

Article

Machine Learning-Assisted Synthesis-to-Optics Screening of Ag@SiO₂/Polymer Nanocomposites for Visible Spectrum Negative Effective Permittivity

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Featured Application

The proposed workflow can be used as an AI-driven tool for designing Ag@SiO₂/polymer nanocomposite films with visible spectrum near-zero or negative effective permittivity response, helping prioritize synthesis-accessible core-shell geometries and filling factor conditions before manufacturing.

Abstract

Machine learning (ML)-assisted design of epsilon-negative polymer nanocomposites requires a clear connection between experimentally controllable synthesis parameters, core-shell nanoparticle geometry, and the resulting effective optical response. The targeted optical response is unusual because the polymer film is predicted to exhibit near-zero or negative real effective permittivity in selected visible spectrum regions, arising from Ag core plasmonic polarizability, SiO₂-mediated dielectric spacing, nanoparticle filling factor, and effective medium coupling rather than from the intrinsic polymer matrix. In this study, a two-stage ML-assisted synthesis-to-optics framework is developed for Ag@SiO₂ core-shell nanoparticle/polymer composite films intended for visible spectrum effective permittivity screening. In the first stage, Stöber synthesis parameters, including water volume, ethanol volume, TEOS content, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration, were used to predict SiO₂ shell thickness. In the second stage, Ag core size, SiO₂ shell thickness, wavelength, and nanoparticle filling factor were used to screen the real effective permittivity of Ag@SiO₂/polymer nanocomposites within an effective medium design space. Using a duplicate-aware validation workflow, Gradient Boosting provided the strongest held-out test performance for shell thickness prediction, with a test R² of 0.8997, MAE of 7.1822 nm, RMSE of 8.8344 nm, and cross-validation R² of 0.5371 ± 0.4648. The relatively large cross-validation variability indicates that the model is useful for interpolation-based synthesis screening but should not be interpreted as fully robust across heterogeneous literature-derived data. For the optical response task, the highest held-out test performance was obtained by a Decision Tree model (test R² = 0.7586), but cross-validation results were unstable, indicating that the epsilon model should be interpreted as a design space screening tool rather than a generalizable predictor. Design window analysis identified candidate negative effective permittivity regions primarily at 400 nm and high nanoparticle filling factor, with predicted Re(ε_{eff}) values ranging from −5.4229 to −0.2086 across selected windows. The main contribution of this work is the treatment of SiO₂ shell thickness as a bridge variable between Stöber-derived synthesis



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control and effective permittivity screening. Experimental validation remains necessary to confirm the predicted design windows, particularly because shell uniformity, Ag core polydispersity, nanoparticle aggregation, polymer dispersion, high-filling-factor feasibility, and effective medium validity can strongly influence the measured optical response.

Keywords: core-shell; Ag@SiO₂; epsilon-negative; Stöber method; machine learning

1. Introduction

Metamaterials and metamaterial-inspired composites have attracted sustained attention in optics, photonics, applied physics, and materials engineering because their electromagnetic response can be engineered through composition, geometry, and mesoscale organization rather than being determined only by the intrinsic properties of a single bulk material [1,2]. In optical materials, one particularly important target is the realization of materials with near-zero or negative effective permittivity, because these responses can enable unusual light-matter interactions, strong field localization, modified scattering, and compact photonic functionalities. For polymer nanocomposite films, however, negative effective permittivity must be interpreted carefully: it is not a property of the polymer matrix alone but an effective optical response arising from the interaction between plasmonic inclusions, dielectric spacing, filling factor, wavelength, and the validity of the homogenized medium approximation.

Metallic nanoparticles provide a practical route for tuning the optical response of composite media because their free-electron oscillations support localized surface plasmon resonance (LSPR). LSPR frequency and strength depend on particle size, shape, dielectric environment, and interparticle spacing. Silver nanoparticles are especially attractive in visible spectrum plasmonics because of their strong optical polarizability and relatively low losses compared with many other plasmonic metals. However, bare Ag nanoparticles are chemically and colloiddally sensitive; they may aggregate, oxidize, or interact directly with neighbouring particles in ways that make the optical response difficult to control.

Ag@SiO₂/polymer nanoarchitectures are particularly relevant because their optical response is governed by coupled structural and electromagnetic effects rather than by composition alone. The Ag core provides strong localized plasmonic polarizability, while the SiO₂ shell regulates dielectric screening, interparticle spacing, and the extent of near-field coupling between adjacent Ag domains. By changing the Ag core size, SiO₂ shell thickness, particle loading, and polymer environment, such nanoarchitectures can support localized field enhancement, plasmonic resonance tuning, scattering modulation, optical absorption control, and transitions toward epsilon-near-zero or epsilon-negative effective permittivity regimes [3–5]. These effects are relevant for sensing, photonic screening, metasurface-inspired coatings, and optical nanocomposite design, provided that the particles remain sufficiently dispersed for an effective medium description to remain meaningful [6,7]. Thus, Ag@SiO₂/polymer composites should be understood not simply as filled polymers but as geometry-controlled plasmonic nanoarchitectures in which the nanoscale core-shell design determines the macroscopic effective optical response.

In other words, Ag@SiO₂ core-shell nanoparticles are a useful model system: the Ag core provides the plasmonic polarizability, while the SiO₂ shell acts as a dielectric spacer, stabilizing layer, and optical screening medium [8–10].

The thickness of the SiO₂ shell is therefore a critical parameter. A very thin or incomplete shell may fail to prevent aggregation or uncontrolled near-field coupling between Ag cores. Conversely, an excessively thick SiO₂ shell can screen the plasmonic response of

the Ag core and increase interparticle separation so strongly that collective optical effects are weakened. Thus, SiO₂ shell thickness has a dual scientific role in Ag@SiO₂/polymer nanocomposites: it is both a synthesis-controlled output of the Stöber coating process and an optical design variable that influences dielectric screening, interparticle spacing, filling factor effects, and effective permittivity. This dual role provides the central link between nanoparticle synthesis and composite optical design [11].

The Stöber method is widely used to form silica coatings around colloidal nanoparticles because it offers a chemically accessible route for controlling silica growth through hydrolysis and condensation of tetraethyl orthosilicate (TEOS) under basic conditions. In Ag@SiO₂ synthesis, shell growth is affected by water and ethanol content, TEOS amount or concentration, catalyst type and volume, reaction time, initial Ag nanoparticle size, and Ag nanoparticle concentration. These variables are interdependent, and their influence on shell thickness is not usually linear. Literature-derived datasets are therefore heterogeneous, with variations in reporting format, missing synthesis parameters, different catalyst systems, and different shell thickness measurement protocols. A purely empirical trial-and-error approach is inefficient because shell thickness control is a multivariable synthesis problem in which several experimental parameters are coupled [12].

Machine learning has become increasingly useful in materials design because it can model nonlinear relationships in tabular experimental datasets, identify predictive trends, and support rapid screening of candidate compositions or processing conditions. In nanoparticle synthesis, ML can be particularly valuable when the target property is controlled by several coupled parameters and when mechanistic equations are incomplete or difficult to apply across heterogeneous literature data [13]. Nevertheless, ML must be used with caution in small- or medium-sized materials datasets. Model performance must be evaluated using reproducible preprocessing, explicit train/test separation, cross-validation, leakage control, and physically interpretable trends; otherwise, high reported accuracy may reflect data duplication, imputation artifacts, or interpolation within a narrow dataset rather than true generalization.

For Ag@SiO₂/polymer nanocomposites, the design problem is broader than predicting shell thickness alone. The optical response of the final composite depends on the Ag core size, SiO₂ shell thickness, nanoparticle filling factor, wavelength, and dielectric response of the polymer host. Effective medium approaches, such as Lorentz–Lorenz or Clausius–Mossotti-type formulations, can relate inclusion polarizability and volume fraction to the effective permittivity of a homogenized composite. In this context, ML will not be presented as replacing electromagnetic theory. Its stronger role is as a support and design space mapping tool that links synthesis-accessible geometry to effective permittivity screening across a multidimensional parameter space.

A key research gap remains: synthesis control and optical composite design are often treated as separate problems. Studies of Ag@SiO₂ synthesis usually focus on controlling shell thickness, morphology, or colloidal stability, whereas optical composite studies often assume nanoparticle geometry and filling factor as predefined inputs. The missing link is a reproducible synthesis-to-optics framework that connects Stöber-derived SiO₂ shell-thickness prediction with visible spectrum effective permittivity screening of Ag@SiO₂/polymer nanocomposite films. Such a framework is useful because the same shell thickness that is controlled during synthesis also governs dielectric screening, interparticle spacing, and the optical polarizability of the final composite.

Accordingly, this study develops a two-stage ML-assisted predictive framework for Ag@SiO₂ core–shell nanoparticle/polymer composite films. In the first stage, Stöber synthesis parameters are used to predict SiO₂ shell thickness. In the second stage, Ag core size, SiO₂ shell thickness, wavelength, and nanoparticle filling factor are used to screen

the effective permittivity of Ag@SiO₂/polymer nanocomposites in the visible spectrum. The objective is not to claim experimental optimization of a final metamaterial structure but to establish a reproducible predictive workflow for identifying candidate geometry–composition–wavelength regions associated with negative effective permittivity.

The main contribution of this work is therefore the integration of synthesis prediction and optical response screening into a single design-oriented workflow. By treating SiO₂ shell thickness as both a Stöber-derived synthetic output and an optical control variable, the framework provides a practical route for connecting nanoparticle fabrication parameters to predicted negative-effective-permittivity design windows in polymer nanocomposite films. The results will be interpreted as ML-assisted design space screening rather than direct experimental demonstration of epsilon-negative behaviour. Experimental validation through nanoparticle characterization, polymer film dispersion analysis, and optical retrieval of effective permittivity remains necessary to confirm the predicted design windows.

2. Materials and Methods

This study was designed as a two-stage machine learning-assisted synthesis-to-optics predictive workflow for Ag@SiO₂ core–shell nanoparticle/polymer nanocomposite films. The first stage addresses the relationship between Stöber synthesis conditions and the resulting SiO₂ shell thickness. The second stage addresses the relationship between Ag@SiO₂ core–shell geometry, nanoparticle filling factor, visible spectrum wavelength, and the predicted effective permittivity of the polymer composite layer. The workflow is therefore framed as predictive modelling and design space screening, not as full mathematical optimization, because no explicit objective function, constraint set, inverse design algorithm, or ranked candidate search is introduced in the present study.

All the features and target values are presented in Table 1. Also, the proposed composite layer structure is shown schematically in Figure 1.

Table 1. Features and the target value for Ag@SiO₂ CS NPs synthesis and negative epsilon composite fabrication using CS NPs.

Ag@SiO ₂ Core–Shell NPs Synthesis with Stöber Method	
Features	H ₂ O volume, ethanol volume, TEOS concentration, catalyser volume, reaction time, Ag NP size, Ag NP concentration
Target value	SiO ₂ shell thickness
Negative-epsilon Ag@SiO ₂ /polymer composite	
Features	SiO ₂ shell thickness, Ag NP size, wavelength, filling factor
Target value	Epsilon

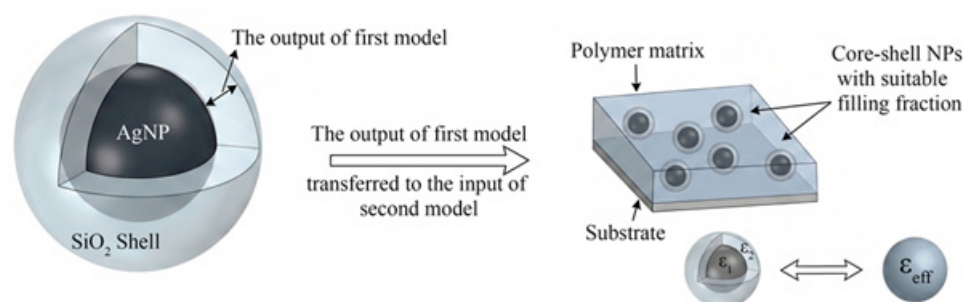
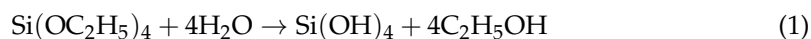


Figure 1. Schematic of the proposed composite layer structure.

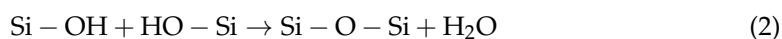
2.1. Methods and Preprocessing

For the first prediction task, the dataset was assembled from literature reports on the Stöber synthesis of monodispersed Ag@SiO₂ core-shell nanoparticles.

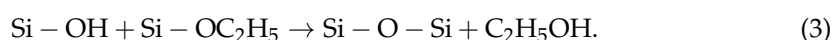
The Stöber-derived SiO₂ coating process is based on the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) under basic conditions. In the presence of water and a catalyst, TEOS first undergoes hydrolysis to form silanol-containing species:



The resulting silanol groups then undergo condensation reactions to form a silica network around the Ag nanoparticle surface:



and/or



In Ag@SiO₂ synthesis, the final shell thickness depends on coupled reaction and colloidal variables rather than on a single reagent ratio. Water participates in TEOS hydrolysis; ethanol controls the solvent environment and colloidal stability; TEOS provides the silica precursor; the catalyst controls the rate of hydrolysis and condensation; reaction time affects shell growth progression; Ag nanoparticle size determines available surface area for silica deposition; and Ag nanoparticle concentration influences the distribution of silica precursor per particle. Therefore, the machine learning model should not be interpreted as determining universal “best ratios” for the Stöber reaction. Instead, it screens literature-derived combinations of water volume, ethanol volume, TEOS amount, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration to estimate the SiO₂ shell thickness expected within the investigated Stöber synthesis domain.

Only studies that reported Ag@SiO₂ particles with identifiable core-shell morphology and sufficient synthesis information were retained. Reports describing poorly defined Ag-SiO₂ mixtures, strongly agglomerated products, or incomplete synthesis conditions were excluded. The input features for this task were water volume, ethanol volume, TEOS amount/concentration, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration. The target variable was the SiO₂ shell thickness. Because the source studies did not report measurement uncertainties in a consistent or comparable format, uncertainty-weighted regression was not applied; instead, uncertainty was handled qualitatively through source-level provenance reporting, measurement method documentation, morphology-based filtering, duplicate-aware validation, and cautious interpretation of model performance. This task links experimentally controllable synthesis parameters to a physically meaningful geometrical output, allowing shell thickness to be treated as a Stöber-derived synthesis response rather than as an arbitrary optical fitting variable. The source-level provenance of the literature-derived Ag@SiO₂ shell thickness dataset is summarized in Table S1. For each source, the extracted records were checked for the availability of the synthesis variables used in the regression model, namely, water volume, ethanol volume, TEOS amount or concentration, catalyst volume, reaction time, Ag nanoparticle size, Ag nanoparticle concentration, and SiO₂ shell thickness. When a variable was not explicitly reported, the corresponding entry was treated as missing and handled only within the leakage-controlled imputation pipeline described below. When a value required unit harmonization, for example, conversion of reaction time or precursor amount into the units used in the dataset, the converted value was recorded in the extraction sheet. The

source-level table is intended to make clear which information was directly measured or reported, which information required conversion, and which entries required imputation.

For the second prediction task, the dataset was constructed to describe the effective optical response of Ag@SiO₂/polymer nanocomposite films. In the optical response task, “composition” is used only in the effective medium sense of Ag@SiO₂ nanoparticle loading or filling factor within the polymer matrix. It does not refer to chemical modification of the Ag core, SiO₂ shell, or polymer host, whose material identities are kept fixed while the Ag core size, SiO₂ shell thickness, wavelength, and filling factor are varied. The input features were Ag core size, SiO₂ shell thickness, incident wavelength, and nanoparticle filling factor. The target variable was the effective permittivity of the composite layer. In this task, SiO₂ shell thickness serves a second role: it is not only the output of the synthesis model but also an optical design variable that controls dielectric screening, interparticle spacing, and the effective polarizability of the Ag@SiO₂ inclusions. The polymer matrix was treated as a dielectric host with a refractive index of 1.5. This assumption simplifies the optical model but should be recognized as a limitation because real polymer matrices may exhibit wavelength-dependent refractive indices, curing-dependent optical properties, and particle–polymer interfacial effects. The generation and provenance of the optical response dataset are summarized in Table S2, including the Ag core size values, SiO₂ shell thickness values, wavelength points, filling factors, polymer host assumptions, effective medium equations, number of raw configurations, duplicate-aware unique configurations, and treatment of repeated feature combinations.

The effective permittivity values used for the optical response task were obtained from an effective medium formulation based on the polarizability of core–shell inclusions and their filling factor in the polymer matrix. The optical response of the composite was interpreted using a Lorentz–Lorenz/Clausius–Mossotti-type framework, in which the effective permittivity depends on the effective polarizability of the Ag@SiO₂ particles, the volume fraction of inclusions, and the dielectric contrast among the Ag core, SiO₂ shell, and polymer host. Accordingly, the ML model in the second task should be understood as a surrogate for rapid design space mapping of geometry–composition–wavelength relationships, not as a replacement for electromagnetic theory or as direct experimental proof of epsilon-negative behaviour [14–21].

The effective permittivity labels used in the optical response dataset were calculated using a quasi-static effective medium formulation for spherical Ag@SiO₂ core–shell inclusions dispersed in a dielectric polymer host. The Ag core radius is denoted by r_{Ag} , the SiO₂ shell thickness by t_{SiO_2} , and the outer core–shell particle radius by

$$r_{\text{out}} = r_{\text{Ag}} + t_{\text{SiO}_2}. \quad (4)$$

The core-to-particle volume ratio is therefore

$$\eta = \left(\frac{r_{\text{Ag}}}{r_{\text{out}}} \right)^3. \quad (5)$$

For a coated spherical inclusion embedded in a polymer host, the dimensionless effective polarizability factor, $\Gamma(\lambda)$, was calculated as

$$\Gamma(\lambda) = \frac{[\varepsilon_{\text{SiO}_2}(\lambda) - \varepsilon_{\text{p}}(\lambda)] [\varepsilon_{\text{Ag}}(\lambda) + 2\varepsilon_{\text{SiO}_2}(\lambda)] + \eta [\varepsilon_{\text{Ag}}(\lambda) - \varepsilon_{\text{SiO}_2}(\lambda)] [\varepsilon_{\text{p}}(\lambda) + 2\varepsilon_{\text{SiO}_2}(\lambda)]}{[\varepsilon_{\text{SiO}_2}(\lambda) + 2\varepsilon_{\text{p}}(\lambda)] [\varepsilon_{\text{Ag}}(\lambda) + 2\varepsilon_{\text{SiO}_2}(\lambda)] + 2\eta [\varepsilon_{\text{SiO}_2}(\lambda) - \varepsilon_{\text{p}}(\lambda)] [\varepsilon_{\text{Ag}}(\lambda) - \varepsilon_{\text{SiO}_2}(\lambda)]}. \quad (6)$$

where $\varepsilon_{\text{Ag}}(\lambda)$, $\varepsilon_{\text{SiO}_2}(\lambda)$, and $\varepsilon_{\text{p}}(\lambda)$ are the wavelength-dependent permittivities of the Ag core, SiO₂ shell, and polymer host, respectively. In the present dataset, the polymer host was approximated as a nondispersive dielectric with refractive index $n_{\text{p}} = 1.5$, so that

$$\varepsilon_{\text{p}} = n_{\text{p}}^2 = 2.25. \quad (7)$$

The effective permittivity of the Ag@SiO₂/polymer nanocomposite was then obtained using the Clausius–Mossotti mixing relation,

$$\frac{\varepsilon_{\text{eff}}(\lambda) - \varepsilon_p}{\varepsilon_{\text{eff}}(\lambda) + 2\varepsilon_p} = f\Gamma(\lambda), \quad (8)$$

which gives

$$\varepsilon_{\text{eff}}(\lambda) = \varepsilon_p \frac{1 + 2f\Gamma(\lambda)}{1 - f\Gamma(\lambda)}. \quad (9)$$

In this expression, f is the nanoparticle filling factor in the polymer matrix. The effective permittivity may be complex if complex wavelength-dependent optical constants are used for Ag. In the present regression task, the scalar target variable was taken as the real part of the effective permittivity,

$$\varepsilon_{\text{target}}(\lambda) = \text{Re}[\varepsilon_{\text{eff}}(\lambda)], \quad (10)$$

because the design objective was to screen geometry–composition–wavelength regions where the real effective permittivity becomes near-zero or negative. The resulting ML model should therefore be interpreted as a surrogate for rapid screening of the effective medium design space, not as an independent electromagnetic solver or experimental retrieval of ε_{eff} .

The effective permittivity formulation used in this study is not an arbitrary self-developed expression. It combines the quasi-static polarizability of a coated spherical inclusion with a Clausius–Mossotti/Lorentz–Lorenz effective medium mixing relation. The coated sphere polarizability term accounts for the dielectric contrast among the Ag core, SiO₂ shell, and polymer host, while the Clausius–Mossotti relation converts the inclusion polarizability and nanoparticle filling factor into the effective permittivity of the homogenized composite medium [12]. As a consistency check, the implementation was verified against physically expected limiting behaviour: when the nanoparticle filling factor approaches zero, the calculated effective permittivity approaches the polymer host permittivity; when the Ag core contribution is removed or strongly screened by a thick SiO₂ shell, the predicted response remains positive and dielectric-like. Direct analytical calculations for selected geometry–wavelength–filling factor points were also compared with the corresponding dataset labels to confirm that the ML target values reproduce the effective medium formulation. Therefore, the purpose of the ML model is not to replace an equation that can be directly evaluated. Rather, ML is used as a synthesis-linked surrogate for rapid design space screening, extraction of negative-effective-permittivity windows, and future integration with inverse design or uncertainty-aware optimization workflows that connect predicted Stöber-derived shell thickness with optical response selection.

Before model development, the datasets were inspected for missing values, physically implausible entries, duplicate rows, repeated feature combinations, and inconsistent target values. This inspection was essential because the datasets were literature-derived and therefore susceptible to heterogeneous reporting, repeated experimental conditions, missing synthesis parameters, and duplicated optical design points. We identified exact duplicate rows and repeated feature combinations, especially in the effective permittivity dataset. These issues can lead to optimistic random-split performance if identical or nearly identical configurations appear in both training and test sets. Therefore, duplicate-aware validation and leakage control are required when interpreting model performance.

Missing numerical values were handled using imputation within the machine learning pipeline. To avoid data leakage, imputation parameters must be fitted only on the training data and then applied to the corresponding validation or test data. This is particularly important for small and heterogeneous synthesis datasets, where imputing missing values before the train/test split can transfer information from the test set into the training process.

Median imputation was used as a conservative baseline in the validation workflow because it avoids overfitting missing values in small datasets. More complex imputation strategies may be used only if their performance is validated within the cross-validation loop and reported transparently.

Feature scaling was applied where required using MinMax normalization. As with imputation, scaling parameters must be fitted only on the training fold during cross-validation and only on the training set during final test set evaluation. Scaling is relevant for linear, distance-based, support vector, and neural network models, while tree-based models are generally less sensitive to feature scaling. Nevertheless, applying the same preprocessing pipeline across algorithms improves comparability and reproducibility.

The computational workflow was implemented in Python 3.10 using standard scientific machine learning libraries. Pandas 3.0.3 and NumPy 2.2.0 were used for data handling and numerical processing; scikit-learn was used for preprocessing, regression models, train/test splitting, cross-validation, and performance metrics; and visualization libraries were used for plotting model performance and variable relationships [22,23].

The preprocessing strategy was designed to ensure that the two ML tasks are interpreted correctly. The shell thickness model predicts a synthesis-derived geometrical variable from Stöber process parameters. The effective permittivity model screens optical responses from geometry, filling factor, and wavelength using effective-medium-derived target values. This distinction is central to the manuscript: the first model addresses synthesis control, whereas the second model addresses optical response screening. The two models are connected through SiO₂ shell thickness, which functions as the bridge between nanoparticle synthesis and composite effective permittivity design.

2.2. Data Inspection and Imputation

Because the datasets used in this study were assembled from literature-derived synthesis reports and effective-medium-based optical calculations, data inspection was performed before model development to identify missing values, extreme entries, duplicate rows, repeated feature combinations, and potential sources of data leakage. This step is especially important for small or heterogeneous materials datasets, where apparently high model performance can result from repeated configurations, preprocessing leakage, or inconsistent target values rather than true regression model generalization.

For the Ag@SiO₂ shell thickness dataset, each record was inspected with respect to the reported Stöber synthesis parameters, including water volume, ethanol volume, TEOS content, catalyst volume, reaction time, Ag nanoparticle size, Ag nanoparticle concentration, and measured SiO₂ shell thickness. The purpose of this inspection was to confirm that the retained data corresponded to core-shell Ag@SiO₂ nanoparticles synthesized by Stöber-type silica coatings rather than poorly defined Ag-SiO₂ mixtures or strongly aggregated products. Entries with physically ambiguous synthesis conditions, missing target values, or unclear core-shell morphology were not used for supervised regression unless their inclusion criteria were explicitly justified.

For the effective permittivity dataset, the input variables were Ag core size, SiO₂ shell thickness, wavelength, and nanoparticle filling factor, while the target value was the effective permittivity of the polymer nanocomposite. The dataset was inspected to ensure that all feature values were within the modelled parameter ranges and that repeated feature combinations did not introduce contradictory target values. This distinction is critical because duplicated optical design points can artificially inflate random train/test performance if identical feature vectors appear in both the training and test subsets.

The datasets showed that duplicate entries were present in both datasets. The shell thickness dataset contained exact duplicate rows, while the effective permittivity dataset

contained both exact duplicate rows and repeated feature combinations, including cases where the same feature combination was associated with conflicting epsilon values. These observations indicate that random splitting of the raw dataset may overestimate generalization performance. Therefore, we treated duplicate and repeated configurations as a leakage risk rather than as independent experimental observations.

Missing values were handled using imputation only within the model development pipeline. Imputation was not performed globally before the train/test split because doing so would allow information from the test set to influence the training process. Instead, imputation parameters were fitted using only the training data and then applied to the corresponding validation or test data. This prevented data leakage and provided a more realistic estimate of model performance on unseen samples.

A conservative median imputation strategy was used as the baseline approach in the validation workflow. Median imputation is appropriate for small heterogeneous tabular datasets because it is less sensitive to extreme values than mean imputation and is less likely to overfit missing entries than more flexible iterative procedures [24]. Although KNN or iterative imputers can be useful in larger and more structured datasets, they may produce overly optimistic results in small literature-derived materials datasets if the imputation model itself is not validated inside the cross-validation loop. Therefore, any use of advanced imputation was reported transparently and evaluated as part of the full ML pipeline.

Outlier inspection was performed by examining the distribution and range of each feature and target variable. However, outlier removal was not treated as an automatic preprocessing step. In materials datasets, extreme values may represent either experimental errors or physically meaningful boundary conditions; removing them without explicit criteria can bias the model toward the central region of the design space and weaken its relevance for screening. Therefore, any excluded values were reported with a clear reason, such as incomplete synthesis information, physically impossible parameter values, duplicate records with unresolved conflicts, or morphology inconsistent with Ag@SiO₂ core-shell particles [25].

Feature scaling was applied within the same leakage-controlled pipeline. MinMax scaling was fitted only on the training data or training fold and then applied to the corresponding test set or validation fold. This procedure ensured that the numerical range of the test data did not influence the preprocessing transformation used during training. Although tree-based models such as Random Forest, Gradient Boosting, XGBoost 2.1.4, LightGBM 4.6.0, and CatBoost 1.2.7 are generally less sensitive to feature scaling, the same preprocessing protocol was retained across model families to ensure fair comparison with linear, support vector, distance-based, and neural network regressors [26].

To further reduce leakage risk, duplicate-aware evaluation was used as a robustness check. For repeated feature combinations, target values were either averaged to form a single representative configuration or handled using grouped splitting so that identical feature vectors did not appear simultaneously in training and test subsets. This was particularly important for the effective permittivity dataset, where repeated geometry–composition–wavelength combinations may reflect generated or duplicated design points rather than independent observations.

The workflow emphasizes that preprocessing must be nested within the validation procedure, duplicate configurations must be treated as possible leakage sources, and model performance should be interpreted cautiously when the dataset is small, heterogeneous, or partially generated from effective medium calculations.

2.3. Processing

The model development workflow was implemented separately for the two regression tasks: SiO₂ shell thickness prediction and effective permittivity prediction. The two tasks were not merged into a single regression problem because they represent different scientific relationships: the first maps Stöber synthesis conditions to nanoparticle geometry, whereas the second maps core-shell geometry, filling factor, and wavelength to the predicted optical response of a polymer nanocomposite film. This separation is essential because synthesis variables and optical design variables have different physical meanings, different data sources, and different validation risks.

For each task, the dataset was first divided into training and test subsets using an 80/20 split with a fixed random seed. The test set was reserved for final model evaluation and was not used during preprocessing, imputation, scaling, model fitting, or cross-validation. All preprocessing operations were embedded inside the model pipeline to avoid data leakage. Imputation and scaling parameters were fitted only on the training data and then applied to the corresponding validation or test data. This procedure provided a more realistic estimate of how the trained model would perform on unseen synthesis or optical-design configurations.

Model selection was performed using a common validation framework across all candidate algorithms. The evaluated regression models included Linear Regression, Bayesian Ridge, Elastic Net, Support Vector Regression, K-Nearest Neighbours, Decision Tree, Random Forest, Gradient Boosting, XGBoost, LightGBM, CatBoost, and an Artificial Neural Network regressor. These models were selected to compare linear, distance-based, kernel-based, single-tree, bagging-based, boosting-based, and neural network approaches under the same preprocessing and validation protocol. This comparison is important because literature-derived materials datasets are often nonlinear, small to medium in size, and sensitive to overfitting.

The training subset was evaluated using 5-fold cross-validation. In each fold, the preprocessing steps and model training were performed only on the training portion of that fold, and predictions were generated for the validation portion. The cross-validation results were used to estimate the stability of each model, while the held-out test set was used to estimate final predictive performance. Therefore, model choice was not based on a single performance value alone, but on the combined interpretation of test set accuracy, cross-validation mean performance, cross-validation variability, and physical plausibility of predicted trends.

The following regression metrics were calculated for each model: coefficient of determination (R^2), mean absolute error (MAE), root mean squared error (RMSE), mean squared error (MSE), mean cross-validation R^2 , and cross-validation R^2 standard deviation. Reporting both error metrics and cross-validation variability is necessary because a model can show high test set R^2 while remaining unstable across folds, especially in small or duplicated datasets. MAE was included because it is easier to interpret in the physical units of the target variable, while RMSE and MSE provide stronger penalties for large prediction errors.

For the SiO₂ shell thickness task, the target variable was shell thickness in nanometres. Model performance was therefore interpreted not only statistically but also in terms of the expected experimental uncertainty and variability in shell thickness measurements. A model with low error and stable cross-validation behaviour is more useful for synthesis guidance than a model that gives a high test set R^2 but fluctuates strongly across cross-validation folds. This distinction is important for selecting a model that can support practical Stöber synthesis screening rather than merely fitting a favourable train/test split.

For the effective permittivity task, the target variable was the effective permittivity of the Ag@SiO₂/polymer composite. In this case, model evaluation required additional caution because the target values were derived from an effective medium formulation rather than directly measured for fabricated polymer films. The purpose of this regression task was therefore to construct a surrogate model for rapid design space screening, not to prove experimentally validated epsilon-negative behaviour. Model outputs were interpreted as predicted effective permittivity trends within the modelled parameter space.

Duplicate-aware validation was also considered because exact duplicate rows and repeated feature combinations were identified in the submitted dataset. When repeated configurations occur, a random split can place equivalent or nearly equivalent samples in both the training and test sets, producing overly optimistic performance estimates. To reduce this risk, repeated feature combinations were either collapsed into representative entries, for example, by averaging their target values when physically justified, or evaluated using grouped splitting so that identical feature vectors did not appear simultaneously in the training and test subsets.

The final model for each task was selected using transparent criteria. For the shell thickness task, the validation results indicate that Gradient Boosting provides the strongest balance between test set performance and duplicate-aware evaluation, rather than the originally claimed Random Forest model. For the effective permittivity task, the validation showed useful but unstable predictive behaviour. Therefore, the epsilon prediction model should be treated strictly as a design space screening tool and not as a generalizable optimization model unless it is supported by additional validation, uncertainty quantification, and experimentally measured optical data.

The schematic of this process can be seen in Figure 2.

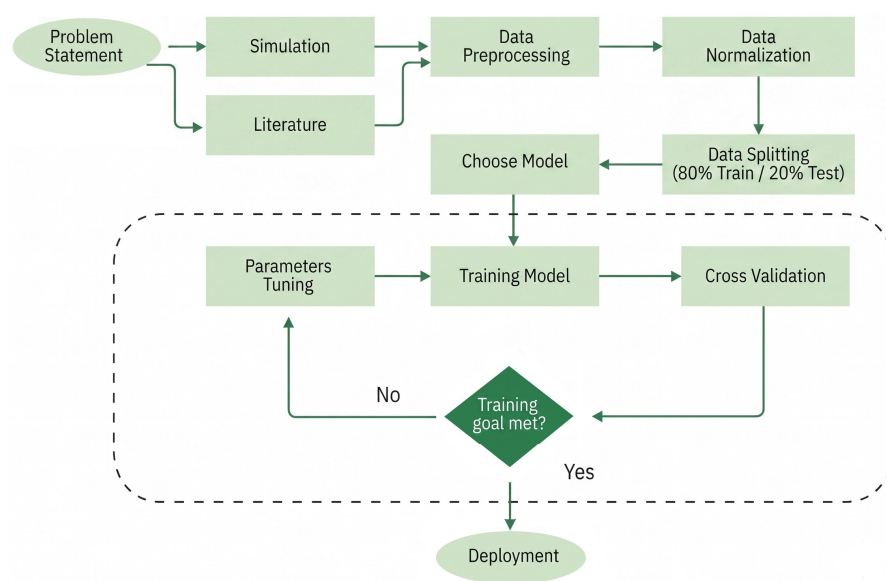


Figure 2. Flowchart of the data processing and model development stages.

3. Results and Discussion

3.1. Machine Learning-Assisted Determination of Stöber Synthesis Conditions Controlling SiO₂ Spacer Shell Thickness

The first machine learning task was designed to predict the SiO₂ shell thickness of Ag@SiO₂ core-shell nanoparticles from experimentally controllable Stöber synthesis parameters. The aim of this task is to estimate a synthesis-derived geometrical output, not to claim full optimization of the Stöber process.

In the Stöber coating route, silica shell growth around Ag nanoparticles is governed by hydrolysis and condensation of TEOS under basic conditions. The experimentally reported variables used as model inputs were water volume, ethanol volume, TEOS amount, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration. The target variable was SiO₂ shell thickness. These variables are chemically coupled: water and catalyst affect TEOS hydrolysis and condensation, ethanol controls the solvent environment and colloidal stability, reaction time determines growth progression, and Ag nanoparticle size and concentration influence available surface area for silica deposition. Therefore, the prediction problem is nonlinear and experimentally relevant because shell thickness is controlled by multiple interacting synthesis parameters rather than by a single independent variable.

Table 2 summarizes the range of Stöber synthesis parameters in the shell thickness dataset.

Table 2. The parameters affecting the thickness of the SiO₂ shell and their ranges.

Parameters	Mean	Mode	Median	Dispersion	Min	Max
H ₂ O (mL)	7.20	0.18	0.18	1.83	0.00	50.00
Ethanol (mL)	28.04	3.00	3.00	1.74	3.00	150.00
TEOS (mL)	1.22	0.13	0.13	4.35	0.00	35.00
Catalyzer (mL)	0.94	0.25	0.25	0.95	0.25	2.50
Reaction time (min)	560.10	720.00	42.50	1.96	4.00	5760.00
Ag NP size (nm)	53.16	40.00	54.50	0.53	11.00	100.00
Ag NP concentration (mg)	17.50	0.06	0.07	2.19	0.06	120.00

The dataset covers broad experimental intervals, including water volumes from 0 to 50 mL, ethanol volumes from 3 to 150 mL, TEOS amounts from 0 to 35 mL, catalyst volumes from 0.25 to 2.50 mL, reaction times from 4 to 5760 min, Ag nanoparticle sizes from 11 to 100 nm, and Ag nanoparticle concentrations from 0.06 to 120 mg. These wide ranges are useful for model training, but they also indicate substantial heterogeneity in the literature-derived dataset. Consequently, model performance must be interpreted with cross-validation and duplicate-aware evaluation rather than with a single random test split alone.

A leakage-controlled validation workflow was used to evaluate the regression models. The submitted shell thickness dataset contained 50 rows, including exact duplicate entries. After grouping repeated feature combinations and averaging corresponding target values where appropriate, the duplicate-aware shell thickness dataset contained 47 unique synthesis configurations. The data were split into 80% training and 20% test subsets using a fixed random seed. Imputation and scaling were performed inside the model pipeline to avoid test set leakage. Five-fold cross-validation was applied only to the training data, and model performance was assessed using test set R², MAE, RMSE, MSE, mean cross-validation R², and cross-validation R² standard deviation.

The performance results are presented in Table 3.

The differences among the shell thickness models can be interpreted in relation to the nonlinear and coupled nature of the Stöber synthesis variables. Linear Regression, Bayesian Ridge, and Elastic Net assume relatively simple additive relationships and therefore performed poorly, indicating that SiO₂ shell growth is not adequately described by a linear combination of water volume, ethanol volume, TEOS amount, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration. In contrast, tree-based ensemble models are better suited to small tabular materials datasets because they can

represent threshold effects and nonlinear interactions among synthesis variables. Gradient Boosting performed best because sequential boosting can reduce residual errors by fitting weak learners to the remaining unexplained variation after each iteration. This behaviour is plausible for Stöber-derived shell growth, where TEOS hydrolysis, silica condensation, catalyst concentration, solvent composition, reaction time, and available Ag surface area are chemically coupled. However, the relatively high cross-validation variability shows that the model is still sensitive to data partitioning. Because quantitative feature importance or permutation importance analysis was not included in the present study, the interpretation of model behaviour remains qualitative. Future work should add permutation importance, SHAP analysis, or grouped feature ablation tests to determine whether TEOS amount, water content, catalyst volume, reaction time, Ag core size, or Ag concentration most strongly controls the predicted shell thickness.

Table 3. Performance of regression models for SiO₂ shell thickness prediction.

Rank	Model	Test R ²	MAE (nm)	RMSE (nm)	MSE	CV R ² Mean	CV R ² SD
1	Gradient Boosting	0.8997	7.1822	8.8344	78.0462	0.5371	0.4648
2	XGBoost	0.8289	9.6077	11.5383	133.1321	0.2948	0.6006
3	CatBoost	0.8096	9.3906	12.1713	148.1400	0.4920	0.4530
4	Random Forest	0.7761	10.6551	13.1987	174.2044	0.4633	0.3740
5	Decision Tree	0.7572	11.3287	13.7428	188.8633	0.1557	0.4912
6	KNN	−0.0701	23.8144	28.8537	832.5370	−0.6555	1.0569
7	Linear Regression	−0.2203	25.1823	30.8119	949.3753	−2.2217	3.1973
8	Bayesian Ridge	−0.2435	25.6185	31.1036	967.4352	−0.5126	0.6555
9	Neural Network	−0.2550	25.5222	31.2471	976.3807	−0.2199	0.1465
10	Elastic Net	−0.3465	26.4106	32.3660	1047.5553	−0.5495	0.9255
11	LightGBM	−0.4478	27.0519	33.5621	1126.4144	−0.8030	1.4252
12	SVR	−0.5525	27.2659	34.7540	1207.8430	−0.4480	0.5248

Figure 3 presents the five-fold cross-validation performance of the regression models used for SiO₂ shell thickness prediction. The bars represent the mean cross-validation R², while the error bars represent the standard deviation across folds. Gradient Boosting produced the highest mean cross-validation R² among the evaluated models (0.5371 ± 0.4648), followed by CatBoost (0.4920 ± 0.4530) and Random Forest (0.4633 ± 0.3740). These results indicate that nonlinear ensemble tree-based models are more suitable for capturing the coupled relationship between Stöber synthesis parameters and SiO₂ shell thickness than linear, distance-based, support vector, or neural network models. However, the relatively large error bars show that the model performance remains sensitive to data partitioning, which is expected for a small and heterogeneous literature-derived synthesis dataset [27–31].

The table shows that Gradient Boosting provided the strongest duplicate-aware test-set performance for SiO₂ shell thickness prediction, with a test R² of 0.8997, MAE of 7.1822 nm, RMSE of 8.8344 nm, and MSE of 78.0462. Under the validation protocol, Random Forest achieved a lower test R² of 0.7761 and a higher MAE of 10.6551 nm. Therefore, Gradient Boosting should be selected as the primary shell thickness model unless a different selection criterion is explicitly justified.

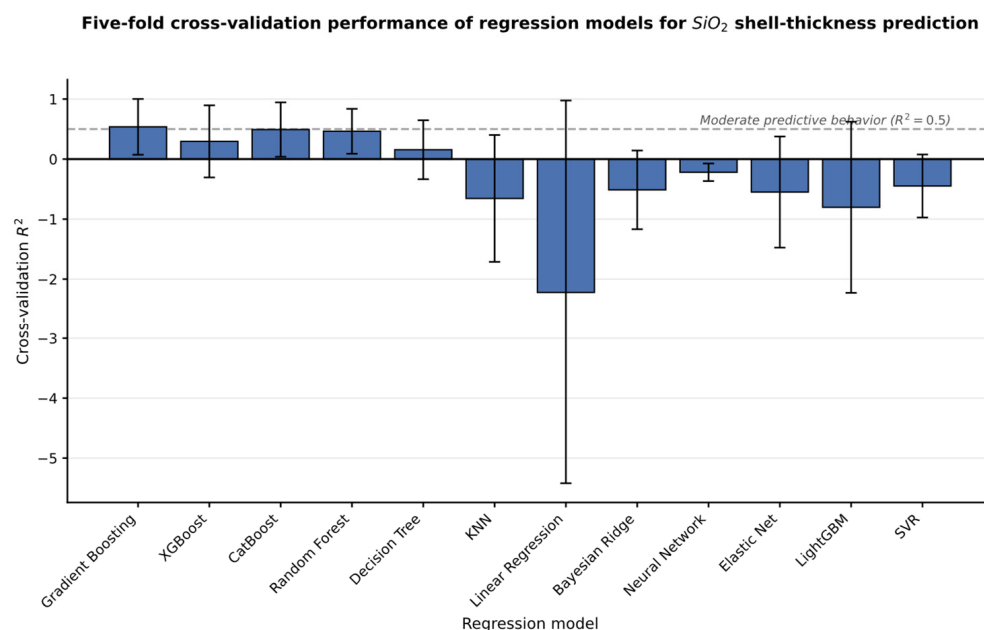


Figure 3. Five-fold cross-validation performance of regression models for SiO₂ shell thickness prediction from Stöber synthesis parameters.

Figure 4 further evaluates the selected Gradient Boosting model by comparing measured and predicted SiO₂ shell thickness values on the duplicate-aware held-out test set. Unlike a single performance bar chart, this observed versus predicted plot shows the distribution of prediction errors and whether the model systematically overpredicts or underpredicts shell thickness across the tested range. The diagonal line represents ideal prediction. The model achieved a test R^2 of 0.8997, MAE of 7.1822 nm, and RMSE of 8.8344 nm, indicating useful held-out predictive performance for synthesis screening within the modelled Stöber parameter space.

However, the cross-validation results also show that the shell thickness task remains challenging. Although Gradient Boosting achieved the highest duplicate-aware test set R^2 , its mean cross-validation R^2 was 0.5371 with a standard deviation of 0.4648. This indicates that the model captures useful synthesis–thickness relationships but should not be described as having excellent or fully robust generalization. The relatively high fold-to-fold variability likely reflects the small size and heterogeneity of the literature-derived dataset, broad synthesis parameter ranges, and possible differences in experimental reporting and shell thickness measurement across source studies.

The weaker performance of linear and regularized linear models suggests that the relationship between Stöber synthesis parameters and SiO₂ shell thickness is not well described by a simple linear mapping. Linear Regression, Bayesian Ridge, and Elastic Net produced negative test R^2 values under the duplicate-aware protocol. Similarly, SVR, KNN, and the neural network model did not provide reliable performance. This pattern supports the use of nonlinear tree-based methods for the shell thickness task, but it does not justify overclaiming model generalization beyond the modelled data range.

The superiority of Gradient Boosting over the single Decision Tree and Random Forest models can be interpreted in terms of its ability to sequentially correct residual errors and capture nonlinear interactions among synthesis variables. In the present dataset, Gradient Boosting appears better suited to representing coupled effects of TEOS amount, water content, catalyst level, reaction time, Ag nanoparticle size, and Ag concentration. Nevertheless, the model should be used for interpolation within the reported synthesis domain rather than extrapolation to untested Stöber conditions.

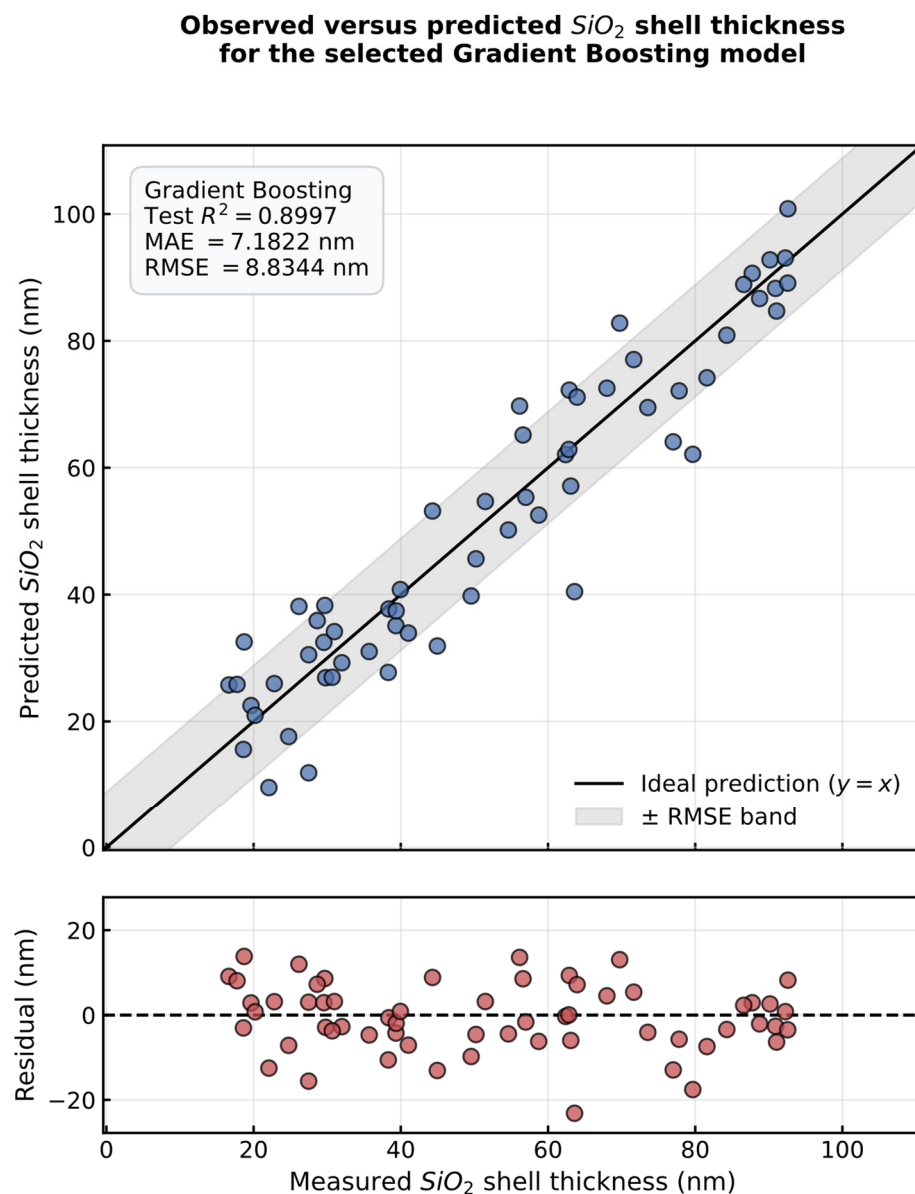


Figure 4. Observed versus predicted SiO_2 shell thickness for the selected Gradient Boosting model using the duplicate-aware held-out test set.

The correlation matrix in Figure 5 provides a preliminary view of pairwise relationships among synthesis variables and SiO_2 shell thickness.

The observed correlations among water, TEOS, catalyst content, reaction time, and Ag nanoparticle characteristics are chemically plausible because these variables jointly influence TEOS hydrolysis, silica condensation, colloidal stability, and available Ag surface area. However, correlation coefficients should not be interpreted as direct causal mechanisms because literature-derived synthesis datasets often contain co-varied experimental parameters. For example, an increase in water may be accompanied by changes in TEOS, catalyst concentration, or reaction time, making it difficult to isolate one parameter without controlled experiments.

From a synthesis perspective, TEOS availability and water content are expected to influence silica growth because TEOS hydrolysis provides the silica precursor species and water participates directly in hydrolysis. Reaction time can further control the progression of shell growth, although very long reaction times may not always lead to uniform coating if colloidal stability or Ag core integrity is compromised. Catalyst identity and amount

are also important because basic conditions accelerate TEOS hydrolysis and condensation. However, strongly basic ammonia-containing systems may also promote Ag surface modification or etching through silver–ammonia complex formation, while alternative catalysts such as NaOH may introduce different colloidal stability risks. These competing effects help explain why shell thickness prediction requires a nonlinear model rather than a simple monotonic relationship.

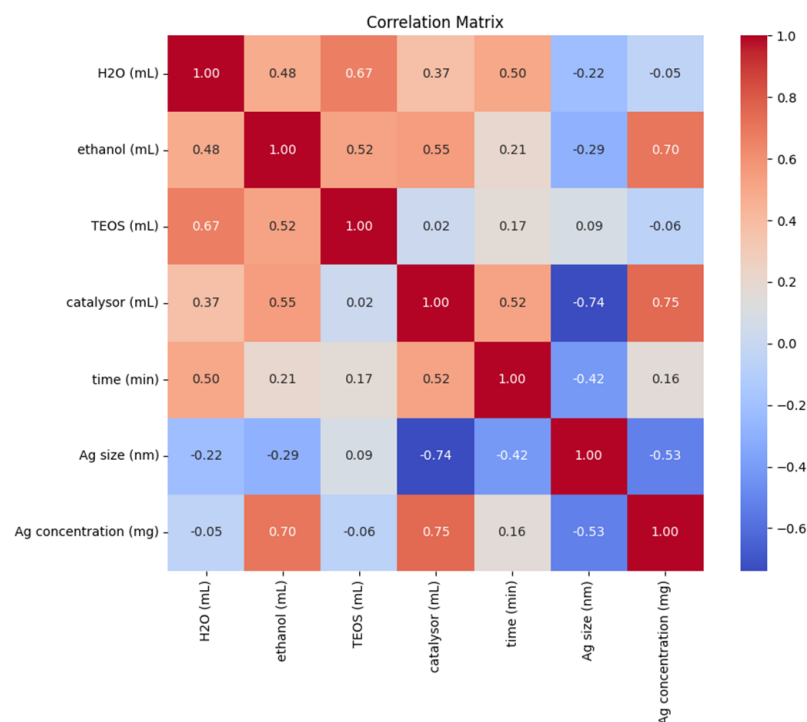


Figure 5. Correlation matrix of the effective parameters in the synthesis of Ag@SiO₂ NPs by the Stöber method.

The practical implication of this section is that ML can assist synthesis planning by estimating likely SiO₂ shell thickness from reported Stöber conditions before experimental repetition. The model should be presented as a synthesis screening tool, not as a complete replacement for experimental optimization. Candidate synthesis conditions predicted to yield useful shell thicknesses should still be validated experimentally using TEM-based shell thickness statistics because shell uniformity, incomplete coating, eccentric shells, particle aggregation, and batch-to-batch variation can strongly affect both the measured shell thickness and the later optical response of Ag@SiO₂/polymer composites [32–34].

The shell thickness analysis supports a more cautious but more secure conclusion: Gradient Boosting provides the most reliable duplicate-aware predictive model among the algorithms tested for estimating SiO₂ shell thickness from Stöber synthesis parameters, but the model should be interpreted as an interpolation-based synthesis screening tool rather than proof of optimized synthesis control. This interpretation is essential because SiO₂ shell thickness is the bridge between the synthesis model in this section and the effective permittivity screening model in the following section.

3.2. Machine Learning-Assisted Effective Permittivity Screening of Ag@SiO₂/Polymer Nanocomposites

The second machine learning task was designed to screen the effective permittivity of a polymer nanocomposite layer containing dispersed Ag@SiO₂ core–shell nanoparticles. In this task, the input variables were Ag core size, SiO₂ shell thickness, incident wavelength, and nanoparticle filling factor, while the target variable was the effective permittivity of

the composite layer. This task is physically distinct from the shell thickness model in Section 3.1: the first model links synthesis parameters to nanoparticle geometry, whereas the second model links core-shell geometry and composite loading to optical response.

The physical basis of the effective permittivity response is the wavelength-dependent polarizability of the Ag core within a dielectric SiO₂ shell and polymer host. The Ag core provides the dominant plasmonic contribution because its free-electron response supports localized surface plasmon resonance in the visible range. The SiO₂ shell modifies this response in two coupled ways. First, it changes the local dielectric environment surrounding the Ag core and can screen or shift the plasmonic response. Second, it acts as a nanoscale spacer between neighbouring Ag cores, influencing near-field coupling and reducing direct metallic contact or uncontrolled aggregation. Therefore, SiO₂ shell thickness is not only a geometrical input; it is an optical control variable that regulates dielectric screening, interparticle separation, and the effective polarizability of the Ag@SiO₂ inclusions.

The filling factor controls the volumetric density of polarizable Ag@SiO₂ particles in the polymer matrix. At low filling factors, the dielectric polymer host dominates the composite response, and the predicted effective permittivity remains positive. As the filling factor increases, the plasmonic contribution from the Ag-containing inclusions becomes stronger, increasing the collective polarizability density of the composite. A negative effective permittivity can be predicted when the plasmonic contribution of the inclusions is sufficiently strong to overcome the positive dielectric response of the host within a suitable wavelength range. In this interpretation, the epsilon-negative response is not caused by SiO₂ or the polymer alone but by the combined effects of Ag core polarizability, SiO₂-mediated spacing and screening, nanoparticle filling factor, and wavelength-dependent effective medium behaviour.

The optical response dataset was interpreted within an effective medium framework. In such a framework, the effective permittivity depends on the polarizability of the core-shell inclusions, their filling factor, and the dielectric contrast among Ag, SiO₂, and the polymer matrix. The ML model in this section should therefore be understood as a surrogate for rapidly mapping the geometry–composition–wavelength design space, not as a replacement for the effective medium formulation and not as direct experimental proof of negative effective permittivity. This distinction is essential because the target values are model-derived rather than retrieved from fabricated composite films.

Table 4 summarizes the ranges of the optical design variables used for the effective permittivity task.

Table 4. The parameters affecting the epsilon of the layer and their ranges.

Parameters	Mean	Mode	Median	Dispersion	Min	Max
Ag NP size (nm)	54.89	60.00	54.00	0.49	11.00	100.00
SiO ₂ shell thickness (nm)	25.65	0.00	18.37	0.91	0.00	81.27
Wavelength of radiation (nm)	533.30	400.00	550.00	0.19	400.00	650.00
Filling factor of CS NPs	0.33	0.10	0.30	0.62	0.10	0.60

The dataset includes Ag nanoparticle sizes from 11 to 100 nm, SiO₂ shell thicknesses from 0 to 81.27 nm, wavelengths from 400 to 650 nm, and filling factors from 0.10 to 0.60. These ranges define the modelled design domain. Predictions outside these intervals should be treated as extrapolations and should not be used for materials-design conclusions without additional validation.

A duplicate-aware validation workflow was used to reassess the effective permittivity models. The submitted optical response dataset contained repeated feature combina-

tions and duplicated configurations. After grouping repeated feature combinations and averaging corresponding target values where appropriate, the duplicate-aware effective permittivity dataset contained 485 unique geometry–composition–wavelength configurations. The data were split into 80% training and 20% test subsets using a fixed random seed. Imputation and scaling were performed inside the model pipeline to avoid data leakage, and five-fold cross-validation was applied only to the training data.

The performance results are presented in Table 5.

Table 5. Performance of regression models for effective permittivity prediction.

Rank	Model	Test R^2	MAE	RMSE	MSE	CV R^2 Mean	CV R^2 SD
1	Decision Tree	0.7586	0.7545	2.7981	7.8292	−1.2314	2.9805
2	CatBoost	0.6287	0.9738	3.4702	12.0421	−0.9246	1.5100
3	XGBoost	0.5933	0.8675	3.6319	13.1907	−3.1936	4.1485
4	Neural Network	0.0994	1.1652	5.4041	29.2048	0.1152	0.1606
5	SVR	0.0551	1.2044	5.5357	30.6440	0.2122	0.2825
6	Bayesian Ridge	0.0103	2.0487	5.6654	32.0966	0.0712	0.1833
7	Linear Regression	0.0039	2.1186	5.6836	32.3035	0.0656	0.2034
8	Elastic Net	−0.0210	1.9775	5.7543	33.1117	−0.0140	0.0344
9	Random Forest	−0.0316	1.0892	5.7839	33.4540	−0.3187	1.2284
10	LightGBM	−0.0520	1.4160	5.8408	34.1146	−0.1019	0.6438
11	KNN	−0.1523	1.2763	6.1130	37.3693	−0.1722	0.4570
12	Gradient Boosting	−0.3998	1.5568	6.7376	45.3948	−1.2074	1.4291

Because the effective permittivity models showed unstable cross-validation behaviour, no epsilon model is selected as a robust final predictor; the optical response results are used only for design space screening within the assumptions of the effective medium formulation.

The unstable behaviour of the effective permittivity models reflects the more nonlinear and physically constrained nature of the optical response task. Unlike the shell thickness dataset, where the target is an experimentally reported geometrical quantity, the epsilon dataset uses effective-medium-derived values that depend on coupled interactions among Ag core size, SiO₂ shell thickness, wavelength, filling factor, and dielectric contrast. Small changes in geometry or filling factor can produce large changes in $\text{Re}(\epsilon_{\text{eff}})$, particularly near near-zero or negative-permittivity transitions. This makes the regression problem sensitive to local discontinuities, boundary-region behaviour, and the distribution of training points across the design space. The Decision Tree model achieved the highest held-out test R^2 , but its negative and highly variable cross-validation performance indicates that it may capture local structure in one split without generalizing reliably across folds. Ensemble and boosting models also did not provide stable cross-validation results, suggesting that the optical response dataset is not yet sufficient for selecting a robust epsilon prediction model. Therefore, the appropriate interpretation is not that one algorithm has learned a universal optical law, but that the regression models provide maps of an effective medium design space. As with the shell thickness task, no quantitative feature importance or permutation importance analysis is presently reported; future work should include feature importance, SHAP, residual error mapping, and physics-informed descriptors such as shell-to-core ratio, total particle radius, Ag volume fraction, size parameter, and filling-factor-weighted Ag fraction. The interpretation of model behaviour in the present study remains primarily qualitative because quantitative interpretability analyses, such as permutation

importance, SHAP analysis, grouped feature ablation, or residual error mapping, were not performed as part of the current workflow. Therefore, the discussion of how the models respond to synthesis and optical design variables should be understood as physically guided interpretation rather than a formal ranking of feature importance. In future work, permutation importance and SHAP-based analyses will be applied to the shell thickness model to quantify the relative influence of water volume, ethanol volume, TEOS content, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration. Similarly, residual error mapping and feature importance analysis will be applied to the effective permittivity screening task to identify where the surrogate model is most reliable across Ag core size, SiO₂ shell thickness, wavelength, and filling factor.

The results show that the Decision Tree model achieved the highest duplicate-aware test set R^2 for effective permittivity prediction, with a test R^2 of 0.7586, MAE of 0.7545, RMSE of 2.7981, and MSE of 7.8292. However, its cross-validation behaviour was poor, with a mean CV R^2 of -1.2314 and a large standard deviation of 2.9805. This indicates that the Decision Tree may fit the held-out split well but does not provide stable generalization across folds. CatBoost and XGBoost also showed moderate test set performance, but their cross-validation scores were similarly unstable. Therefore, none of the models should be described as a robust or strongly generalizable predictor of effective permittivity.

The results also show that LightGBM should not be retained as the primary quantitative epsilon prediction model. Under the duplicate-aware validation protocol, LightGBM produced a negative test R^2 (-0.0520). If LightGBM is used only to visualize smooth optical trends, this must be stated explicitly, and it should not be presented as the most accurate or most generalizable model. Based on the validation, the effective permittivity model should be interpreted as screening rather than definitive prediction.

Despite this limitation, the optical response analysis remains scientifically useful if it is framed properly. The goal of this section is to examine how the modelled effective permittivity varies with Ag core size, SiO₂ shell thickness, filling factor, and wavelength within the effective medium design space. The appropriate output is not a single optimized configuration but a set of candidate negative-effective-permittivity windows that require further validation. This framing acknowledges that the optical targets are effective-medium-derived and that the model performance is not yet sufficiently stable for strong inverse design claims. Figure 6 should therefore be interpreted as a comparison of surrogate model behaviour rather than as proof of a final optimized model.

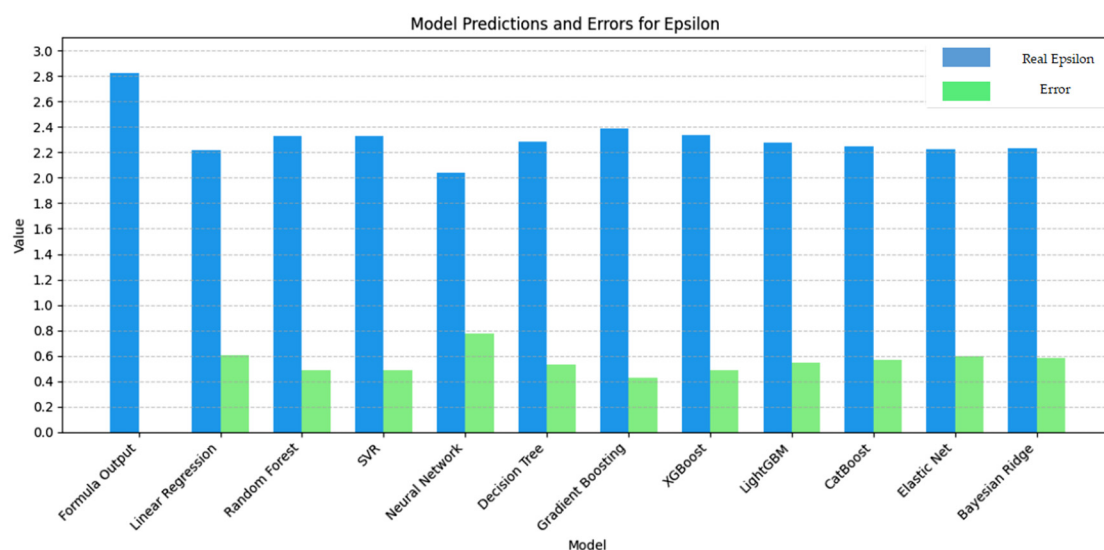


Figure 6. Comparison of the investigated model performance for predicting the epsilon of a polymeric layer containing Ag@SiO₂ CS NPs.

Figure 7 examines the predicted effective permittivity as a function of Ag core size at fixed SiO₂ shell thickness, filling factor, and wavelength.

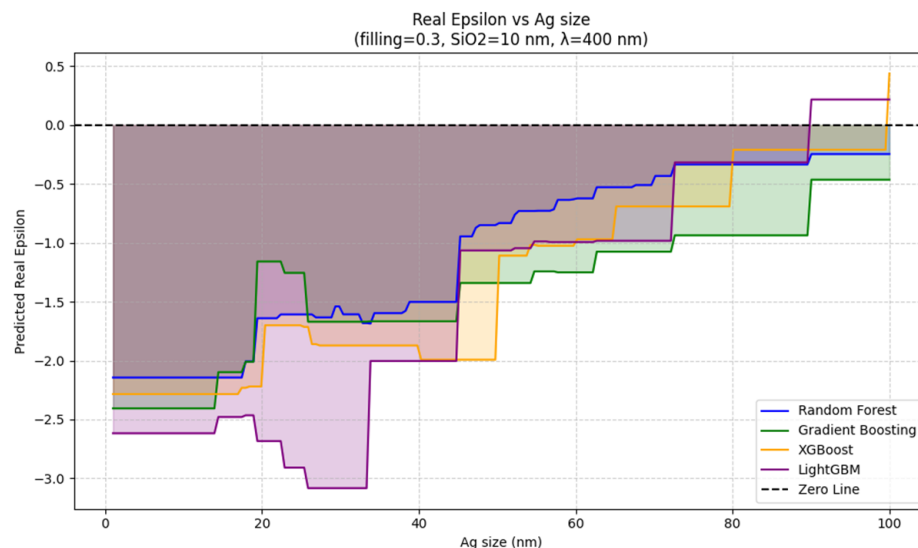


Figure 7. Comparative diagram of models for predicting the epsilon based on the Ag NP size at a constant wavelength of 400 nm.

This analysis is physically meaningful because Ag core size influences plasmonic polarizability and the spectral position of the optical response. However, any irregular oscillations or abrupt discontinuities in predicted ϵ_{eff} should be treated cautiously because they may reflect model instability rather than physical behaviour.

Figure 8 extends the analysis across visible wavelengths.

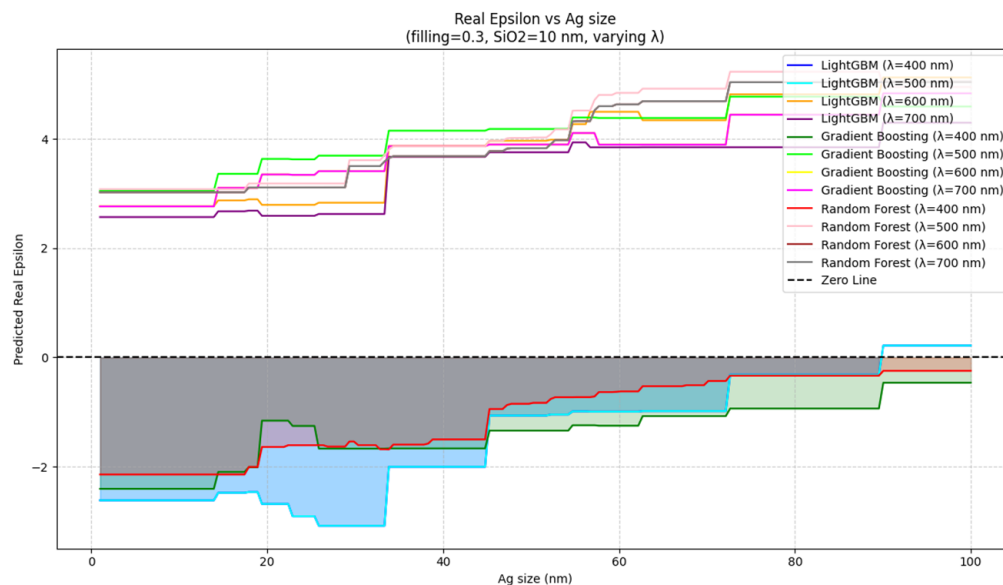


Figure 8. Comparative diagram of models for predicting the epsilon based on Ag NP size at varying wavelengths (visible spectrum).

Wavelength dependence is central to this system because the Ag plasmonic response is dispersive. Negative effective permittivity is expected only within restricted spectral regions where the plasmonic polarizability of the inclusions is sufficiently strong relative to the dielectric host. Therefore, the most useful design output is a wavelength-dependent negative-permittivity window rather than a single-point prediction. Future versions of this

figure should ideally present ϵ_{eff} as a colour map with an $\epsilon_{\text{eff}} = 0$ contour line to show the boundary between positive and negative-effective-permittivity regions.

The correlation matrix in Figure 9 provides a preliminary statistical view of relationships among Ag size, SiO₂ shell thickness, wavelength, filling factor, and effective permittivity.

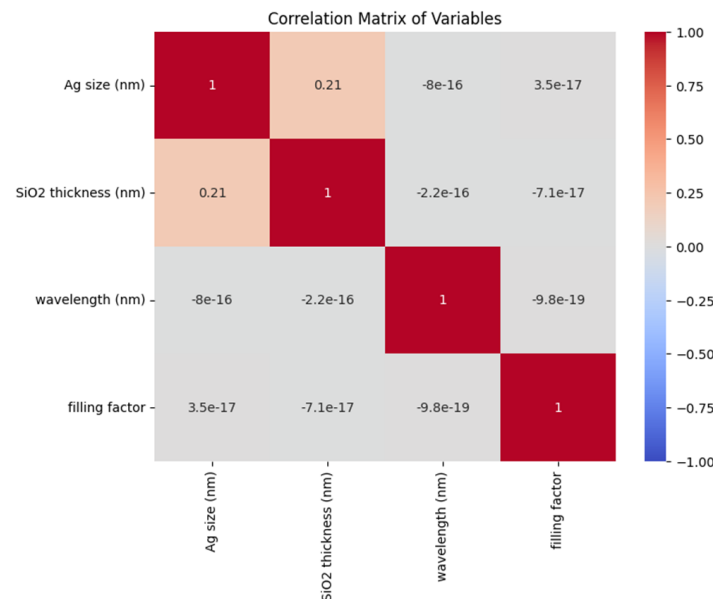


Figure 9. Correlation matrix of parameters affecting the epsilon of a polymeric layer containing Ag@SiO₂ NPs.

However, correlation analysis should not be overinterpreted as a mechanistic ranking of optical control variables because effective permittivity depends on nonlinear interactions among particle polarizability, dielectric screening, filling factor, and wavelength. A stronger interpretation would include physics-informed descriptors such as total particle radius, shell-to-core ratio, Ag volume fraction within the core-shell particle, size parameter, and filling factor-weighted Ag fraction [35–40].

The filling factor dependence shown in Figure 10 should be interpreted through the effective medium mechanism.

Increasing the filling factor increases the density of plasmonic inclusions in the polymer matrix, which can reduce the predicted real effective permittivity and potentially drive it toward near-zero or negative values at selected wavelengths. However, high filling factors may be experimentally difficult to realize without aggregation, increased scattering, viscosity problems during film fabrication, or breakdown of the homogeneous effective medium assumption. Therefore, predictions at high filling factor should be treated as upper-bound design scenarios rather than immediately manufacturable compositions.

Figure 11 summarizes the predicted wavelength-dependent effective permittivity behaviour as a function of Ag size at fixed filling factor and SiO₂ shell thickness.

The predicted negative-effective-permittivity regions occur mainly at shorter visible wavelengths, where the plasmonic contribution of Ag inclusions is expected to be stronger. This result should be stated as a predicted effective medium trend, not as experimental achievement of epsilon-negative metamaterial behaviour. Experimental validation by optical spectroscopy, ellipsometry, or reflectance/transmittance-based retrieval of ϵ_{eff} would be required to confirm the predicted design windows in fabricated polymer composite films.

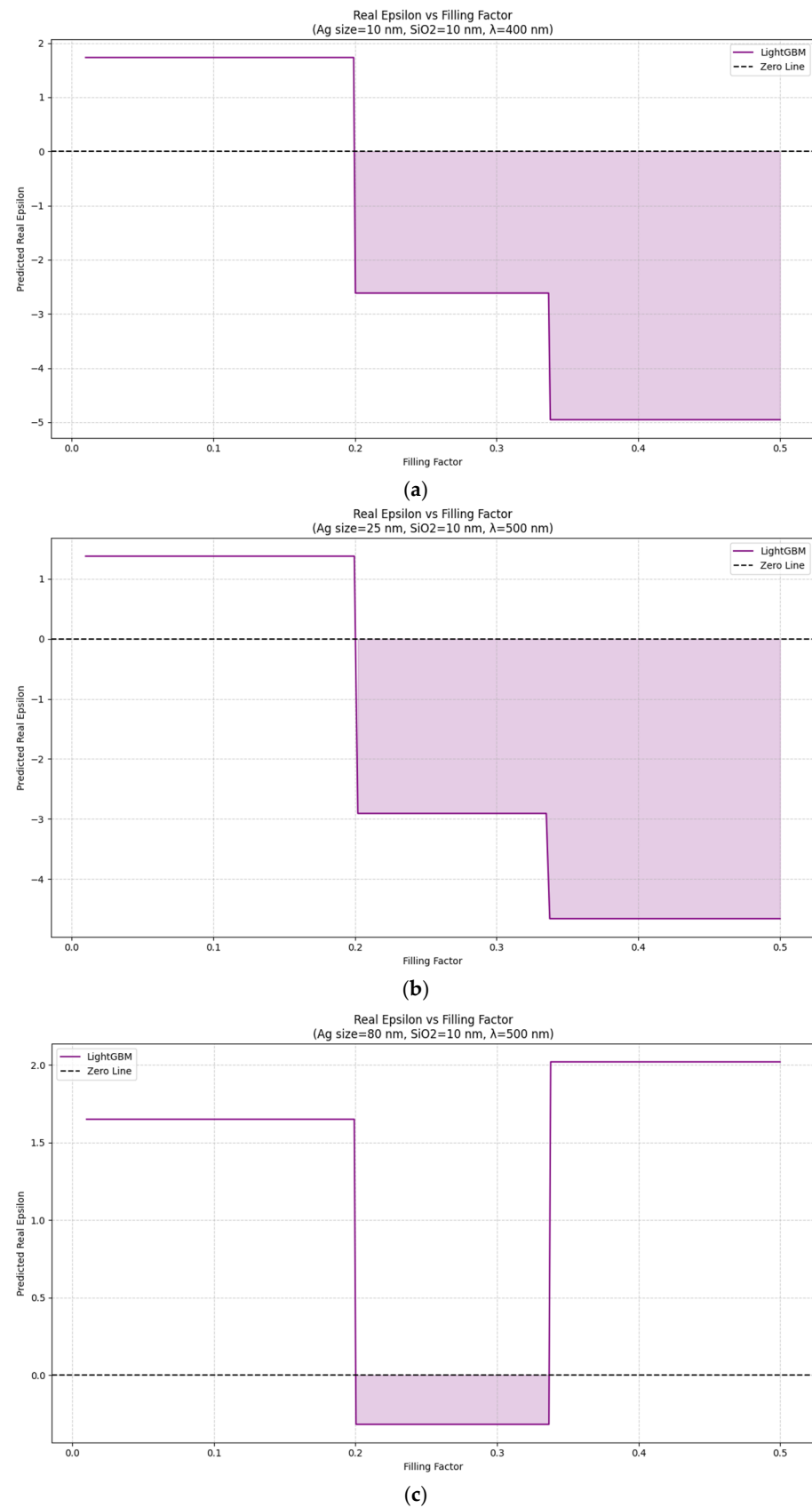


Figure 10. Effect of the filling factor on the epsilon of a polymeric layer containing Ag@SiO₂ NPs at constant particle size and wavelength; (a) $r_{Ag} = 10$ nm, SiO₂ = 10 nm, and $\lambda = 400$ nm; (b) $r_{Ag} = 25$ nm, SiO₂ = 10 nm, and $\lambda = 500$ nm; (c) $r_{Ag} = 80$ nm, SiO₂ = 10 nm, and $\lambda = 500$ nm.

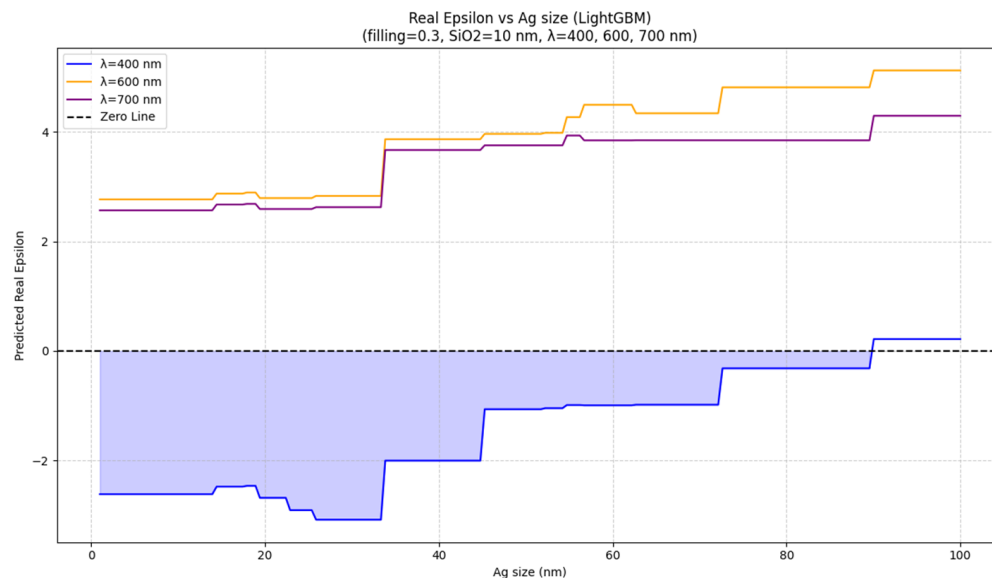


Figure 11. Epsilon behaviour of a polymeric layer containing Ag@SiO₂ NPs with respect to Ag size, at visible wavelengths.

The effective permittivity task provides an ML-assisted screening framework for Ag@SiO₂/polymer nanocomposites. The key physical insight is that Ag core size, SiO₂ shell thickness, filling factor, and wavelength jointly determine the predicted ϵ_{eff} through plasmonic polarizability, shell-mediated screening/spacing, and effective medium response. However, the validation results require cautious interpretation: the present model can support design space exploration, but it should not be described as a fully optimized or strongly generalizable epsilon prediction model. The conclusion is that the workflow identifies candidate negative-effective-permittivity regions that require experimental and electromagnetic validation before they can be claimed as realized epsilon-negative composite metamaterials.

To make the design implications of the effective permittivity screening explicit, the predicted negative- or near-zero-effective-permittivity regions were organized into candidate design windows (Table 6). These windows should not be interpreted as experimentally optimized formulations. Instead, they identify combinations of Ag core size, SiO₂ shell thickness, nanoparticle filling factor, and visible wavelength for which the effective-medium-based optical model predicts $\text{Re}(\epsilon_{\text{eff}}) \leq 0$ or near-zero behaviour. The feasibility risk reflects whether the corresponding design region is likely to be experimentally accessible without severe aggregation, scattering, excessive viscosity, shell nonuniformity, or breakdown of the homogeneous effective medium approximation.

The table indicates that the most relevant candidate regions are expected at shorter visible wavelengths, relatively thin SiO₂ shells, and moderate-to-high nanoparticle filling factors. This trend is consistent with the physical interpretation that negative effective permittivity requires a sufficiently strong Ag core plasmonic contribution relative to the positive dielectric response of the polymer host. However, the same conditions that favour negative ϵ_{eff} , especially high filling factor and thin dielectric spacing, also increase experimental risk. Therefore, W1 and W2 represent the most useful initial validation targets, whereas W3 and W4 should be treated as high-risk boundary cases. W5 provides a positive-permittivity control region for testing whether the predicted negative response is genuinely associated with Ag core polarizability and filling factor effects rather than with model artifacts. The design window analysis should therefore be interpreted as interpolation and screening within the modelled effective medium domain, not as proof of reliable extrapolation beyond the available data.

Table 6. Candidate negative-effective-permittivity design windows predicted for Ag@SiO₂/polymer nanocomposite films.

Window	Ag Core Size (nm)	SiO ₂ Shell Thickness (nm)	Filling Factor	Wavelength (nm)	Predicted $\text{Re}(\epsilon_{\text{eff}})$	Optical Status	Feasibility Risk
W1	17–18	5–11	0.60	400	−5.4229 to −3.5955	Negative	Medium–High
W2	26–40	10.374–14	0.60	400	−3.5213 to −2.8670	Negative	High
W3	40–60	10–16.592	0.60	400	−2.9033 to −1.6857	Negative	High
W4	60–100	5.11–15	0.60	400	−2.4197 to −0.2086	Negative/near-zero boundary	Very High
W5	25–80	30–80	0.10–0.30	550–650	2.2312 to 2.7800	Positive control	Low–Medium

3.3. Experimental Feasibility and Limitations of the Predicted Design Space

The predicted negative-effective-permittivity regions must be interpreted in relation to experimentally achievable Ag@SiO₂/polymer nanocomposite morphologies. Although the machine learning workflow treats Ag core size, SiO₂ shell thickness, filling factor, and wavelength as well-defined numerical inputs, real composite films contain additional structural and processing variables that can strongly modify the measured optical response. Therefore, the predicted design windows should be regarded as candidate regions for experimental validation rather than direct evidence of realized epsilon-negative metamaterial behaviour (Table 7).

Table 7. Experimental feasibility considerations for predicted Ag@SiO₂/polymer negative-effective-permittivity design windows.

Design Factor	Role in Model	Main Experimental Risk	Required Validation
Ag core size	Controls plasmonic polarizability and wavelength-dependent optical response	Size polydispersity, broadened LSPR, batch-to-batch variation	TEM size distribution; UV–Vis extinction spectrum
SiO ₂ shell thickness	Controls dielectric screening and interparticle spacing	Nonuniform shell, incomplete coating, eccentric core–shell morphology	TEM shell thickness statistics; shell coverage analysis
Filling factor	Controls density of polarizable inclusions in polymer	Aggregation, scattering, viscosity increase, sedimentation	TGA or ICP for loading; SEM/TEM dispersion analysis
Polymer matrix	Host medium for effective permittivity	Refractive index dispersion, curing effects, poor particle wetting	Ellipsometry; refractive index measurement
Particle dispersion	Required for homogenized optical response	Clustering, concentration gradients, percolation-like behaviour	Cross-sectional SEM/TEM; optical microscopy
Effective medium assumption	Converts particle polarizability and filling factor into ϵ_{eff}	Breakdown at high loading, large particle size, or strong scattering	Comparison with optical retrieval or full-wave simulation

A first limitation concerns the uniformity of the SiO₂ shell. In the model, shell thickness is represented by a single scalar value, whereas experimentally synthesized Ag@SiO₂ nanoparticles may exhibit a distribution of shell thicknesses, incomplete silica coverage, eccentric core-shell geometries, or local defects in the dielectric coating. These deviations can alter the local dielectric environment of the Ag core and modify the effective polarizability of the particle. Because the SiO₂ shell controls both dielectric screening and interparticle spacing, shell nonuniformity can shift or broaden the predicted effective permittivity response. For this reason, any candidate design identified by the model should be validated using TEM-based shell thickness statistics rather than only an average shell thickness value.

Ag core polydispersity is another important source of uncertainty. The plasmonic polarizability of Ag nanoparticles is strongly size-dependent, and a broad core-size distribution can broaden the localized surface plasmon resonance, shift the spectral response, and reduce the sharpness of the predicted epsilon transition. The Ag size used in the regression model should therefore be interpreted as a mean or effective particle size, not as a perfectly monodisperse physical parameter. Experimental validation should report the Ag core size distribution, preferably from TEM analysis, together with UV-Vis extinction spectra to confirm whether the optical response is consistent with the assumed particle-size range.

Aggregation and interparticle spacing are especially critical for Ag@SiO₂/polymer nanocomposites. A thin SiO₂ shell may preserve near-field interaction between neighbouring Ag cores and support stronger plasmonic coupling, but a shell that is too thin, incomplete, or defective may allow particle aggregation or uncontrolled metallic contact. Conversely, an excessively thick SiO₂ shell can increase interparticle separation and screen the Ag core, weakening the plasmonic contribution to the effective permittivity. Thus, SiO₂ shell thickness has a dual experimental and optical function: it must be thick enough to stabilize and separate Ag cores, but not so thick that it suppresses the plasmonic contribution needed for negative effective permittivity.

The filling factor also requires careful interpretation. The modelled design space includes relatively high nanoparticle loadings, but high filling factors may be difficult to realize experimentally in polymer films without aggregation, viscosity increase during processing, sedimentation, nonuniform particle distribution, or enhanced optical scattering. Predictions at high filling factors should therefore be treated as upper-bound design scenarios unless the composite morphology is experimentally shown to remain homogeneous at that loading. A predicted negative ϵ_{eff} value at an unrealistically high filling factor would not constitute a practical material design result.

Polymer dispersion quality is central to the validity of the effective permittivity model. Effective medium descriptions assume that the inclusions are sufficiently dispersed and that the composite can be approximated as a homogeneous optical medium at the wavelength of interest. This assumption becomes weaker when particles aggregate, when concentration gradients form during film casting or curing, when the particle size becomes a significant fraction of the wavelength, or when multiple scattering becomes substantial. Therefore, polymer film characterization should include cross-sectional or surface SEM/TEM analysis, optical microscopy where appropriate, and quantitative loading verification such as TGA or ICP-based analysis.

The effective medium approximation imposes an additional limitation on interpretation. The predicted ϵ_{eff} values depend on assumptions about particle geometry, dielectric functions, filling factor, and host matrix refractive index. In this study, the polymer refractive index was treated as constant, which simplifies the optical model but neglects wavelength dispersion, curing-dependent refractive index changes, and particle-polymer interfacial effects. Consequently, the ML-predicted negative-effective-permittivity regions

should be verified using optical measurements such as ellipsometry, UV–Vis spectroscopy, or reflectance/transmittance-based retrieval of ϵ_{eff} from fabricated films.

These limitations do not eliminate the usefulness of the framework, but they define its valid scope. The model is most useful for prioritizing candidate Ag@SiO₂/polymer configurations for experimental testing, not for proving that a final epsilon-negative composite has already been fabricated. The strongest interpretation is that the framework identifies synthesis-accessible and optically relevant regions of the design space where negative effective permittivity may occur, subject to validation of shell uniformity, particle dispersion, filling factor feasibility, and effective medium validity.

Future work should therefore couple the present predictive workflow with experimental verification at three levels: nanoparticle-level characterization, film-level morphology analysis, and optical property retrieval. Nanoparticle-level validation should include TEM measurement of Ag core size, SiO₂ shell thickness, shell uniformity, and particle polydispersity. Film-level validation should assess particle dispersion, aggregation, loading fraction, and spatial uniformity in the polymer matrix. Optical validation should determine whether the measured effective permittivity agrees with the predicted negative-epsilon windows. Only after these validation steps can the predicted design windows be promoted from ML-assisted candidates to experimentally supported epsilon-negative polymer nanocomposites.

4. Conclusions

This study developed a machine learning-assisted synthesis-to-optics screening framework for Ag@SiO₂ core-shell nanoparticle/polymer nanocomposite films. The work should be interpreted as predictive modelling and design space screening rather than full optimization because the present study does not include an explicit objective function, constrained inverse design algorithm, uncertainty-aware candidate ranking, or experimental validation of final composite formulations.

The first part of the workflow addressed the prediction of SiO₂ shell thickness from Stöber synthesis parameters. Water volume, ethanol volume, TEOS content, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration were used as input variables, while SiO₂ shell thickness was treated as the target output. Under the duplicate-aware validation workflow, Gradient Boosting provided the strongest held-out test performance among the evaluated regressors, achieving a test R^2 of 0.8997, MAE of 7.1822 nm, RMSE of 8.8344 nm, and MSE of 78.0462. However, the cross-validation result of 0.5371 ± 0.4648 indicates substantial fold-to-fold variability. The shell thickness model should therefore be regarded as an interpolation-based synthesis screening tool within the investigated Stöber parameter space, not as a fully generalizable predictor of all Ag@SiO₂ synthesis conditions.

The second part of the workflow examined the effective permittivity of Ag@SiO₂/polymer nanocomposite films using Ag core size, SiO₂ shell thickness, wavelength, and nanoparticle filling factor as optical design variables. The validation results showed that the effective permittivity task is more fragile than the shell thickness task. Although the Decision Tree model achieved the highest held-out test R^2 of 0.7586, its cross-validation performance was unstable. Therefore, no epsilon model should be presented as a robust standalone predictor. The optical response analysis maps effective-medium-derived relationships among geometry, composition, and wavelength and identifies candidate negative-effective-permittivity regions for future validation. From an algorithmic perspective, the results show both the usefulness and the limitations of machine learning for this type of materials-design problem. Gradient Boosting provided the strongest shell thickness prediction because nonlinear tree-based ensemble methods can capture coupled relationships among Stöber

synthesis variables, including TEOS amount, water content, catalyst volume, reaction time, Ag nanoparticle size, and Ag nanoparticle concentration. However, the relatively large cross-validation variability indicates that this model should not be interpreted as broadly generalizable beyond the investigated literature-derived synthesis domain. For the effective permittivity task, the evaluated epsilon models showed unstable cross-validation behaviour, even when some models achieved moderate held-out test performance. Therefore, the optical response models should be used for screening within the assumptions of the effective medium formulation, not as robust final predictors or as evidence of experimentally validated negative-effective-permittivity behaviour.

The design window analysis showed that negative $\text{Re}(\epsilon_{\text{eff}})$ is predicted mainly at $\lambda = 400$ nm and a high nanoparticle filling factor. The extracted candidate windows gave predicted $\text{Re}(\epsilon_{\text{eff}})$ values from -5.4229 to -3.5955 for small Ag cores with thin SiO_2 shells, from -3.5213 to -2.8670 for small-to-intermediate cores, from -2.9033 to -1.6857 for intermediate cores, and from -2.4197 to -0.2086 for larger-core boundary cases. A thick-shell, lower-filling-factor control region remained positive, with predicted $\text{Re}(\epsilon_{\text{eff}})$ values from 2.2312 to 2.7800 . These results support the interpretation that negative effective permittivity requires a sufficiently strong Ag core plasmonic contribution, moderated by SiO_2 shell-mediated spacing/screening and enhanced by high inclusion density.

The main conceptual contribution of the study is the use of SiO_2 shell thickness as a bridge variable between synthesis and optical response. In the synthesis task, shell thickness is the Stöber-derived output controlled by hydrolysis, condensation, catalyst conditions, reaction time, and Ag nanoparticle characteristics. In the optical task, the same shell thickness becomes a design variable influencing dielectric screening, interparticle spacing, Ag plasmonic polarizability, filling factor effects, and the resulting effective permittivity of the polymer composite. In this sense, the framework supports the pre-selection of candidate Ag@ SiO_2 /polymer design windows with defined geometrical and optical parameters before experimental fabrication. The ML workflow is therefore used to identify promising synthesis-accessible and optically relevant design regions, rather than to claim autonomous material creation or experimental proof of epsilon-negative behaviour.

The predicted negative-effective-permittivity regions should not be interpreted as experimentally demonstrated epsilon-negative metamaterial films. The optical targets were derived from an effective medium framework, and the effective permittivity model did not show robust cross-validation stability. In addition, real polymer nanocomposite films may contain shell thickness distributions, Ag core polydispersity, incomplete silica coating, nanoparticle aggregation, concentration gradients, scattering losses, and processing-induced changes in the polymer matrix. High filling factors are particularly important because they may promote negative effective permittivity in the model while also increasing the risk of aggregation, optical scattering, viscosity limitations, and breakdown of the homogeneous effective medium approximation.

Future work should validate the predicted windows experimentally by combining nanoparticle-level characterization, film-level morphology analysis, and optical property retrieval. TEM should be used to quantify Ag core size, SiO_2 shell thickness, shell uniformity, and polydispersity. Polymer film characterization should assess nanoparticle loading, dispersion quality, aggregation, and spatial uniformity. Optical validation should include ellipsometry, UV-Vis spectroscopy, or reflectance/transmittance-based retrieval of effective permittivity. A stronger next-generation framework should also include physics-informed descriptors, uncertainty quantification, grouped or duplicate-free validation, and a true constrained optimization module with defined objective functions, manufacturability constraints, and ranked candidate designs.

The contribution of this study is not the experimental realization of an optimized epsilon-negative metamaterial, but the establishment of a coupled ML-assisted screening workflow that links Stöber-derived Ag@SiO₂ shell thickness prediction to effective permittivity design space exploration in polymer nanocomposite films.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/app16126068/s1>, Table S1: Source-level provenance of the literature-derived Ag@SiO₂ shell-thickness dataset used for Stöber synthesis modelling. Table S2: Provenance and generation protocol of the effective-permittivity optical-response dataset used for Ag@SiO₂/polymer nanocomposite screening.

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