (5 mM)
A8	PCL/Cur/GLE-Ag hybrid NPs (10 mM)

example, poly(oxyethylene)isooctyl phenyl ether micelles were used as capping agents to control the shape and size of gold NPs [37], and also the poly(vinyl pyrrolidone) was beneficial as a stabilizer upon fabrication of Ag nanowires by a solution-phase method [38]. Moreover, different polymers have been widely explored as stabilizers or scaffolds for immobilization of metallic NPs such as dendrimers and block copolymer micelles [39,40].

In this study we report the photo-induced green synthesis and antimicrobial evaluation of PCL/Cur/GLE-Ag hybrid NPs. Firstly, PCL/Cur/GLE NPs were synthesized via emulsion-solvent evaporation method in the presence of PVA as a surfactant. The NPs were prepared in such



**Scheme 1.** (a) Major phenolic compounds in the aqueous GLE [11,12], and (b) a schematic illustration of the developed antimicrobial PCL/Cur/GLE-Ag hybrid NPs.

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