Room temperature cured silver nanoparticle embedded hybrid nanocomposite coatings: processing and property evaluation†

Srikrishna Manna, ab Prabir Pal, ab Milan Kanti Naskar ab and Samar Kumar Medda ab

Room temperature (RT) curable inorganic–organic hybrid hydrophobic coatings embedded with in situ formed silver nanoparticles (Ag NPs) were developed on glass substrates by a sol–gel based wet chemical method using a spray/dip coating technique. Tetraethyl orthosilicate (TEOS), 3-glycidoxypropyl)trimethoxysilane (GLYMO), titanium(IV) isopropoxide (TTIP), polydimethyl siloxane (PDMS) trimethylsiloxy terminated, diamine based curing agent and silver nitrate (AgNO3) were used as precursors to prepare a hybrid nanocomposite polymeric sol prior to coating. The coated surface displays a notable brownish yellow color indicating the formation of Ag NPs under ambient conditions. In-depth characterizations of the Ag NPs incorporated hybrid coated surface were reported using UV-visible absorption spectroscopy, X-ray diffractometry (XRD), attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), water contact angle (WCA) measurements, abrasion testing, pencil hardness testing and adhesion testing. The coating with embedded Ag NPs inside the matrix was mechanically robust, easy to produce and stable in the long term with little change in color even after a period of 210 days. RT cured hybrid coatings surrounded by Ag NPs on the surface have potential applications in the medical field with antibacterial properties and could also be explored for applications in the food and beverage industry as well as other sectors of society.

1. Introduction

Because of their optical, electronic, plasmonic, catalytic and anti-bacterial properties,1–5 silver nanoparticles (Ag NPs) have great potential applications in diverse sectors of society, especially in the bio-medical field in health care products to protect humans from harmful germs. Ag NPs destroy harmful germs such as different types of bacteria (Gram positive and Gram negative), viruses and fungi to protect our environment.6 The development of antimicrobial properties in thin film hybrid coatings on different substrates such as glass, plastic, metal, and cotton has been reported by thermal or UV curing using suitable metal ions like silver (Ag+), copper (Cu2+) and zinc (Zn2+).7,8 The sustainability of composite nanoparticle coatings on different substrates with long-term stability is one of the most important issues for the fight against harmful bacteria. Ag NPs are the main candidates to promote the highest antimicrobial properties compared with other metal nanoparticles.9–14 The generation of Ag NPs with mechanically hard and durable coatings curable at room temperature offers great advantages in terms of reduced energy consumption and sustainability. Various methods have been reported by the scientific research community towards the formation of Ag NPs coatings by controlling some of the factors known to increase the durability, antibacterial properties and curing temperature. One common method is the in situ synthesis of Ag NPs films by thermal curing with layer by layer deposition using weak organic–inorganic acids and their derivatives.15–17 Rivero et al. have used a polymeric solution using a sol–gel wet chemical process by adjusting the pH to 7 to 9 for the preparation of an Ag NPs incorporated thin film by layer by layer deposition using two alternative wet chemical methods followed by a thermal curing process.18 Mukhopadhyay et al. have reported antibacterial properties of anatase TiO2 and Ag NP doped silica films on soda lime glass substrates by a sol–gel method, with curing at 450 °C in air and an H2/Ar atmosphere.19 Pal et al. have shown the growth of Ag NPs in an inorganic–organic hybrid system using a dip coating process on
glass and polymer plastic substrates followed by thermal curing at 80 °C, for the development of antibacterial activity. Tarannum et al. have reported the green synthesis of Ag NPs with controlled shape and size by reducing coupling agents using natural sources, like plants, various types of microbes and biopolymers, for antibacterial activity. Dai et al. have shown antibacterial activity with the help of curing wound healing using an e-polylysine/silver nanocomposite solution following a wet chemical technique. Jia et al. prepared a nanocomposite cluster of Ag–TiO₂ coating by reduction of silver ions with UV-A radiation for surface plasmon applications. Liu et al. have reported Ag NPs synthesis at room temperature using an aldehyde and nitro group functionalized porous polymer matrix. The in situ reduction of Ag NPs using the amine group of poly diamine–copper phosphate in a hybrid system was developed by Zhang et al. for anti-microbial activity. Poortavasoly et al. have used aminohydrolated polyster fabric to generate Ag NPs with triethanolamine to enhance antimicrobial and hydrophilic properties. Three types of fumed silica were used and functionalized with thiol and amine groups that reacted with diamine silver ions to form Ag NPs in the silica composites. Zienkiewicz-Strzalka et al. have reported thermal cured coatings on various substrates with the formation of Ag NPs.

Most of the previous work has been reported for either UV or thermal cured coatings with the formation of Ag NPs on various substrates. However, these methods are expensive in terms of energy consumption, time consuming, and suffer from long-term stability issues. Therefore, there is a critical need for alternative room temperature cured durable hydrophobic coatings with the formation of Ag NPs by spray or dip coating techniques.

The research work shown in this paper is to prepare in situ Ag NPs embedded in the polymeric network structure of an inorganic–organic hybrid system on glass substrates cured at room temperature (30 ± 5 °C) under ambient conditions. The sol–gel based wet chemical method was adopted with in situ reduction of silver nitrate to Ag NPs followed by the deposition of the coating on glass substrates by spray and dip coating techniques. The developed room-temperature cured AgNPs embedded nanocomposite coatings have great potential applications, particularly in the bio-medical field, and food and beverage industry, with antibacterial activity, which are important from an environmental and health point of view.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) 98%, (3-glycidoxypropyl)trimethoxysilane (GLYMO) 98%, titanium(IV)isopropoxide (TTIP) 97%, and poly(propylene glycol)bis(2-aminopropyl ether) MW 400 g mol⁻¹ were obtained from Sigma Aldrich, while silver nitrate 99.99% and polydimethyl siloxane (PDMS) trimethyl-siloxoy terminated (MW 4000 g mol⁻¹) were obtained from Alfa Aesar, USA. Acetyl acetone (acac), 1-propanol and nitric acid (HNO₃) were procured from Merck. Mili-Q (Millipore) water (18.2 MΩ) was used throughout the experiments.

2.2. Preparation of sols

Fig. 1 schematically shows the preparation of the Ag NPs embedded inorganic–organic hybrid nanocomposite sol. In step 1, TTIP and acac (1 : 0.5 mol ratio) in 1-propanol (112 mmol) were stirred for 45 min to control the rapid hydrolysis of TTIP by partially chelating with acac. In step 2, a mixed solution of TEOS and GLYMO (2 : 1 mole ratio) in 1-propanol (165 mmol) was prepared under stirring for 5 min followed by the addition of 1 M HNO₃ (4 mmol) in 1-propanol (100 mmol), maintaining a TEOS : HNO₃ = 0.8 – 0.9 mol ratio. The above chelated TTIP solution (step 1) was slowly added into the step 2 solution under stirring for 2 h for the hydrolysis polymerization reaction. The PDMS in 1-propanol (0.09 mmol) was added into the above polymeric sol under stirring for 2 h followed by ageing at room temperature (30 ± 5 °C) for 24 h under static conditions. The total equivalent SiO₂ content (11 wt%) was minimized to 5 wt% by diluting with 1-propanol (0.5 mol). In step 3, an optimized amount of poly(propylene glycol)bis(2-aminopropyl ether) (0.5 mol%) as a curing agent in 1-propanol was added into the above polymeric sol under stirring for another 30 min. For the formation of the Ag NPs embedded inorganic–organic hybrid nanocomposite, 1.3, 2.6, 3.8, 5.0 and 6.3 mol% of AgNO₃ with respect to equivalent SiO₂ obtained from TEOS and GLYMO was added into the sol as prepared in step-3 under stirring for 2 h followed by aging for 24 h. The prepared sols were designated as SA-0, SA-1, SA-2, SA-3, SA-4 and SA-5 for Ag⁺ contents of 0, 1.3, 2.6, 3.8, 5.0 and 6.3 mol%, respectively (Table 1).

2.3. Coating development

Glass substrates were cleaned with neutral detergent followed by washing with tap water and rinsing with Millipore water and 1-propanol, then by dipping in warm isopropanol, prior to coating deposition. The different sols were coated on glass slides by dip coating techniques with a withdrawal speed of
Various compositions of sols were used to deposit on the glass substrate and cure at room temperature highlighting optimum conditions of curing of 7 days (SA-4) as compared to in the absence of Ag NPs (SA-0) (Fig. 2a). The sols SA-0 and SA-4 were used to coat on larger size glass substrates (300 mm x 300 mm x 3 mm) with 3 mm thickness (Fig. 2b) by a spray coating technique (Fig. 2c).

### 2.4. Characterization

The developed coated samples were characterized by transmission electron microscopy (TEM-JEOL), X-ray diffraction (XRD) and ATR-Fourier-transform infrared spectroscopy (Bruker ECO, ALPHA) studies. Surface morphology and elemental analyses of RT cured coated films were carried out using field emission scanning electron microscopy (FESEM) (ZEISS, SUPRA™ 35VP). The thicknesses of the Ag NPs embedded coated films along with the surface roughness were measured by atomic force microscopy (AFM, Nanosurf Easy scan 2, Switzerland). The absorption properties of the Ag NPs in the coated film were studied using a UV-visible spectrophotometer (Cary 50 scan). The surface chemical compositions of the samples were studied by monochromatic aluminum Kα (1486.7 eV) X-ray photoelectron spectroscopy (XPS). Room temperature cured samples were kept under identical conditions for several days (30 days) prior to XPS measurements. The C 1s core-level spectra at 284.7 eV were used to calibrate the binding energy. A nonlinear background was subtracted from the raw data before fitting. The hydrophobic properties of the coated surface were measured using a contact angle meter (OCA 15 pro Data Physic, Germany). To evaluate the mechanical strength, adhesion (ASTM D 3359), abrasion, pencil hardness (ASTM D 3363) and thermal durability tests were carried out.

### 3. Results and discussion

#### 3.1. Solution chemistry and its mechanism

The preparation of a sol by the sol–gel technique for deposition on various substrates cured at RT is the most important aspect in terms of its stability. Fig. 3 schematically shows the formation of an inorganic–organic hybrid network structure with ring opening of GLYMO in the presence of TEOS, Ti(IV) isopropoxide, PDMS and diamine based curing agent followed by hydrolysis–polycondensation reaction at an acidic pH. Herein, poly(propylene glycol)bis(2-aminopropyl ether) acts as a curing and reducing agent. It helps to facilitate the opening of the epoxy part of GLYMO by nucleophilic attack on the carbon terminus during hydrolysis and condensation reaction at the time of curing. GLYMO has polymerizable alkoxy groups as well as epoxy groups bonded with Si through –(CH₂)₃–O– chains.²⁸

### Table 1 Sol composition of the Ag NPs incorporated inorganic–organic hybrid nanocomposite

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>TEOS : GLYMO (in mol ratio)</th>
<th>Mol% of AgNO₃ with respect to equivalent SiO₂ from (TEOS + GLYMO)</th>
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<tr>
<td>SA-0</td>
<td>2.0 : 1</td>
<td>0</td>
</tr>
<tr>
<td>SA-1</td>
<td>2.0 : 1</td>
<td>1.3</td>
</tr>
<tr>
<td>SA-2</td>
<td>2.0 : 1</td>
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<td>2.0 : 1</td>
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<tr>
<td>SA-5</td>
<td>2.0 : 1</td>
<td>6.3</td>
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</table>

Fig. 2  (a) The colour of the coated films in various compositions were developed after 7 days of ageing, (b) SA-4 and SA-0 coated glasses (300 mm x 300 mm x 3 mm) developed by a spray coating technique, and (c) spray coating system.
Therefore, during hydrolysis-condensation reactions, the alkoxy group results in a –Si–O–Si– network, whereas the epoxy group generates a polyethylene oxide (PEO) network. In this system, polydimethyl siloxane (PDMS) trimethylsiloxy terminated (MW 4000 g mol\(^{-1}\)) is incorporated to enhance the hydrophobic surface by weak van der Waals interaction in the polymeric network. It increases the chemical durability, abrasion resistance, and mechanical stability of the coated film due to the large bond energy of –Si–CH\(_3\) (452 kJ mol\(^{-1}\)) and low surface tension (20.4 mN m\(^{-1}\)).\(^{29,30}\) The hybrid end product obtained from GLYMO increases the formation of polyethylene oxide (PEO) linkages bonding with silica (from TEOS) and titania network. In the presence of AgNO\(_3\), the diamine based curing precursor reduces Ag\(^+\) ions to Ag NPs with a changed brownish yellow color in the coated glass substrates after 7 days of curing at RT. The Ag NPs in the coated glass substrates were stable for more than 200 days under ambient conditions. It is reported that the formation of silver nanoparticles requires thermal and/or UV curing processing.\(^{18–20,27}\) In the present study, we have established the formation of silver nanoparticles cured at room temperature using a Ti(IV) catalyst and diamine based curing agent. Fig. 4 schematically shows the Ag NPs embedded inorganic–organic hybrid network structure formed during the curing stage.

3.2. ATR-FTIR spectra of nanocomposite solution and coatings

An ATR-FTIR study was performed to understand the bonding nature of the inorganic–organic hybrid network structure of the RT cured coatings. Fig. 5 shows the ATR-FTIR spectra of the room temperature cured hybrid coated film (a) without Ag NPs (obtained from sample SA-0) and (b) with Ag NPs (obtained from sample SA-4) after 7 days of ageing. The absorption band at 3747 cm\(^{-1}\) signifies the formation of a Si–OH bond in the coated film in the absence of Ag NPs (Fig. 5a), which is diminished in the presence of Ag NPs (Fig. 5b). The bands at 2864–2947 and 1375–1455 cm\(^{-1}\) are attributed to C–H/CH\(_2\) stretching and bending vibrations, respectively.\(^{28,31,32}\) A broad stretching vibration at 3200–3500 cm\(^{-1}\) represents –OH and –NH, and their corresponding bending vibrations appear at 1600–1700 cm\(^{-1}\).\(^{31,32}\) The characteristic peaks in the skeletal system of the polymeric network at 1056, 913 and 785 cm\(^{-1}\) are due to Si–O–Si/Ti–O–C, and the corresponding C–O stretching vibration is at 1276 cm\(^{-1}\).\(^{28,32–34}\) It is worth noting that the intensity of the N–H bending vibration is reduced in the embedded Ag NPs in the polymeric network structure, which is due to the interaction between amino groups and Ag NPs.\(^{33}\) In the solution stage, the peak intensity of –NH bending at 1630 cm\(^{-1}\) appeared low due to chemical interactions with other species (Fig. S1, ESI†).

3.3. UV-visible absorption due to Ag NPs in the room temperature cured film

The evolution of Ag-NPs in the coating surface was examined by UV-visible absorption spectroscopy. Fig. 6a shows UV-visible absorption spectra of the samples SA-0, SA-1, SA-2, SA-3, SA-4 and SA-5 after 7 days of curing time at RT. The absorption peak located at 415 nm confirms the presence of Ag NPs, except for
the sample SA-0 where no Ag is present. This sharp peak is due to the localized surface plasmon resonance (LSPR), which originates from the collective oscillations of the surface of plasmonic silver nanoparticles induced by the incident light. The light absorption covered the entire visible region (400–700 nm). The intensity and broadening of the LSPR absorption increased with an increase in the Ag content with respect to the SiO₂ equivalent from 1.3 to 6.3 mol% (SA-1 to SA-5). The LSPR absorption peak is highly sensitive to the concentration of free carriers of Ag⁰ ions, which depends on the size and shape of the nanoparticles. The size and shape of the Ag nanoparticles are modulated by controlling the AgNO₃ concentration. However, as expected, SA-0 remained colorless and showed no absorption peak in the visible wavelength region, indicating no Ag⁺ ions in the polymeric hybrid matrix.

To investigate the effect of aging time on LSPR absorption, the SA-4 sample was used for UV-visible measurements and spectra were taken at different intervals of curing time (Fig. 6b). Interestingly, the intensity of the absorption peak progressively increased up to 60 days, followed by a gradual decrease up to 120 days. It is worth mentioning that for longer curing times of over 60 days, there could have been the possibility of the formation of a passive layer of dangling –OH on the surface of the Ag nanoparticles as Ag–OH, resulting in a decrease in the intensity of LSPR absorption. The key purpose of the formation of Ag NPs in the SiO₂–PEO network composite is to preserve the reactivity with a diamine based curing agent and increase the longevity by protecting the Ag⁰ nanoparticles. The observation of the surface SiO₂–PEO network layer helps in suppressing the reaction with OH⁻ ions and prevents the aggregation of the Ag nanoparticles. Thus, the lifetime of Ag⁰ nanoparticles is increased. It is therefore clear from ATR-FTIR (Fig. 5) and UV studies that the formation of the silica (SiO₂) network started at the sol stage, which gradually intensified during the room temperature curing process with the formation of polyethylene oxide leading to the generation of the SiO₂–PEO network associated with Ag NPs formation and yellow color coating.

3.4. XRD

XRD analysis was adopted to characterize the formation of Ag NPs in the hybrid matrix. Fig. 7 shows the XRD patterns of (a) SA-0 (without Ag NPs) and (b) SA-4 (with Ag NPs) after 7 days of curing at RT. The characteristic peaks of Ag (JCPDS Card 04 0783) were determined at 2θ values of 38.1 and 44.2° corresponding to hkl values of (111) and (200) with inter-planar d spacings of 2.35 and 2.04 Å, respectively, for a face centered cubic structure.³⁵–³⁷ Thus, XRD patterns confirmed the presence of Ag NPs in the inorganic–organic hybrid material. The appearance of a broad peak at 21° is attributed to the amorphous inorganic–organic hybrid silica based polymeric matrix.³⁵

4. Microstructure analysis

4.1. TEM study

Fig. 8 shows (a) a TEM image, (b) an image at a higher magnification with a selected area electron diffraction (SAED) pattern in the inset, (c) energy-dispersive X-ray analysis (EDAX) and (d) high resolution-TEM (HR-TEM) of the sample SA-4 (in the presence of Ag NPs in the hybrid composite) after 7 days of curing at RT. It shows the presence of uniformly distributed

![Fig. 6](a) UV-visible absorption spectra of the samples SA-0, SA-1, SA-2, SA-3, SA-4 and SA-5 (after 7 days of curing at RT) and (b) UV-visible absorption spectra of the sample SA-4 for different curing time periods at RT.

![Fig. 7](XRD patterns of (a) SA-0 and (b) SA-4 after 7 days of curing at RT along with (c) reference JCPDS Card for Ag.)

![Fig. 8](a) TEM image, (b) image at a higher magnification with a selected area electron diffraction (SAED) pattern in the inset, (c) energy-dispersive X-ray analysis (EDAX) and (d) high resolution-TEM (HR-TEM) of the sample SA-4 (in the presence of Ag NPs in the hybrid composite) after 7 days of curing at RT.
nearly spherical particles with average diameters of about 7.2 ± 3.0 nm, which are determined from the histogram in Fig. 8(a and b), ESI†. The Ag NPs in the coating matrix are highly crystalline in nature, which is confirmed by the SAED pattern, indicating (111) and (200) planes corresponding to d spacing values of 2.35 and 2.00 Å (Fig. 8(b), inset). The TEM-EDS spectrum (Fig. 8c) shows signals of Si, Ti, and Ag in addition to C and O. The high resolution image also shows the lattice fringe with d spacing of 2.3 Å for the (111) plane. Fig. S3, ESI† shows the (a) TEM image, (b) HR-TEM image and (c and d) SAED pattern of the Ag NPs embedded inorganic–organic hybrid composite after 210 days of ageing, confirming the stability of the coating. Fig. 9 shows (a and b) the TEM image, (c) EDAX and (d) SAED of the sample SA-0 after 7 days of curing at RT. It indicates no crystallinity in the hybrid composite in the absence of Ag NPs.

4.2. Field emission scanning electron microscopy (FESEM)

Fig. 10 shows the FESEM images of (a) SA-4 with (b) EDAX and (c) SA-0 with (d) EDAX after 7 days of curing at RT. The presence of Ag NPs with other elements such as Si, Ti, O and C is confirmed from the EDAX analysis of SA-4, while the sample SA-0 shows a crack-free smooth coating in the absence of Ag NPs. Fig. S2, ESI† shows particle size distributions with the histogram for the sample SA-4 obtained from (a and b) TEM images and (c and d) FESEM images. It indicates an average particle size of 7.3 ± 2.9 nm. From microstructural analysis, it is revealed that some of the Ag NPs in the matrix undergo cluster formation with ageing.

4.3. XPS study

Fig. 11a shows survey spectra of the control (SA-0) and Ag NPs embedded (SA-4) samples. We have identified Si, O, C, Ti and Ag core level spectra in the survey scan. No other impurity was identified. The Ag related XPS peaks were visible in the case of the Ag NPs sample (SA-4). To understand elemental oxidation states and chemical compositions of the surfaces, XPS analysis of the control (SA-0) and Ag NP embedded (SA-4) samples were performed, and comparative analysis is presented here. The high resolution Ti 2p XPS spectrum of the control sample shows Ti 2p3/2 and 2p1/2 spin–orbit doublet peaks located at around ~459.0 and ~464.7 eV, respectively (Fig. 11b). The fitted Ti 2p spectrum highlights characteristic doublet peaks of Ti4+ ions (TiO2).35 The Ti 2p spectrum of Ag NPs shows similar features to the control, with Ti 2p3/2 and Ti 2p1/2 doublet peaks located at ~459.0 and ~464.7 eV, respectively related to the Ti4+ ions. The Si 2p spectrum of the control sample shows that Si is predominantly present as Si–O–C with reduced SiOx component (Fig. 11c). In addition, an excess amount of SiO2 of around 33.3% is due to the formation of the –Si–O–Si–network in the coated surface. The Si 2p spectrum of Ag NPs shows similar reduction capability of Si into Si–O–C with reduced SiOx. The relative percentage of Si–O–C with reduced SiOx component was found to be identical for both
the samples (66.6%). The O 1s core-level spectrum of the control shows a lower binding component of Si–O–C/SiO$_2$/SiO$_x$ located at 532.0 eV and OH$^-$ species located 532.9 eV (Fig. 11d). The Ag NPs result in a similar O 1s spectrum with a small decrease of OH$^-$ species compared with the control sample. The relative percentages of Si–O–C/SiO$_2$/SiO$_x$ and OH$^-$ species were found to be around 90.3% and 9.6%, respectively, for the control, and 92.7% and 7.2%, respectively, for the Ag NPs. 

Fig. 11e displays the C 1s peaks of the control sample fitted with three prominent features, one at a lower binding energy, another at an intermediate binding energy, and the third at a higher binding energy. These components are assigned to C–H/C–C, C–O–C and C(O)C, located at 284.6, 286.0 and 288.7 eV, respectively. We have fitted the C 1s spectrum of the Ag NPs with three components, keeping the energy positions, widths and line shapes the same as for the control. The relative percentage of each component is shown in the inset of the figure.

The Ag 3d spectrum of the Ag NPs is shown in Fig. 11f. The spectrum shows that silver is mainly in the Ag$^0$ state, and the peaks are located at $\sim$367.8 and $\sim$373.8 eV for Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$, respectively. Additional shoulder doublet peaks were observed at the higher binding energy side, which indicates the presence of Ag$^+$ states located at $\sim$368.8 and $\sim$374.8 eV, respectively. We have estimated the relative percentage of Ag$^0$ and Ag$^+$ states by carefully fitting the Ag 3d XPS spectra using two pairs of doublet components corresponding to Ag$^0$ (purple) and Ag$^+$ (gray) ions, as displayed in Fig. 11f. In the $\chi^2$ iterative fitting programme, we used same line shapes, widths and branching ratios for the two pairs of doublet peaks. The relative percentages of Ag$^0$ and Ag$^+$ ions were found to be $\sim$73.1% and $\sim$26.8%, respectively. Thus, the surface of the Ag NPs is predominantly embedded with inner Ag$^0$ nanoparticles covered with a small amount of silver oxide (Ag$^+$). The increase in reactivity towards Ag$^+$ is enhanced for longer aging times. XPS analysis of the control sample determines C–H/C–C, C–O–C.
and C(O)C components formed in different proportions at the coated surface, which is directly related to the degree of inorganic organic polymerization. The polymerization affects reactive sites and influences the reactivity of the sample surface. The XPS analysis suggests that the coating was stable in the long term with Ag$_0$ nanoparticles embedded in the network chain without any significant influence of additional aging.

5. Physicomechanical properties

The thickness of the Ag NPs embedded film (SA-4) was found to be around 600 ± 20 nm (Fig. S4, ESI†). Fig. S5 (a and b), ESI† represents the surface morphology (2D top and 3D view) of the hybrid coating surface on the glass substrate, while Fig. S5(c), ESI† shows that the root mean square roughness value was obtained as 3.0 nm, which indicates a smooth and homogeneous surface of the coating. The coated film gives a brownish yellow color and is optically transparent. Table 2 summarizes the physicomechanical properties of the Ag NPs embedded hybrid composite (SA-4). The adhesion test was performed by the standard ASTM D3359 method (cross-cut adhesive tape test). The coated surface was examined by optical microscopy using 100X magnification after the tape test. It shows no peeling off of the coatings from the substrate and can be classified as ASTM 5B (highest standard) (Fig. S6, ESI†). Fig. S7, ESI† shows the static WCA, which is found to be around 101° ± 2° on the coated surface (SA-4). It shows that the surface of the Ag NPs coated sample exhibits self-cleaning properties. Pencil hardness testing was carried out as per ASTM-3363 to evaluate the hardness of the coated film (SA-4).

In this method, different grades of pencils (6B to 9H) were used to apply a constant force (750 g) with a 45° angle using a pencil hardener tester. As per the ASTM procedure, the pencil hardness was found to be 3H grade pencil hardness. Visually, no scratch was observed after 5 times of marking up to 2 cm on different parts of the coated surface, and this can be easily applicable to commercial purposes. For durability of the coating, sand abrasion resistance testing was also performed on the RT cured coated film (SA-4), with respect to the WCA measurements. This method was adopted as per a survey of the literature.²⁸,⁴¹,⁴² In this test, 80 mesh sand paper was positioned on the coated surface with a load of 100 g weight and observed upon pulling the sand paper at a 180° angle across a 4 cm travel distance on the coated surface for up to 30 cycles. A change of the WCA value from 101° (before the abrasion test) to ~92° (after 20 cycles) was observed, and it reached 65° after 30 cycles (Fig. S8, ESI†). This suggests that the coating has a hydrophobic effect for up to 20 cycles of abrasion testing, showing no significant changes of peel off or delamination. The coating film is identified to have hydrophilic properties after 30 cycles of abrasion. Thermal stability testing of the Ag NPs embedded RT cured coating (SA-4) was carried out up to 200 °C for 2 h, and it was observed that there is no significant change in the WCA and colour of the coated film on the glass substrate.

6. Understanding the stability of in situ generated Ag NPs in the nanocomposite coating

In this work, Ag NPs have been formed inside the inorganic–organic hybrid matrix due to proper selection of the diamine based curing agent and the use of a minimum calculated quantity of the acid–water mixture (1 M HNO$_3$) for complete hydrolysis and condensation reaction of the precursors to avoid excess –OH or polar groups in the hybrid inorganic–organic matrix. The diamine-based curing agent and titanium(IV) ions in the hybrid matrix demonstrated the formation of a polymeric network structure by the opening of the epoxy group of GLYMO. The polymeric network structure (–SiO$_2$–PEO, –Si–O–Si–, –Si–O–Ti–, –Si–O–Ti– and CH$_3$–NH–) formation was evident from ATR-FTIR and XPS analysis, with a significant decreased amount of the –OH group in the coating hybrid materials. The estimated amount of –OH is 7.2% in the hybrid matrix, as obtained from XPS analysis. Conversely, the presence of the amine components of the curing agents in the polymeric matrix acts as reducing atmosphere via lone pair interaction with Ag$^+$ ions. As a result, Ag NPs (Ag$_0$) were formed in the hybrid matrix with a lower content of –OH, and the reducing environment rendered the stability of Ag NPs at RT. This helps us to increase the surface area of the polymeric network encapsulated with Ag NPs in the host hydrophobic (non-polar surface) polymeric matrix where weak van der Waals attractive forces between the surface of the Ag NPs and hybrid matrix are developed. Host hydrophobic polymeric nanocomposites also act as a long-term stabilizer, which protects the Ag NPs (Ag$_0$) from degradation because of the external atmosphere.

Table 2. Physicomechanical properties of the RT cured Ag NP incorporated hybrid coating

<table>
<thead>
<tr>
<th>Test performed</th>
<th>Specifications</th>
<th>Characteristics</th>
</tr>
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<tr>
<td>Visual appearance</td>
<td>—</td>
<td>Transparent brownish yellow coated surface</td>
</tr>
<tr>
<td>Absorption study</td>
<td>—</td>
<td>417 nm due to formation of Ag NPs</td>
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<tr>
<td>Thickness</td>
<td>—</td>
<td>600 ± 20 nm</td>
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<td>Adhesion</td>
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<td>ASTM class 5B (highest standard)</td>
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<td>Pencil hardness</td>
<td>ASTM D 3363</td>
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<td>Abrasion resistance</td>
<td>20 cycles of abrasion testing for RT cured substrate</td>
<td>After the abrasion test, the WCA value decreased from 101° to 92°, indicating that coated materials exist on the glass substrate</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>The RT cured sample was heated up to 200 °C for 2 h</td>
<td>There are no significant changes in the coating properties up to 200 °C, and a yellow colour appeared</td>
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7. Anti-bacterial study

We have evaluated the antibacterial properties of the coating using an incubation method. For incubation on the film, Gram-positive bacteria (Staphylococcus aureus) growth was carried out at 37 °C for 24 h on both coated samples (size: 5 mm × 5 mm) with the Ag NPs embedded hybrid matrix (SA-4) (Fig. S9a, ESI†) and control sample without Ag NPs (SA-0) (Fig. S9b, ESI†). Incubation of the Ag NP embedded coating over 24 h shows no bacteria growth, while the coated glass without Ag NPs shows a significant amount of bacteria growth, and an inhibition zone was not observed. This suggests that the Ag NPs coated film is effective in eliminating the bacterial growth. The antibacterial activity of the Ag NPs coated film demonstrated that the in situ formation of Ag NPs in the nanocomposite matrix with greater durability could find applications in the medical sector and food and beverage industries.

8. Conclusions

The present work demonstrates the development of the in situ formation of Ag NPs inside an inorganic–organic hybrid nanocomposite cured at room temperature (30 ± 5 °C). The uniformly coated hydrophobic hybrid nanocomposite with a WCA of 101 ± 2° exhibits self-cleaning properties. The embedded Ag NPs in the hybrid nanocomposite, with a particle size of 7.2 ± 3 nm, provide significant long-term stability (≥ 200 days) under ambient conditions. In terms of durability, the coated surface exhibits mechanical robustness, and it shows Gram-positive antibacterial activities, which could be applicable in the food and beverage industry for the preservation of food grains. The present study of RT cured hybrid nanocomposites with the in situ formation of Ag NPs with a simple processing route that could be applicable for the formation of hybrid nanocomposites embedded with other nanoparticles, such as Cu and Zn, toward self-cleaning antibacterial applications. Instead of using Ti(IV), other catalysts, such as Zr(IV) and Sn(IV), could be used for further study. The present process is advantageous in terms of low energy consumption, environmental friendliness and scalability, with long-term stability.

Author contributions

Srikrishna Manna: investigation, conceptualization, methodology, visualization, writing – original draft. Dr Prabir Pal: investigation, supervision, writing – review & editing. Dr Milan Kanti Naskar: supervision, writing – review & editing, visualization. Dr Samar Kumar Medda: supervision, investigation, methodology, writing – review & editing, funding acquisition.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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Notes and references