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POLYLACTIC ACID-COATED COPPER OXIDE-SILICA NANOPARTICLES AS A COST-EFFECTIVE ALTERNATIVE TO SILVER-BASED ANTIMICROBIAL MATERIALS

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The escalating threat of antimicrobial resistance (AMR) and the high cost of silver (Ag)-based nanomaterials have intensified the search for affordable, efficient, and sustainable alternatives [1, 2]. Copper oxide (CuO) has emerged as a promising candidate due to its low cost, broad-spectrum activity, and compatibility with inorganic supports [3, 4]. Recent studies have demonstrated that CuO-based composites can achieve antimicrobial efficacy through reactive oxygen species generation while offering significant economic advantages over silver—copper is priced at approximately \$3.50 per pound compared to \$400 per pound for silver [5]. Polylactic acid (PLA) functionalization offers a strategy to tailor surface chemistry and introduce biodegradability [6, 7], yet the impact of PLA on the antimicrobial performance of CuO-based systems relative to Ag-based counterparts remains poorly understood. In this work, we systematically evaluate the antimicrobial activity of fumed silica nanocomposites functionalized with either silver (SiO₂–Ag) or copper oxide (SiO₂–CuO), before and after PLA coating, to determine whether PLA-modified CuO can serve as a cost-effective alternative without compromising efficacy.

All materials were characterized by X-ray photoelectron spectroscopy (XPS) and nitrogen physisorption to confirm successful PLA attachment and preservation of the mesoporous architecture. XPS analysis of SiO₂–Ag–PLA and SiO₂–CuO–PLA showed characteristic ester-related C 1s components (C–O, O–C=O) and attenuation of inorganic signals, consistent with a conformal polymer overlayer of a few nanometres. Importantly, the Ag 3d and Cu 2p core-level spectra revealed no change in oxidation state after functionalization, indicating that the PLA deposition process does not alter the active metal phase. Physisorption measurements showed that both SiO₂–Ag and SiO₂–CuO possess Type IV isotherms with high surface areas (264 m²/g and 256 m²/g, respectively). After PLA coating, surface areas decreased moderately (to 187 m²/g for Ag and 172 m²/g for CuO), while the characteristic mesopore size distributions remained unchanged, confirming that the porous framework is retained. These findings are consistent with recent reports on PLA–silica composites, where polymer incorporation preserves the mesoporous architecture while enhancing functional properties [6, 8].

Table

Antimicrobial activity was assessed by determining minimum inhibitory concentrations (MIC, mg/mL) against a panel of clinically relevant bacteria:

Strain	SiO ₂ -Ag	SiO ₂ -Ag-PLA	SiO ₂ -CuO	SiO ₂ -CuO-PLA
<i>E.coli</i> 148 (clinical isolate)	3.125	12.5	25	12.5
<i>K.pneumoniae</i> ATCC BAA-1705 (KPC)	3.125	12.5	–	12.5
<i>E.coli</i> ATCC 33876	3.125	12.5	6.25	12.5
<i>K.pneumoniae</i> ATCC 10031	3.125	3.125	12.5	12.5
<i>S.aureus</i> ATCC 29213	3.125	6.25	25	–
<i>S.aureus</i> ATCC BAA-1026 (MRSA)	6.25	12.5	12.5	12.5

The unmodified SiO₂-Ag composite exhibited potent activity against all tested strains (MIC 3.125–6.25 mg/mL). PLA coating reduced its activity by two- to four-fold (MIC 6.25–12.5 mg/mL), likely due to partial shielding of the silver phase. In contrast, the SiO₂-CuO composite showed strain-dependent activity, with notable efficacy against *E. coli* ATCC 33876 (MIC 6.25 mg/mL) and *K. pneumoniae* ATCC 10031 with *S. aureus* ATCC BAA-1026 (MIC 12.5 mg/mL). Remarkably, PLA modification of the CuO system did not uniformly reduce activity. SiO₂-CuO-PLA maintained MICs of 12.5 mg/mL against *E. coli* 148, *E. coli* ATCC 33876, *K. pneumoniae* ATCC BAA-1705, and *K. pneumoniae* ATCC 10031, and was active against the KPC-producing strain where the uncoated CuO was ineffective. This preservation of activity suggests that the PLA layer may modulate copper ion release or improve surface interactions with bacterial cells without fully passivating the active sites. Recent studies have shown that CuO nanoparticles generate •OH radicals that damage cellular components, providing a mechanism for their antimicrobial action [3, 4, 9]. Furthermore, copper oxide dressings have demonstrated antimicrobial efficacy alongside stimulation of angiogenesis and extracellular matrix remodeling, offering dual functionality that silver-based systems lack [2, 10].

Taken together, the XPS and textural data confirm that PLA functionalization preserves the chemical state of the inorganic phase and the open mesoporous architecture essential for mass transport. While Ag-based materials possess higher intrinsic potency, the PLA-modified CuO nanocomposite offers a compelling alternative: it exhibits broad-spectrum activity against clinically relevant Gram-negative and Gram-positive pathogens, retains efficacy after polymer coating, and benefits from the substantially lower cost of copper. Recent clinical evidence suggests that copper oxide dressings may accelerate healing in refractory wounds and offer cost advantages over silver-based alternatives, though large-scale trials remain limited [2]. These findings establish SiO₂-CuO-PLA as a cost-effective, structurally robust antimicrobial platform, suitable for applications such as wound dressings, coatings, and biomedical devices where balancing performance, stability, and economic viability is critical.

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VITAMIN K-DEPENDENT PROCESSES AND POTENTIAL INTERACTIONS WITH ANTICOAGULANTS

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Vitamin K is a family of lipophilic 2-methyl-1,4-naphthoquinones, which includes phyloquinone (K_1) and menaquinones (K_2 , MK-n). Its fundamental function in biology is to ensure post-translational modification of proteins – γ -carboxylation of glutamate residues (Glu→Gla) with the formation of calcium-binding Gla clusters. It is these clusters that form a structural module that provides Ca^{2+} -dependent binding to phospholipid membranes and determines the activity of most vitamin K-dependent proteins (VKDP) [2, 9].

The classic “hepatic” group of VKDPs determines hemostasis: prothrombin (factor II), factors VII, IX, X, and natural anticoagulants protein C and protein S. The formation of complete Gla domain(s) is necessary for the assembly of coagulation complexes on platelet/endothelial membranes. At the same time, modern biomedical chemistry considers VKDP as a broader system that includes extrahepatic proteins—matrix Gla protein (MGP), osteocalcin (OC), Gas6, Gla-rich protein (GRP/UCMA), etc., which are involved in the regulation of bone mineralization, inhibition of vascular calcification, cell survival, and inflammation [1, 4].

Biochemically, γ -carboxylation occurs in the endoplasmic reticulum and is catalyzed by γ -glutamyl carboxylase (GGCX). The reaction requires CO_2 and O_2 , and the reduced form of vitamin K, hydroquinone (KH_2), is used as a redox cofactor, which is converted to vitamin K epoxide (KO) during the process. Thus, carboxylation and epoxidation are tightly coupled stages of a single enzymatic event, which determines the sensitivity of the system to K deficiency and recycling inhibitors [3].

The “vitamin K cycle” maintains the carboxylation flow: KO is reduced back to quinone/hydroquinone mainly with the participation of VKORC1 (vitamin K epoxide reductase complex subunit 1) and related reductases. Vitamin K antagonists (VKAs), primarily warfarin, inhibit VKORC1 and cause functional KH_2 deficiency, resulting in the synthesis of partially carboxylated (biologically deficient) coagulation factors and increased INR [7].

From the perspective of drug chemistry, it is critically important to distinguish between “vitamin K deficiency” and “carboxylation deficiency.” Even with normal K intake, situations with impaired VKDP activation are possible due to drug effects (VKA), genetic variants of enzymes (VKORC1, GGCX), impaired absorption of lipophilic vitamins, or changes in the microbiota. For extrahepatic VKDPs, particularly MGP, a clinically relevant marker is the accumulation of uncarboxylated forms (e.g., dp-ucMGP), which is associated with the risk of vascular calcification and cardiometabolic complications in various cohorts [4].

The most significant interactions between vitamin K and anticoagulants concern VKAs and are predominantly pharmacodynamic in nature. Fluctuations in the intake of K_1 from food (greens, cabbage, liver) or K_2 from fermented products/supplements alter the availability of the cofactor for γ -carboxylation and modulate the effectiveness of warfarin [1]. In practice, this manifests as a decrease in the anticoagulant effect (INR ↓) with a sudden increase in vitamin K intake and, conversely, a tendency toward hypocoagulation (INR ↑) with a sharp decrease in its intake [7].