Heterostructured TiO$_2$/SiO$_2$/γ-Fe$_2$O$_3$/rGO Coating with Highly Efficient Visible-Light-Induced Self-Cleaning Properties for Metallic Artifacts

Maryam Mokhtarifar, Reyhaneh Kaveh, Mojtaba Bagherzadeh, Andrea Lucotti, MariaPia Pedeferri, and Maria Vittoria Diamanti*

Cite This: ACS Appl. Mater. Interfaces 2020, 12, 29671−29683

ABSTRACT: A novel nanohybrid composite of TiO$_2$, SiO$_2$, γ-Fe$_2$O$_3$, and reduced graphene oxide (TiO$_2$@Si:Fe:rGO) is fabricated by the sol−gel method. The properties of the coated film were examined by structural and self-cleaning analyses using simulated discoloration/soiling and roofing tests. The fabricated transparent TiO$_2$@Si:Fe:rGO composite showed excellent photocatalytic activity and wettability, behaving well in self-cleaning applications. The addition of SiO$_2$ improved the crystalline structure and surface hydroxylation of TiO$_2$ nanoparticles. γ-Fe$_2$O$_3$ decreased the recombination rate of e$^-$/h$^+$ pairs, and significantly improved photocatalytic activity under visible light. Moreover, rGO sheets as excellent electron acceptors and transporters also reduced recombination, as well as affected wettability, achieving superhydrophilicity under irradiation. The coated substrate showed excellent resistance to simulated acid rain and significantly preserved the substrate from soiling in roofing tests.

KEYWORDS: self-cleaning, TiO$_2$, γ-Fe$_2$O$_3$, SiO$_2$, reduced graphene oxide, superhydrophilic photocatalyst, transparent coating

1. INTRODUCTION

Preservation of current and future artifacts that have left a valuable visual art legacy is of great importance in today’s world. However, atmospheric deterioration continues to threaten tangible architectural heritages, especially those buildings and monuments made out of metals that are highly prone to various types of outdoor declines, including degradation and discoloration.$^{1−3}$

To overcome this challenge, many studies have been dedicated to the elimination of pollutants by using photoactive metal oxides such as WO$_3$, ZnO, and TiO$_2$. Among them, TiO$_2$ is one of the most considerable materials in the built environment due to its high photocatalytic efficiency and good integration with building materials. Indeed, its physicochemical properties, such as high chemical stability, easy availability, and the possibility to be easily added as coating or in mass to cementitious materials or to be deposited in the form of a thin film and reaching the superhydrophilic state, make it a great candidate for the preservation of metallic artifacts. The effect is that of reducing maintenance time and cost and protecting them from soiling by means of its self-cleaning features.$^{9−13}$

Besides, some of the general aspects of suitable coatings to preserve metallic historic and modern buildings exposed to harsh environmental situations are proper adhesion, chemical stability, colorlessness, and transparency to maintain the aesthetic characteristics of the original material.$^{14}$

To furtherly increase the photocatalytic efficiency, it is essential to engineer TiO$_2$ hydrophilic surfaces to maximize the removal of contaminants and counteract soiling and discoloration. However, the wide band gap of the semiconductor for both anatase and rutile forms of TiO$_2$ limits both its hydrophilic conversion and photocatalytic activity and, consequently, its self-cleaning ability to happen only at 5% of the solar spectrum, i.e., the UV region of sunlight.$^{15}$

Within this context, heterojunction structures that combine other narrow band gap metal oxides with TiO$_2$ can be used to achieve better light-harvesting and charge transport properties. On the other hand, the presence of the metal oxides in TiO$_2$ composites could promote the electron transfer reactions between the photocatalyst and pollutant molecules. Moreover, materials with high specific surface area such as carbon-based
materials can be utilized as an excellent supporting material to amplify photocatalytic activity by increasing surface sites.\textsuperscript{16,17} 

Trying to face this challenge, the present work aims at the synthesis and characterization of a nanocomposite coating including silicon dioxide (SiO\textsubscript{2}), y-iron oxide (γ-Fe\textsubscript{2}O\textsubscript{3}), and reduced graphene oxide (rGO) on titanium substrates. The synergistic effects of the components above with TiO\textsubscript{2} are investigated in terms of resulting film morphological, structural and functional characteristics with special reference to self-cleaning practical applications.

2. MATERIALS AND METHODS

2.1. Preparation of Sols and Coatings. Iron chloride tetrahydrate (FeCl\textsubscript{3}·4H\textsubscript{2}O), propylene oxide, tetaethyl orthosilicate (TEOS), tetrabutyl titanate (TBT), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), graphene oxide solution (GO), sodium borohydride (NaBH\textsubscript{4}), ethanol (C\textsubscript{2}H\textsubscript{5}OH), and methylene blue (MB) were purchased from Sigma–Aldrich and used as received. To prepare the γ-Fe\textsubscript{2}O\textsubscript{3} nanoparticles, FeCl\textsubscript{3}·H\textsubscript{2}O (5 mmol) was dissolved in ethanol (0.3 M) and then added to propylene oxide (50 mmol), sonicated for 15 min, and followed by stirring for 6 h. Then, the resulting solution was heated at around 100 °C to obtain a brown powder.

To synthesize rGO, NaBH\textsubscript{4} (6 mmol) was dissolved in diluted ethanol and then a drop of mixed solution was withdrawn and dried on an aluminum plate. XRD was used to investigate the crystalline structures in the coated samples; diffraction patterns were recorded on a Philips PW1830 powder diffractometer operating at 40 kV voltage and 40 mA filament current. Spectra were acquired at the scanning rate of 2.5 deg/min with Cu K\textalpha\textsubscript{1} radiation in the 2θ range 20–60°. The weight fractions of anatase and rutile were calculated according to eq 1,\textsuperscript{29} where \(I_a\) and \(I_r\) are the intensity of the strongest reflections for rutile and anatase in (110) and (101) phases, individually.

\[ \frac{f_a}{f_r} = \frac{1}{(1 + 1.2(\frac{I_a}{I_r}))} \]  

For the composition analysis XRF was employed (ARL PERFORMA-II). The optical properties were investigated by UV–vis–near-IR diffuse reflectance spectra, recorded in the 220–2600 nm range with a Shimadzu UV 3600 Plus spectrophotometer equipped with an ISR-603 integrating sphere, and BaSO\textsubscript{4} was used as the reference material. The band gap was calculated on the basis of the reflectance UV–vis spectra after Kubelka–Munk conversion using the Tauc plot method.\textsuperscript{11} The FT-IR spectra of the prepared samples were recorded on a Bruker Tensor 27 spectrometer using a KBr pellet for sample preparation at room temperature. The Raman spectra were measured with a LABRAM HR800 equipped with a Pellet cooled CCD detector, and \(\lambda = 514\) nm excitation was done by an argon ion laser (Stabilite 2017, Spectra-Physics). The laser radiation was filtered by an interference filter and focused on the sample by an Olympus BX41 microscope. A 50x Olympus objective with a 0.7 numerical aperture was utilized. The Rayleigh radiation was rejected using Notch filters for the \(\lambda = 514\) nm laser line. Surface roughness of the coated samples was studied by atomic force microscopy (AFM) using a NT-MDT Specimen with an initial mirror polish surface was allowed to allow the deposition. Optical microscopy (OM) was used to assess possible cracking of the film before and after photodegradation test, in order to give a first evaluation of film structural stability (Leica INM 200). In addition, adhesion was evaluated by comparing OM images before and after making a scratched line at the coated samples using a diamond tip.

To evaluate self-cleaning properties, the wettability of the coated thin films was examined from the contact angle (CA) of a water droplet. These measurements were done on five predefined positions by a CCD camera connected to the computer via a PCI card. For each sample, the average contact angle was measured both under dark and after illumination for 30 min. Measurements were repeated after discoloration tests to check whether the coatings maintained their self-cleaning attitude also after possible discoloration.

2.3. Photocatalytic Degradation Performance. The photocatalytic activity of the coated thin films was characterized in methylene blue degradation under UV and visible light irradiation by spectrophotometry (UV–vis spectrophotometer, Thermo Scientific...
at the beginning of each month.

facing South. The colors of specimens were monitored for 6 months
them on a rack that was placed on the roof of a building, 45° dipping angle was chosen for

deposition of the soiling agents with 45° dipping angle was chosen for
These individual components were selected to simulate soiling of

soiling: black carbon, mineral dust, humic acids (organics), and
soiling agents that were selected in this experimental work to mimic natural

soiling present on urban surfaces is mostly including four soiling

compounds, respectively.

metallic roofs. Other environmental factors such as air-borne salts and ultraviolet rays are not investigated here because they were found to have a marginal effect on metals discoloration. The solution pH for the immersion tests was controlled in a range of 3–7 by changing the ratio of sulfuric acid and sodium hydroxide, and the specimens were immersed in the solution kept at 65 °C for 7 days to accelerate the procedure.

3. RESULTS AND DISCUSSION

3.1. Structure of the Coated Films. FESEM morphology images of synthesized composites are reported in Figure 1. On the basis of Figure 1a, TiO\textsubscript{2}@Si:Fe:rGO thin film shows apparently a uniform coating structure though more detail on particles distribution could be figured out from powder SEM morphology. Hence, images of the TiO\textsubscript{2}@Si and TiO\textsubscript{2}@Si:Fe:rGO composites are presented in Figure 1ab, respectively.

Table 1. Volume Fractions of Soiling Mixtures Used to Mimic the Soiling of Roofing Materials

| site               | artifact                | soiling components (%) |
|--------------------|-------------------------|------------------------|
| Cleveland, OH, USA | Peter B. Lewis building | carbon black 8, humic acid 0, dust 61, salt 31 |
| Glasgow, United Kingdom | Glasgow Science Centre | carbon black 6, humic acid 15, dust 52, salt 27 |
| Normandy, France  | Juno Beach Centre       | carbon black 12, humic acid 36, dust 28, salt 24 |
| Patras, Greece    | Patras museum           | carbon black 5, humic acid 8, dust 63, salt 24 |

Figure 1. SEM images of (a) structure of TiO\textsubscript{2}@Si:Fe:rGO thin film, (b, c) distribution of the nanoparticles in TiO\textsubscript{2}@Si and TiO\textsubscript{2}@Si:Fe:rGO composites, respectively.

Spectronic 200E) at the wavelength 686 nm where MB has its maximum absorbance.

In a typical experiment, the MB solution was prepared by adding dye to deionized water (10 to M), and then the coated specimens (1.7 × 1.9 cm\textsuperscript{2}) were put in the MB solution (40 mL). Before photodegradation, the specimens were kept in the dark for 50 min to reach adsorption−desorption equilibrium. The samples were then illuminated for 6 h under UV LED (500 mA, 3.8 V) and visible LED (700 mA, 3 V) with 3 cm LED−sample distance. Eventually, the photodegradation of MB was calculated as a function of the relative MB concentration versus time of reaction, C/C\textsubscript{0}, where C\textsubscript{0} is the initial concentration of MB solution and C is the concentration at sampling time, as derived from absorption values. Pseudo-first-order kinetics was hypothesized to control the rate of MB photodegradation, as observed in related scientific literature, so the slope of the curve of ln(C/C\textsubscript{0}) versus time of reaction was taken as MB photodegradation rate constant k.

2.4. Simulated Artificial Soiling. The typical composition of soiling present on urban surfaces is mostly including four soiling agents that were selected in this experimental work to mimic natural soiling: black carbon, mineral dust, humic acids (organics), and inorganic salts. The four soiling agents were mixed in different ratios in an aqueous mixture and applied to the samples’ surfaces. Dip deposition of the soiling agents with 45° dipping angle was chosen for ease of control and because soot deposition is typically waterborne. These individual components were selected to simulate soiling of metallic roo-

2.5. Simulated Acid Rain Test. Metals freshly exposed to atmosphere as building roofs and walls are immune to pitting or crevice corrosion; nevertheless, these metals may undergo color changing after prolonged exposure. In the case of titanium, discoloration is a result of the formation of oxide films on the surface, which show interference colors by interacting with light. It is proved that discoloration is accelerated in the presence of titanium carbide (TiC) on the titanium surface, which is introduced in the sheet during the manufacturing process. Even though color changing does not adversely affect the structural function of the metal components, it sometimes spoils the building appearance. Furthermore, it is proved that the rate of discoloration changed depending on the building location and material factors, even though different sheets were adjacent to each other on the same building.

To evaluate discoloration resistance of the samples, bare and coated titanium pieces were immersed in solutions of prescribed pH values simulating acid rain, obtained by adding H\textsubscript{2}SO\textsubscript{4} and NaOH to distilled water. Other environmental factors such as air-borne salts and ultraviolet rays are not investigated here because they were found to have a marginal effect on metals discoloration. The solution pH for the immersion tests was controlled in a range of 3–7 by changing the ratio of sulfuric acid and sodium hydroxide, and the specimens were immersed in the solution kept at 65 °C for 7 days to accelerate the procedure.
Figure 1b reveals that TiO$_2$ nanoparticles have smaller diameter and are dispersed on SiO$_2$ particle surfaces uniformly. In panel c, it could be observed that particles of TiO$_2$, SiO$_2$ and $\gamma$-Fe$_2$O$_3$ are well distributed on the surface of the rGO nanosheets and well served as substrate for the homogeneous distribution of the nanoparticles.

XRF analysis results are presented in Table 2. This table shows the chemical compositions in the sample of TiO$_2$@Si:Fe:rGO. According to the obtained results, the atomic ratios Ti/Si and Ti/Fe were calculated as 0.83 and 44, respectively.

XRD patterns and crystalline structures of the coated samples calcined at 600 °C are presented in Figure 2a,b and Table 3, respectively. It can be observed that the addition of SiO$_2$ to TiO$_2$ enhanced the thermal stability of anatase TiO$_2$, resulting in the retardation of the anatase-to-rutile phase transition. Indeed, the presence of SiO$_2$ can prevent the nucleation of rutile.$^{42}$ No peak for silica was observed; hence, SiO$_2$ is amorphous. Crystallite sizes obtained by Scherrer

| sample     | TiO$_2$ | SiO$_2$ | Fe$_2$O$_3$ | Na$_2$O | Al$_2$O$_3$ | K$_2$O | MnO | P$_2$O$_5$ | LOI     |
|------------|---------|---------|-------------|---------|-------------|--------|-----|------------|---------|
| analysis (%)| 38.79   | 34.85   | 0.915       | 0.1     | 0.09        | 0.07   | 0.01| 0.009      | 25.127  |

Figure 2. XRD patterns of (a) TiO$_2$@Si:Fe:rGO coated film and (b) anatase (101) and rutile (110) peaks of the samples after heat treatment at 600 °C. Raman spectra of (c) TiO$_2$ and TiO$_2$@Si:Fe:rGO and (d) GO samples in the wavenumber range from 100 to 1800 cm$^{-1}$.

| sample     | anatase (%) | rutile (%) | particle size (nm) |
|------------|-------------|------------|--------------------|
| TiO$_2$    | 54          | 46         | 31                 |
| TiO$_2$@Si | 64          | 36         | 28                 |
| TiO$_2$@Si:Fe | 59      | 41         | 24                 |
| TiO$_2$@Si:Fe:rGO | 71    | 29         | 23                 |

Table 2. XRF Analysis Results of the TiO$_2$@Si:Fe:rGO Sample

Table 3. Anatase Percentage in Crystalline TiO$_2$ (Calculated by Spurr Equation) and Anatase Particle Size (Calculated by Scherrer Equation)
equation were about 31 and 27 nm for the samples of TiO2 and TiO2@Si calcined at 600 °C, respectively. From literature it is known that for this transition to occur, anatase particles need to grow to a sufficient size, anatase being thermodynamically more stable for small nanoparticles. However, the contribution of bulk energy to total energy increases along with particle size. The transition to rutile takes place in a reconstructive process to decrease the total energy. In this way, the presence of SiO2 prevented phase transition by inhibiting the growth of the primary particles. The presence of SiO2 around TiO2 could efficiently delay the growth of nanoparticles likely due to the formation of the Ti–O–Si bond and because of the presence of amorphous SiO2 in contact with TiO2, which would hinder the growth of particles of TiO2.

In the TiO2@Si:Fe composite, since the ionic radius of Fe3+ (0.64 Å) is similar to the ionic radius of Ti4+ (0.68 Å), the replacement of iron in the matrix of titania is not only possible but also favorable. Thus, structural deformations and the presence of defects in the TiO2 crystals might have formed by the substitution of Ti4+ by Fe3+, which marginally reduces the crystallinity of TiO2. In the presence of Fe2O3 in the TiO2@Si:Fe composite, anatase TiO2 peaks decrease in intensity while peaks for rutile phase start appearing. This observation indicates that Fe(III) ions have substantial influence on the anatase titania phase in binary TiO2−Fe2O3 compounds. The incorporation of Fe2O3 in the titania matrix might have facilitated the anatase–rutile phase transformation, indicating the presence of Fe4+ ions as substitutes in titania crystals.

Also, the XRD pattern of this sample shows diffraction peaks corresponding to the (220), (311), (400), (511), and (440) planes of γ-Fe2O3 (Figure 2b) but no separate peak for rGO in the composite, possibly due to the low amount and low intensity of rGO. Moreover, the characteristic peak of rGO at 23.5° may be screened by the main peak of anatase TiO2 at 25.3°.

Interestingly, TiO2 phase transformation from anatase to rutile was retarded, as the anatase/rutile ratio increased by adding rGO in the sol; hence, the presence of carbon retarded the anatase-to-rutile transformation, as already reported in literature related to activated carbon. This may be attributed to the high surface area of rGO, as well as to a reduction of acidity and promotion of the dehydration of Ti4+ complex, by forming edge shared bonds, thus producing anatase phase by adding rGO in the nanocomposite. Indeed, a variation in the number of OH ligands in the Ti complex produced from Ti4+ hydrolysis was observed to change acidity.

Crystallographic structures of the prepared samples were also investigated by Raman spectroscopy and exhibited in Figure 2cd. Scattering at 145, 393, and 638 cm−1 are characteristic of anatase, while the one at 445 cm−1 is related to rutile. Given a smaller crystallite size and consequent relaxation of surface atoms, which are lacking adjacent atoms, peaks are slightly shifted in TiO2@Si:Fe:rGO. For this sample both characteristic bands of D and G peaks of GO, located at 1323 and 1570 cm−1, have shifted to lower frequencies in comparison with pure GO. This issue can be good evidence that GO was successfully reduced. Also, the intensity of I/I ratio peaks of TiO2@Si:Fe:rGO compared to pure GO was enhanced. It can be related to the reduced average size of sp2 domains during the reduction process of GO in TiO2@Si:Fe:rGO nanocomposite. Moreover, peaks at 513 and 700 cm−1 were attributed to the presence of γ-Fe2O3 in this nanocomposite.

The FT-IR spectra of the TiO2, TiO2@Si, γ-Fe2O3, and TiO2@Si:Fe:rGO samples is shown in the wavenumber range from 300 to 4000 cm−1 (Figure 3). TiO2 shows three bands including a broad absorption band at around 3500 cm−1, related to the stretching vibration of hydroxyl groups O–H bound to the surface of TiO2, an absorption band at 1627 cm−1, due to bending of Ti–OH, and an absorption band at 1381 cm−1 for Ti–O modes. In TiO2@Si, at ~970 cm−1 Ti–O–Si bonds appear, which are responsible for delayed anatase-to-rutile transformation (see XRD results). Moreover, the absorption band at 1104 cm−1 is attributed to the asymmetric Si–O–Si stretching vibration. γ-Fe2O3 shows strong bands at 453 and 544 cm−1 (Fe–O groups); these peaks were shifted to 448 and 538 cm−1 in TiO2@Si:Fe:rGO probably due to surface augmentation. Eventually, in TiO2@Si:Fe:rGO, the absorption peak at 1542 cm−1 could be related to the skeletal vibration of graphene.

3.2. Roughness and Transmittance. Figure 4 shows the surface topography of the coated films investigated by AFM. The AFM results imply that the average roughness (Ra) of the
films coated with TiO₂, TiO₂@Si, TiO₂@Si:Fe, and TiO₂@Si:Fe:rGO are 40, 47, 69, and 200 nm, respectively. As can be seen, R, has a slight increase with the addition of SiO₂ and γ-Fe₂O₃ and a sharp increase with the addition of rGO. This result could be correlated to sloppy stacking of rGO sheets, which results in larger channels around the rGO stacks, compatible with the variation in surface roughness. In other words, the rGO assembled layers in TiO₂@Si:Fe:rGO coating probably are in random order and, therefore, are very rough on the surface.

As highlighted above, only such protective coatings which satisfy the maintaining of the aesthetic appearance of artifacts through a transparent and colorless layer can be acceptable. Hence, coatings producing an apparent color difference with the substrate are not appropriate for metal protection from discoloration in modern and ancient artifacts, analogously to pointing already drawn in the case of glass both in the solar cell field and in the built environment.

Transmittance spectra in the range of 300–1000 nm were measured on glass slides coated with the different coating materials. As can be seen in Table 4, all coated layers have high transmittance over the entire visible wavelengths range, higher than 80% also in the case of the most complex TiO₂@Si:Fe:rGO coating. This proves that all coatings have good transparency.

Although transmittance slightly decreased with the addition of SiO₂, γ-Fe₂O₃, and rGO, all samples were still satisfactory from an aesthetic viewpoint. The increased surface roughness could be responsible for the slight loss in optical transmission in the TiO₂@Si:Fe:rGO coating (see Figure 4). Furthermore, TiO₂@Si:Fe film was observed to have a higher absorption intensity than TiO₂@Si (Figure S3). This issue could be a result of electronic interactions between TiO₂@Si and γ-Fe₂O₃ and efficient surface hybridization between these components. Moreover, the TiO₂@Si:Fe:rGO coated film exhibits the highest absorption compared to the other samples, which is expected due to the large optical absorption of both γ-Fe₂O₃ and rGO. None of these coatings generated a color perceivable by naked eyes easily. Spectrophotometric measurements in reflectance mode were performed as well to observe color differences with more details (Table 4). These measurements were done by placing the glass slide on a reference white surface before and after dip coating, to evaluate color changes induced by the application of the coating.

Table 4 also reports the average L*, a*, and b* color coordinates for uncoated and coated samples and the ΔE values calculated using the uncoated sample as reference. In all specimens, the coating induced a slight whitening, observable as a small increase in the luminance parameter (L*) in TiO₂ and TiO₂@Si. However, L* decreased again for samples TiO₂@Si:Fe and TiO₂@Si:Fe:rGO, while still higher than uncoated glass. The a* parameter increased in TiO₂@Si:Fe and TiO₂@Si:Fe:rGO samples as a result of the inherent red color brought about by γ-Fe₂O₃. Also, the b* coordinate slightly increased with the application of the coating, indicating a small reduction in the blue hue intensity. The values of the overall color difference ΔE (Table 4) indicate that the TiO₂ coating had no effect on the aesthetic appearance of the specimen with ΔE < 1, meaning not perceptible by human eyes. However, by adding other components, particularly γ-Fe₂O₃, ΔE values increased slightly, but still below 3, which means the color differences are perceptible only by close observation and are therefore more than acceptable.

3.3. Photocatalytic Degradation of MB under UV and Visible Light. The photocatalytic degradation of MB with TiO₂, rGO, TiO₂@Si, TiO₂@Si:Fe, and TiO₂@Si:Fe:rGO coated films under UV and visible light was investigated (Figure 5). First, samples were immersed in the dye solution in dark: the equilibrium adsorption state was reached in 30 min, and MB adsorption on all of the samples was negligible. Degradation extents after 6 h UV irradiation were about 32% for pure TiO₂, 20% for pure rGO, 54% for TiO₂@Si, and more than 76% and 83% for TiO₂@Si:Fe and TiO₂@Si:Fe:rGO, respectively. These amounts decreased to about 9%, 8%, 32%, 54%, and 71% under visible light.

Results were plotted as ln(C/C₀) versus time, obtaining linear trends with correlation coefficients (R²) higher than 0.9 as expected in the pseudo-first-order kinetics model. Kinetic constant (k) and band gaps of TiO₂, TiO₂@Si, TiO₂@Si:Fe, and TiO₂@Si:Fe:rGO coated films are reported in Table S5. The direct band gap values reported were determined by extrapolating the linear region of the Tauc’s plot of (αhν)½ against photon energy, starting from absorbance data reported in Figure S3.

The increased efficiencies obtained in each addition of a compound to the sol are explained in the following. SiO₂ both increased the anatase content and reduced particle size, avoiding agglomeration. γ-Fe₂O₃ improved charge separation and reduced electron–hole recombination by receiving in its conduction band (CB) electrons photogenerated in TiO₂ and transferring holes photogenerated in its valence band (VB) to that of TiO₂. The incorporation of rGO into the composite led to band gap reduction. In fact, as shown in Figure S3 light absorption increased in the TiO₂@Si:Fe:rGO nanocomposite, suggesting that this sample could exhibit an enhanced photocatalytic activity. Moreover, photogenerated electrons can easily migrate to the rGO sheets, leading to effective separation and decreased recombination rate of photogenerated electron and hole pairs. In fact, the sheets of rGO can act as an excellent speed charge transfer channel to...
enhance the charge separation efficiency. Also, rGO sheets keep nanoparticles dispersed, preventing agglomeration.68−71

3.4. Evaluation of Coating Integrity. As mentioned above, mechanical durability and excellent adhesion of coatings could guarantee them undamaged in long-term use in cultural heritage field. We compared durability and surface structure of the TiO2@Si:Fe:rGO and TiO2 coated films by OM analysis (Figure 6). While TiO2 presents several cracks on its surface, the TiO2@Si:Fe:rGO coated film presents a uniform and dense structure without cracks. Surface structure was evaluated even after long-time immersion and photocatalysis tests. While the TiO2@Si:Fe:rGO film remains unchanged during degradation tests, the amount of cracks in the TiO2 coating increased significantly after exposure to the acid environment due to its weak stability.

Scratch test was performed as a destructive method to test the adhesion of such soft coatings deposited on hard substrates such as titanium72 (Figure 6). As revealed by OM images, in the TiO2 film, dense networks of lateral cracks could be observed alongside the scratch trail on the surface. These cracks are much more apparent compared to the TiO2@Si:Fe:rGO film, with considerably fewer nucleation regions to cracking; in the latter case, by rubbing the scratched region with fingers, the scratched film was not easily removed.

Generally, the improvement in interfacial adhesion and mechanical stability could be related to better interactions

Figure 5. Photocatalytic activity for degradation of MB under (a,b) UV and (c,d) vis lights for MB, TiO2, TiO2@Si, TiO2@Si:Fe, and TiO2@Si:Fe:rGO coated films.

Table 5. Kinetic Constants of Photocatalytic MB Degradation under UV and Visible Light and Band Gaps of TiO2, rGO, TiO2@Si, TiO2@Si:Fe, and TiO2@Si:Fe:rGO Thin Films

| sample   | UV     | visible | band gap (eV) |
|----------|--------|---------|---------------|
|          | $K$ (min$^{-1}$) | $R^2$ | $K$ (min$^{-1}$) | $R^2$ | band gap (eV) |
| MB       | n/a    | 0.95    | n/a           | 0.93  | 3.20          |
| rGO      | n/a    | 0.94    | n/a           | 0.95  | 2.87          |
| TiO2     | −0.0013 | 0.93    | n/a           | 0.91  | 2.03          |
| TiO2@Si  | −0.0024 | 0.98    | −0.0012       | 0.94  | 2.30          |
| TiO2@Si:Fe| −0.0040 | 0.97    | −0.0022       | 0.97  | 2.87          |
| TiO2@Si:Fe:rGO | −0.0053 | 0.98    | −0.0032       | 0.98  | 2.26          |

*n/a = too low to be evaluated.
between the TiO$_2$@Si:Fe:rGO film and titanium surface. According to previous reports, the addition of SiO$_2$ and Fe$_2$O$_3$ to TiO$_2$ thin films could display very high adhesive and cohesive strengths in comparison with pure TiO$_2$ thin films.$^{73-78}$ Besides, the unique two-dimensional carbon-based structures such as GO (and rGO) sheets could act effectively at deflecting cracks at the metal/film interface, also improving coating density and adhesion through a multilayer structure.$^{79-84}$

### 3.5. Self-Cleaning and Discoloration Resistance Tests.

Wettability, measured by water contact angle (CA), is a critical property in self-cleaning studies depending on the chemical composition and the morphology of the solid surfaces.$^{85-87}$ The surface wettability of the coated surfaces was investigated by measuring CA in the dark and after light irradiation for 30 min. The shape of the water droplet and CA values are given in Figure 7.

CA values measured before and after light irradiation show significant differences between coated substrates. In particular, water CA on TiO$_2$@Si coating decreases after exposure to light, probably due to SiO$_2$, which suppresses the transformation of anatase to rutile and the crystal growth of anatase (see Figure 2a,b). Furthermore, it favors water adsorption as shown by increased surface hydroxyl groups observed in FTIR characterization, which helps superhydrophilicity be maintained for an extended period.$^{88}$

Clearly, by adding γ-Fe$_2$O$_3$ to TiO$_2$/SiO$_2$ structure, wettability under light irradiation further increased thanks to the improved charge separation and decreased recombination phenomena.$^{89}$ Indeed, the introduction of Fe$^{3+}$ ions in TiO$_2$@Si:Fe film is responsible for a reduction in the photogenerated hole–electron recombination rate. Then, more photogenerated holes can oxidize the lattice O$_2^-$ anions, creating more oxygen vacancies; eventually, water molecules may coordinate into the oxygen vacancy sites, leading to dissociative adsorption of water molecules on the surface, increasing surface hydroxyl content and reducing CA upon irradiation.$^{30}$

The decrease in CA appeared much more abrupt by adding rGO, both in the dark and under light. Indeed, rGO had a major effect on wettability: after illumination, water CA changed clearly from hydrophilic (CA 41.3°) to superhydrophilic with CA < 2°. Furthermore, CA remained relatively constant even after turning off light and approached the initial dark state gradually.

The role of rGO on coating wettability could be attributed to the following mechanism. With the aid of UV irradiation, oxygen molecules on graphene are motivated from the ground spin-triplet state to a higher energy spin-singlet, resulting in electron–hole pairs which in turn form superoxide anions.$^{91,92}$ This leads to depletion of a large number of oxygen atoms, which in turn results in a continuous diffusion of oxygen vacancies on the rGO surface. Water molecules in air capture these vacancies to generate hydroxyl radicals, which bind to the carbon atom of the rGO in a supramolecular form (rather than in the form of a covalent bond) converting the hydrophilic TiO$_2$@Si:Fe:rGO composite (in the dark) into superhydrophilic TiO$_2$@Si:Fe:rGO under irradiation.$^{93,94}$ The adsorption of water molecules on the rGO defect surface further imparts it with superhydrophilicity. Under dark, these supramolecules gradually disappear on account of a lack of adequate energy supply.$^{94}$ Subsequently, oxygen molecules substitute for water molecules deposited on the graphene defect surface, which induces the return to hydrophilicity. If hydroxyl radicals were attached to the carbon atom of rGO by covalent bonds, they would not disappear in the absence of light. In the case of rGO, the hydroxyl groups are covalently bound to carbon atoms, so after a time in the dark storage, the rGO surface is not capable of converting into the initial CA.
enhancing hydrophilicity.95,96 by the increasing surface roughness (Figure 4), and thus presence of TiC on the surfaces decreases significantly (see Figure 8). Indeed, TiC dissolves more than ten times more easily in a sulfuric acid solution than metallic titanium does.37 It is presumed that discoloration in the atmosphere is an interference color caused by the dissolution of titanium in acid rain, which forms TiO2 on the sheet surfaces; the oxide film grows thicker, causing the interference color when thickness exceeds a few tens of nanometers.4 Namely, the color difference of TiO2 and TiO2@Si sheets increased with immersion time in acid rain, reaching values of 7 and 10, respectively.

Furthermore, results in Figure S6 and Table S2 demonstrate that the wettability of the TiO2@Si:Fe:rGO thin film is not affected significantly by the discoloration tests. Interestingly, the film not only could protect titanium from discoloration but also kept its own integrity against chemical or physical decomposition, which could result in crack formation. In contrast, TiO2 wettability (as a comparison) showed an increase by about 10° to 15° both in dark and under illumination after discoloration. As the TiO2 film could not prevent titanium from changing color, i.e., from oxidizing (see Figure 9), then the new oxide film growth may have damaged the sol–gel derived TiO2 film.37 Consequently, this led to a change in wettability, tending more to hydrophobicity.

Figure 10 shows the color difference developed in simulated soiling tests for uncoated and coated titanium specimens exposed to the five different soiling conditions simulating the different environments considered. As can be seen, the self-cleaning performance of the specimens depends on the type of pollutants, which are different on the basis of the place. As expected, all of the coated sheets show lower ΔE than the bare sheet, while coated films do not show similar behaviors. On the basis of the results, it can be discussed that TiO2@Si:Fe:rGO coated film could act more efficiently than other films thanks to its significant self-cleaning properties. This result was
expected considering its superhydrophilicity and excellent photoactivity after illumination, as discussed above. Furthermore, results (Figure S7 and Table S3) confirm that the TiO₂@Si:Fe:rGO film could keep its appearance almost unchanged even after the soiling tests.

Soiling in real outdoor conditions was actually performed by exposing samples to the polluted atmosphere of Milan, Italy. Figure 11 shows ΔE values measured at the beginning of each month during the six months exposure. Moreover, the local average rainfall and sunlight irradiation index obtained from “air.plumelabs” and “weather-atlas” databases during this period are indexed in the graph.

The high pollution concentration in September (41.2 μg/m³) (Table 6) gave rise to an initial steep increase of ΔE values for all samples, coated and uncoated. As expected, bare titanium showed higher ΔE due to the lack of any protective self-cleaning layer on the surface. Interestingly, in the case of the TiO₂@Si and TiO₂@Si:Fe films, the coated layers preserved the titanium sheet by setting self-cleaning conditions, benefiting from considerable rainfall and UV irradiation. Afterward, color-changing increased unfavorably, especially on bare titanium and TiO₂ coated substrates. In the case of TiO₂@Si and TiO₂@Si:Fe films, these changes were more significant compared to the contribution of the first month, due to low related rainfall and UV which decreased the chances of self-cleaning.

The most noticeable results were obtained once again on the TiO₂@Si:Fe:rGO coated film after six months of exposure, with an overall ΔE lower than 1, meaning that the appearance did not show any color difference detectable by eye, meaning that it maintained self-cleaning properties also in a period of low rainfall and UV.

4. CONCLUSION

The fabricated transparent TiO₂@Si:Fe:rGO composite showed excellent photoactivity and wettability, behaving well in self-cleaning applications. Addition of SiO₂ improves the morphology, crystalline structure, and surface hydroxylation of TiO₂ nanoparticles and γ-Fe₂O₃ decreases the recombination rate of e⁻/h⁺ pairs and largely improves photocatalytic activity under visible light. Moreover, the rGO sheets also reduce recombination and improve nanoparticle dispersion. rGO also showed a significant effect on wettability, leading to a lower contact angle of the TiO₂@Si:Fe:rGO coated surface in dark and to superhydrophilicity under irradiation. On the basis of this study, the prepared TiO₂@Si:Fe:rGO composite coating is an efficient photocatalyst for degradation of contaminants under UV and visible light illumination and allows one to convert surface wettability to superhydrophilicity. Furthermore, the film revealed a proper adhesion integrity even after photodegradation tests, as well as superhydrophilicity even after discoloration tests.

Concerning the self-cleaning behavior, all coatings were sufficiently transparent to avoid alteration of the substrate color. Moreover, simulation of contact with acid rain caused negligible color change for TiO₂@Si:Fe:rGO coated surface. On the basis of simulated soiling tests, the same coating allowed efficient self-cleaning thanks to its significant superhydrophilicity and excellent photoactivity. These results were confirmed by roofing tests, where again negligible color changes were induced by atmospheric exposure of the coated samples. These results pave the way for potential use of the produced coating as a protective layer on metallic substrates working outdoors, such as in the built environment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c06792.

Synthesis schematic representation, artifacts photographs, samples’ absorbance spectra, discoloration photographs, samples’ color differences, XRD results, contact angle photographs, and photographs of samples after soiling tests (PDF)
AUTHOR INFORMATION

Corresponding Author
Maria Vittoria Diamanti − Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan 20133, Italy; orcid.org/0000-0003-4785-2473; Email: mariavittoria.diamanti@polimi.it

Authors
Maryam Mokhtarifar − Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan 20133, Italy
Reyhaneh Kaveh − Department of Chemistry, Sharif University of Technology, Tehran 11365-11155, Iran
Mojtaba Bagherzadeh − Department of Chemistry, Sharif University of Technology, Tehran 11365-11155, Iran
Andrea Lucotti − Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan 20133, Italy
Maria Pia Pedefferi − Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan 20133, Italy

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c06792

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by MIUR, Grant PRIN 2015WBEP3H "Monitoraggio, Consolidamento, Conservazione e Protezione di Beni Culturali".

REFERENCES

(1) Mokhtarifar, M.; Pedefferi, M. P.; Diamanti, M. V. Towards a Better Preservation of Current and Future Outdoor Architectural Heritage: Maximum Suppression of Discolouration in Anodized and Non-Anodized Titanium Sheets. Environ. Technol. Rev. 2020, 9, 37.
(2) Screpans, A.; De Marco, A. Corrosion on Cultural Heritage Buildings in Italy: A Role for Ozone? Environ. Pollut. 2009, 157 (5), 1513–1520.
(3) Bernard, M. C.; Joiret, S. Understanding Corrosion of Ancient Metals for the Conservation of Cultural Heritage. Electrochim. Acta 2009, 54 (22), 5199–5205.
(4) Diamanti, M. V.; Aliverti, S.; Pedefferi, M. P. Decoupling the Dual Source of Colour Alteration of Architectural Titanium: Soiling or Oxidation? Corros. Sci. 2013, 72, 125–132.
(5) Goidanich, S.; Brunk, J.; Herting, G.; Arenas, M. A.; Odnevall Wallinder, I. Atmospheric Corrosion of Brass in Outdoor Applications. Patina Evolution, Metal Release and Aesthetic Appearance at Urban Exposure Conditions. Sci. Total Environ. 2011, 412–413, 46–57.
(6) Pelegrini, R. T.; Freire, R. S.; Duran, N.; Bertazzoli, R. Photoassisted Electrochemical Degradation of Organic Pollutants on a DSA Type Oxide Electrode: Process Test for a Phenol Synthetic Solution and Its Application for the E1 Bleach Kraft Mill Effluent. Environ. Sci. Technol. 2001, 35 (13), 2849–2853.
(7) Vohra, M. S.; Tanaka, K. Photocatalytic Degradation of Aqueous Pollutants Using Silica-Modified TiO2. Water Res. 2003, 37 (16), 3992–3996.
(8) Hepel, M.; Luo, J. Photoelectrochemical Mineralization of Textile Dye Dye Pollutants Using Nanocrystalline WO3 Electrodes. Electrochim. Acta 2001, 47 (5), 729–740.
(9) Pauporté, T.; Rathousky, J. Electrodeposited Mesoporous ZnO Thin Films as Efficient Photocatalysts for the Degradation of Dye Pollutants. J. Phys. Chem. C 2007, 111 (21), 7639–7644.
(10) Paolini, R.; Borroni, D.; Pedefferi, M. P.; Diamanti, M. V. Self-Cleaning Building Materials: The Multifaceted Effects of Titanium Dioxide. Constr. Build. Mater. 2018, 182, 126–133.
(11) Diamanti, M. V.; Paolini, R.; Rossini, M.; Aylan, A. B.; Zinzi, M.; Poli, T.; Pedefferi, M. P. Long Term Self-Cleaning and Photocatalytic Performance of Anatase Added Mortars Exposed to the Urban Environment. Constr. Build. Mater. 2015, 96, 270–278.
(12) Puzeat, E.; Pichat, P. Studying TiO2 Coatings on Silica-Covered Glass by O2 Photosorption Measurements and FTIR-ATR Spectrometry: Correlation with the Self-Cleaning Efficacy. J. Photochem. Photobiol., A 2003, 160 (1–2), 127–133.
(13) Kalousek, V.; Tscharich, J.; Bahnemann, D.; Rathousky, J. Mesoporous Layers of TiO2 as Highly Efficient Photocatalysts for the Purification of Air. Superlattices Microstruct. 2008, 44 (4–5), 506–513.
(14) Zvonkina, I. J.; Hilt, M. Strategies for Developing Multi-Functional, Self-Healing Coatings for Corrosion Prevention and Other Functions. In Handbook of Smart Coatings for Materials Protection 2014, 105–120.
(15) Banerjee, S.; Pillai, S. C.; Falaras, P.; O’Shea, K. E.; Byrne, J. A.; Dionysiou, D. D. New Insights into the Mechanism of Visible Light Photodegradation. J. Phys. Chem. Lett. 2014, 5 (15), 2543–2554.
(16) Nguyen, P. T. N.; Salim, C.; Kurniawan, W.; Hinode, H. A Non-Hydrolytic Sol-Gel Synthesis of Reduced Graphene Oxide/TiO2 Microsphere Photocatalysts. Catal. Today 2014, 230, 166–173.
(17) Rezaei, M.; Salem, S. Photocatalytic Activity Enhancement of Anatase-Graphene Nanocomposite for Methylene Removal: Degradation and Kinetics. Spectrochim. Acta, Part A 2016, 167, 41–49.
(18) Kwon, C. H.; Kim, J. H.; Jung, I. S.; Shin, H.; Yoon, K. H. Preparation and Characterization of TiO2-SiO2 Nano-Composite Thin Films. Ceram. Int. 2003, 29, 851.
(19) Sun, S.; Deng, T.; Deng, H.; Chen, Y.; Chen, W. Preparation of Nano-TiO2-Coated SiO2Microsphere Composite Material and Evaluation of Its Self-Cleaning Property. Nanomaterials 2017, 7, 367.
(20) Dai, X.; Lu, G.; Hu, Y.; Xie, X.; Wang, X.; Sun, J. Reversible Redox Behavior of Fe 2 O 3 /TiO2 Composites in the Gaseous Photodegradation Process. Ceram. Int. 2019, 45, 13187.
(21) Alsharaee, E. H.; Bora, T.; Soliman, A.; Ahmed, F.; Bharath, G.; Ghoniem, M. G.; Abu-Salah, K. M.; Dutta, J. Sol-Gel-Assisted Microwave-Derived Synthesis of Anatase Ag/TiO2/Go Nanohybrids toward Efficient Visible Light Phenol Degradation. Catalysts 2017, 7, 133.
(22) Weinstein, S. J.; Ruschak, K. J. Dip Coating on a Planar Non-Vertical Substrate in the Limit of Negligible Surface Tension. Chem. Eng. Sci. 2001, 56, 4957.
(23) Hu, Z.; Zhang, J.; Xiong, S.; Zhao, Y. Annealing-Free, Air-Processed and High-Efficiency Polymer Solar Cells Fabricated by a Dip Coating Process. Org. Electron. 2012, 13, 142.
(24) Rajabi, N.; Heshmatpour, F.; Malekfar, R.; Bahari-Poor, H. R.; Abyar, S. A Comparative Study of Dip Coating and Spray Pyrolysis Methods for Synthesizing ITO Nanolayers by Using Ag Colloidal Sol. Mater. Sci.-Pol. 2014, 32, 102.
(25) Grosso, D. How to Exploit the Full Potential of the Dip-Coating Process to Better Control Film Formation. J. Mater. Chem. 2011, 21, 17033.
(26) Faustini, M.; Louis, B.; Albouy, P. A.; Kuemmel, M.; Grosso, D. Preparation of Sol-Gel Films by Dip-Coating in Extreme Conditions. J. Phys. Chem. C 2010, 114, 7637.
(27) Guglielmi, M.; Colombo, P.; Peron, F.; Mancinelli Degli Esposti, L. Dependence of Thickness on the Withdrawal Speed for TiO2 and SiO2 Coatings Obtained by the Dipping Method. J. Mater. Sci. 1992, 27, 5052.
(28) Ceratti, D. R.; Louis, B.; Paquez, X.; Faustini, M.; Grosso, D. A New Dip Coating Method to Obtain Large-Surface Coatings with a Minimum of Solution. Adv. Mater. 2015, 27, 4958.
(29) Bottein, T.; Loizillon, J.; Grosso, D. Full Investigation of Angle Dependence in Dip-Coating Sol-Gel Films. J. Phys. Chem. B 2017, 121, 6220.
(67) Husain, A. A. F.; Hasan, W. Z. W.; Shafie, S.; Hamidon, M. N.; Pandey, S. S. A Review of Transparent Solar Photovoltaic Technologies. Renewable Sustainable Energy Rev. 2018, 49, 797–806.

(68) Wen, X.; Zhao, S.; Asuha, S. Preparation of Nitrogen-Doped Mesoporous TiO2/RGO Composites and Its Application to Visible Light-Assisted Photocatalytic Degradation. J. Nanomater. 2019, 1, 1.

(69) Liu, Y. Hydrothermal Synthesis of TiO2-RGO Composites and Their Improved Photocatalytic Activity in Visible Light. RSC Adv. 2014, 4, 36040.

(70) Tan, L.-I.; Ong, W.-J.; Chai, S.-P.; Mohamed, A. Reduced Graphene Oxide-TiO2 Nanocomposite as a Promising Visible-Light-Active Photocatalyst for the Conversion of Carbon Dioxide. Nanoscale Res. Lett. 2013, 8, 465.

(71) Hu, X. S.; Shen, Y.; Zhang, Y. T.; Nie, J. Preparation of Flower-like CuS/Reduced Graphene Oxide(RGO) Photocatalysts for Enhanced Photocatalytic Activity. J. Phys. Chem. Solids 2013, 74, 562.

(72) Bull, S. J.; Berasategui, E. G. An Overview of the Potential of Quantitative Coating Adhesion Measurement by Scratch Testing. Tribol. Int. 2006, 39, 99.

(73) Jia, Q.; Zhang, Y.; Wu, Z.; Zhang, P. Tribological Properties of Anatase TiO 2 Sol-Gel Films Controlled by Mutually Soluble Dopants. Tribol. Lett. 2007, 26, 19.

(74) Chun, H. D.; Kim, J. S.; Yoon, S. M.; Kim, C. G. Physical Properties and Photocatalytic Performance of TiO2 Coated Stainless Steel Plate. Korean J. Chem. Eng. 2001, 18, 908.

(75) Dam Le, D.; Dung Tang, T. M.; Thanh Chau, V.; Chien, P. The Fabrication of Visible Light Responsive Ag-SiO2 Co-doped TiO2 Thin Films by the Sol-Gel Method. Adv. Nat. Sci.: Nanosci. Nanotechnol. 2010, 1, 015007.

(76) Li, Z.; Hou, B.; Xu, Y.; Wu, D.; Sun, Y.; Hu, W.; Deng, F. Comparative Study of Sol-Gel-Hydrothermal and Sol-Gel Synthesis of Titania-Silica Composite Nanoparticles. J. Solid State Chem. 2005, 178, 1395.

(77) Momeni, M.; Golestani-Fard, F.; Saghafian, H.; Barati, N.; Khanamahdi, A. Development of Visible Light Activated TiO2 Thin Films on Stainless Steel via Sol Spraying with Emphasis on Microstructural Evolution and Photocatalytic Activity. Appl. Surf. Sci. 2015, 357, 1902.

(78) Momeni, M.; Saghafian, H.; Golestani-Fard, F.; Barati, N.; Khanamahdi, A. Effect of SiO2 Addition on Photocatalytic Activity, Water Contact Angle and Mechanical Stability of Visible Light Activated TiO2 Thin Films Applied on Stainless Steel by a Sol Gel Method. Appl. Surf. Sci. 2017, 382, 80.

(79) Zhang, X.; Fan, X.; Yan, C.; Li, H.; Zhu, Y.; Li, X.; Yu, L. Interfacial Microstructure and Properties of Carbon Fiber Composites Modified with Graphene Oxide. ACS Appl. Mater. Interfaces 2012, 4, 1543.

(80) Da, S. X.; Wang, J.; Geng, H. Z.; Jia, S. L.; Xu, C. X.; Li, L. G.; Shi, P. P.; Li, G. High Adhesion Transparent Conducting Films Using Graphene Oxide Hybrid Carbon Nanotubes. Appl. Surf. Sci. 2017, 392, 1117.

(81) Lu, H.; Yao, Y.; Huang, W. M.; Hui, D. Covalently Functionalized Carbon Fiber by Grafted Self-Assembled Graphene Oxide and the Synergistic Effect on Polymeric Shape Memory Nanocomposites. Composites, Part B 2014, 67, 290.

(82) Ning, H.; Li, J.; Hu, N.; Yan, C.; Liu, Y.; Wu, L.; Liu, F.; Zhang, J. Interlaminar Mechanical Properties of Carbon Fiber Reinforced Plastic Laminates Modified with Graphene Oxide Interleaf. Carbon 2015, 91, 224.

(83) Son, G. C.; Hwang, D. K.; Jang, J.; Chee, S. S.; Cho, K.; Myoung, J. M.; Ham, M. H. Solution-Processed Highly Adhesive Graphene Coatings for Corrosion Inhibition of Metals. Nano Res. 2019, 12, 19.

(84) Moon, I. K.; Kim, J. I.; Lee, H.; Hur, K.; Kim, W. C.; Lee, H. 2D Graphene Oxide Nanosheets as an Adhesive Over-Coating Layer for Flexible Transparent Conductive Electrodes. Sci. Rep. 2013, 3, 1112.

(85) Wang, J.; Zhang, Y.; Wang, S.; Song, Y.; Jiang, L. Bioinspired Colloidal Photonic Crystals with Controllable Wettability. Acc. Chem. Res. 2011, 44 (6), 405–415.

(86) Wang, J.; Wen, Y.; Hu, J.; Song, Y.; Jiang, L. Fine Control of the Wettability Transition Temperature of Colloidal-Crystal Films: From Superhydrophilic to Superhydrophobic. Adv. Funct. Mater. 2007, 17 (2), 219–225.

(87) Li, Q.; Guo, Z. Lubricant-Infused Slippery Surfaces: Facile Fabrication, Unique Liquid Repellence and Antireflective Properties. J. Colloid Interface Sci. 2019, 536, 507–515.

(88) Huang, T.; Huang, W.; Zhou, C.; Sito, Y.; Huang, H. Superhydrophobicity of TiO2/SiO2 Thin Films: Synergistic Effect of SiO2 and Phase-Separation-Induced Porous Structure. Surf. Coat. Technol. 2012, 213, 126–132.

(89) Yu, J. C.; Ho, W.; Lin, J.; Yip, H.; Wong, P. K. Photocatalytic Activity, Antibacterial Effect, and Photoinduced Hydrophilicity of TiO2 Films Coated on a Stainless Steel Substrate. Environ. Sci. Technol. 2003, 37 (10), 2296–2301.

(90) Yu, J.; Zhou, M.; Yu, H.; Zhang, Q.; Yu, Y. Enhanced Photoinduced Super-Hydrophilicity of the Sol-Gel-Derived TiO2 Thin Films by Fe-Doping. Mater. Chem. Phys. 2006, 95 (2–3), 193–196.

(91) Feng, X.; Zhai, J.; Jiang, L. The Fabrication and Switchable Superhydrophilicity of TiO2 Nanorod Films. Angew. Chem., Int. Ed. 2005, 44 (32), S115–S118.

(92) Kim, S. B.; Hwang, H. T.; Hong, S. C. Photocatalytic Degradation of Volatile Organic Compounds at the Gas-Solid Interface of a TiO2 Photocatalyst. Chemosphere 2002, 48 (4), 437–444.

(93) Luo, Z.; Pinto, N. J.; Davila, Y.; Charlie Johnson, A. T. Controlled Doping of Graphene Using Ultraviolet Irradiation. Appl. Phys. Lett. 2012, 100 (25), 253108.

(94) Duong, D. L.; Han, G. H.; Lee, S. M.; Gunes, F.; Kim, E. S.; Kim, S. T.; Kim, H.; Ta, Q. H.; So, K. P.; Yoon, S. J.; Chae, S. J.; Jo, Y. W.; Park, M. H.; Chae, S. H.; Lim, S. C.; Choi, J. Y.; Lee, Y. H. Probing Graphene Grain Boundaries with Optical Microscopy. Nature 2012, 490 (7419), 235–239.

(95) Bharti, B.; Kumar, S.; Kumar, R. Superhydrophilic TiO2 Thin Film by Nanometer Scale Surface Roughness and Dangling Bonds. Appl. Surf. Sci. 2016, 364, 51–60.

(96) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. Light-Induced Amphiphilic Surfaces [4]. Nature 1997, 388, 431–432.

(97) Maeda, H.; Kobayashi, T.; Konishi, S. Patternning of Wettability Using the Photocatalytic Decomposition of Hydrophobic Self-Assembled Monolayer on the TiO2 Pattern. Jpn. J. Appl. Phys. 2017, 56, 06GN09.