

## Titania-coated glass microballoons and cenospheres for environmental applications

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**Abstract** Functional titania coatings on glass microballoons (GMBs) and cenospheres have a broad range of potential environmental applications, primarily in purification of drinking water and treatment of industrial wastewater. The heterogeneous photocatalytic capabilities of titania films and particles have been extensively examined in the literature as effective alternatives to current technologies. Although the chemistry of titania films for photocatalysis has been studied, titania-coated GMBs have not yet been extensively considered and the materials science aspects of the titania-GMB and titania-cenosphere systems have not been addressed. We have examined the microstructure, morphology, and mechanical properties of titania coatings on both cenospheres and commercially produced GMBs. Scanning electron microscopy was used to examine coating coverage and defects. Energy dispersive X-ray spectroscopy and Raman spectroscopy were used for element and phase identification, respectively. Hardness and modulus measurements of the titania coatings and the GMB and cenosphere materials were done by nanoindentation. Additionally, the photocatalytic activity of the titania-coated GMB system was tested on Procion

Red dye using two different types of mixing, a magnetic stirrer and an aeration bubbler apparatus. The titania coatings showed good coverage and retention except in the case of magnetic stirring, where significant coating loss was observed.

### Introduction

Glass microballoons (GMBs) without functional coatings are being applied in an expanding range of applications primarily due to improvements in manufacturing processes and corresponding improvements in the available range of physical and mechanical properties. Generally, these hollow spheres have wall thicknesses of 1–3  $\mu\text{m}$  and diameters between 5 and 120  $\mu\text{m}$ , although larger and smaller GMBs are also produced. GMBs have good specific mechanical properties, good sound and thermal damping and low densities, and because of these characteristics they have been used extensively in certain polymer composites and syntactic foams. Although GMBs have been predominantly used as filler materials since their development in the mid-twentieth century, the improved properties that have been realized are opening new applications [1]. Beyond the traditional applications that incorporate GMBs into various composites, these materials are being considered for applications in which functional coatings are applied and the GMBs are not bound within a composite matrix.

Among the metal, polymer and ceramic coatings applied to GMBs, titania is of particular interest because of its semiconducting properties in water. In the presence of UV radiation greater or equal in energy to its band gap,  $E_G = 3.02 \text{ eV}$ , or a wavelength less than or equal to

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approximately 400 nm, titania creates electron-hole pairs [2]. The electrons and holes combine with dissolved oxygen and water to form aggressive free radicals, such as hydroxyls, peroxides, and superoxides, which are destructive to many organic compounds and microorganisms found in water. Thus, titania is being studied for its profound potential impact on water purification. Heterogeneous photocatalysis using titania films or particles can break down organic solvents, pesticides, oils, and dyes, as well as, destroy and break down microbiological water pollutants such as bacteria, protozoa, and viruses [2–13]. Although the implications of titania to the purification of drinking water and to the treatment of wastewater from numerous industries is quite profound, the search for an appropriate substrate for the titania has emerged as an obstacle. While coatings of large structures lack sufficient surface area for effective reaction rates, aqueous slurries of small titania particles also have disadvantages. The titania particles must be removed from the water by flocculation and sedimentation processes, complicating the processing and adding significant capital and operational expense.

The use of GMBs as a substrate has the advantage of providing large surface area to volume ratios, while having low densities. The low density of the coated GMBs allows them to float on water, thus simplifying their separation in industrial scale processes, while simultaneously positioning them on the surface of the water where ambient UV radiation is strongest. Additional benefits of the system include the nontoxic nature of titania, the use of ambient solar UV radiation as an energy source and the fact that titania, being a catalyst, is not consumed in the reactions.

As a result of the noted photocatalytic properties of titania and the stated potential advantages of titania-coated hollow microspheres, research has been conducted to consider the capability of titania-coated cenospheres and GMBs to breakdown several classes of pollutants. Shifu and Gengyu examined the effect of UV-irradiated titania-coated cenospheres on the breakdown of organophosphorus pesticides [14]. The results of their experiments showed that after 420 minutes of solar UV radiation, the organophosphorus pesticides were completely photocatalytically degraded into  $\text{PO}_4^{-3}$ . In a study performed by Preis et al. [15], aromatic aminocompounds, which are residues from rocket fuel and are a contributor to groundwater pollution in Estonia, were discovered to be effectively degraded through the treatment of UV-irradiated titania in its anatase form. Furthermore, because Preis et al. [15] examined the effectiveness of both slurries of titania particles and of titania attached to hollow glass microspheres, this study allowed a comparison of these two possible techniques. They concluded that the use of titania-coated microspheres had produced the advantage of treating wastewater pollution without constant agitation, unlike slurries of titania

particles which require continuous stirring to have an effect. Furthermore, without the act of agitation, Preis et al. [15] concluded that the titania coating would be less likely to become separated from its substrate. Despite these postulations, no evidence has been noted in the literature examining the coating integrity of titania-coated cenospheres or GMBs. In this paper, we report on the microstructure, morphology, and mechanical properties of titania-coated cenospheres and GMBs to elucidate their viability as candidate materials for environmental applications.

Additionally, we investigated the ambient solar photocatalysis of Procion Red, an industrial dye, using two different forms of mixing, a magnetic stirrer and an aeration bubbler apparatus. Synthetic dyes are generally very stable compounds that are difficult to breakdown by conventional techniques, such as biodegradation, adsorption, or oxidation [11]. Due to toxicity and esthetic considerations, these dyes are undesirable waste byproducts of textile industrial effluent.

## Materials and experimental procedure

Titania-coated GMBs and cenospheres were produced via proprietary processes and provided by Trelleborg Emerson Cuming, Inc. (Mansfield, MA, USA). The uncoated GMBs used were also produced by Trelleborg Emerson Cuming, Inc., ranging in average diameter from 47 to 54  $\mu\text{m}$ . The uncoated cenospheres were produced by Trelleborg Fillite (Norcross, GA, USA). Cenospheres are derived from fly ash, a waste byproduct of coal fired power plant operation and the cenospheres tested had average diameter ranging from 63 to 67  $\mu\text{m}$ .

Samples for scanning electron microscopy (SEM) were prepared on adhesive carbon mounting tabs and sputter coated with Au–Pd for conductivity. A Philips 515 SEM (Eindhoven, Netherlands) equipped with a lanthanum hexaboride filament and a JEOL 7000 (Tokyo, Japan) with a field emission source were used. The Philips SEM was also equipped with a Fisons-KeveX energy dispersive X-ray spectrometer (San Carlos, CA, USA). Particle size measurements were performed with a Coulter LS200 particle size analyzer (Beckman Coulter, Fullerton, CA, USA).

Hardness and modulus measurements were made on an XP-II nanoindenter (MTS-Nano, Oak Ridge, TN, USA). Micro-Raman spectroscopy was performed on a Labram-HR and a Dilor XY instruments, both by Jobin-Yvon, a division of the Horiba Group. All Raman experiments used a green excitation at 514.532 nm wavelength with approximately a 1  $\mu\text{m}$  beam diameter.

Preliminary experiments were initiated to investigate the viability of titania-coated GMBs in industrial applications

and to verify the photocatalytic activity of the system. The photocatalytically assisted degradation of Procion Red MX-5B dye (Sigma Aldrich, St. Louis, MO, USA) was tested under ambient solar UV radiation using two types of mixing, a magnetic stirrer and an aeration bubbler apparatus. The dye was mixed with tap water from Birmingham, Alabama at a ratio of 23 mg/L. Two control samples were used that did not contain titania-coated GMBs, one kept in complete darkness and the other exposed to the same ambient solar UV radiation as the test samples. Approximately 1 g of titania-coated GMBs were put in each of two beakers containing 50 mL of water. One beaker used a magnetic stirrer and the other an aerating stone with forced air. These two beakers were placed along with one of the controls in direct sunlight during June and July of 2007 at a latitude of 33.57° N. The aqueous dye solution was separated from the GMBs by settling followed by centrifuging, and the breakdown of color was measured by absorbance at a wavelength of 510 nm with a Cary 100 UV–visible spectrophotometer (Varian, Inc., Palo Alto, CA, USA).

## Results and discussion

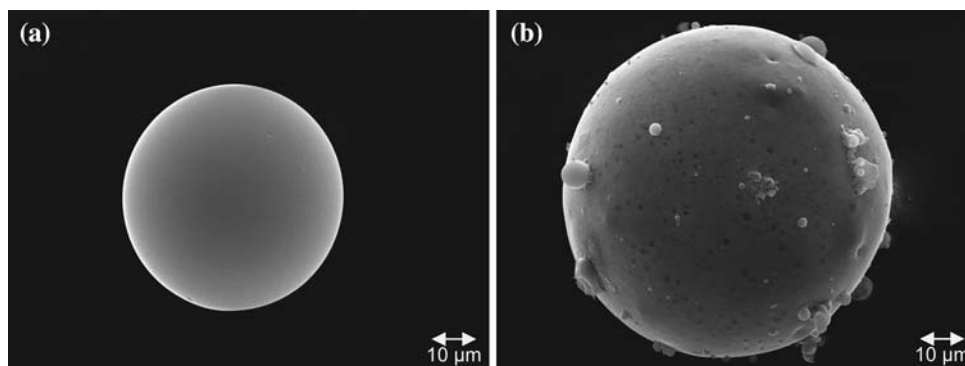
### Microstructure and morphology

The two types of hollow microspheres that were investigated included manufactured GMBs, which have an

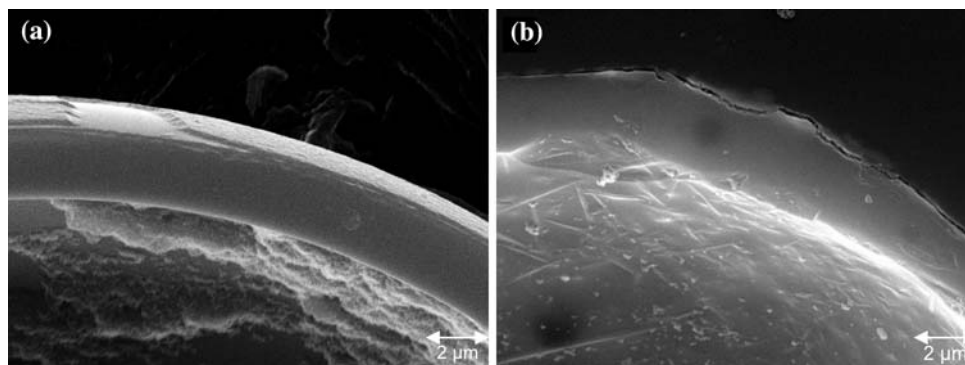
amorphous structure of borosilicate glass, and cenospheres, which are predominantly amorphous glass but with a component of aluminosilicate crystal structure. Figure 1 shows examples of each of these materials. GMBs have a spherical morphology and smooth surface. Cenospheres had a rougher surface and a more complex morphology with much higher incidence of multiple hollow compartments and a higher incidence of surface defects. These defects take the form of holes, depressions, surface asperities, and micrometer scale hollow structures that can penetrate into the wall thickness of the cenospheres. Defects that penetrate through the walls of the hollow microspheres have been seen in earlier work to act as stress concentrators in similar materials through the analysis of finite element modeling [16]. Figure 2 shows a titania-coated GMB with a smooth surface and uniform wall thickness. The polished cenosphere in Fig. 2 shows a rougher inner and outer surface and a more irregular wall thickness. The asperities and surface irregularities act as stress risers when the microspheres experience loading, and depressions at thin sections of the wall are likely crack initiation sites.

The sol–gel deposited titania coatings had a microstructure of fused submicrometer titania particles, Fig. 3. Cenospheres and GMBs showed continuous coatings, but the cenospheres also showed agglomerated asperities and the GMBs often showed elongated depressions of open voids. Cracking of the titania coating was noted on some

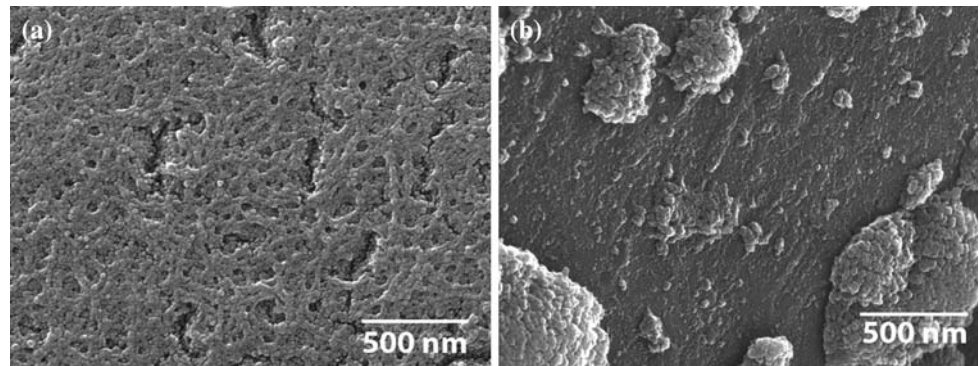
**Fig. 1** (a) GMB showing a spherical morphology and smooth surface and (b) a cenosphere, showing rougher surface with a higher density of surface defects (SEM)



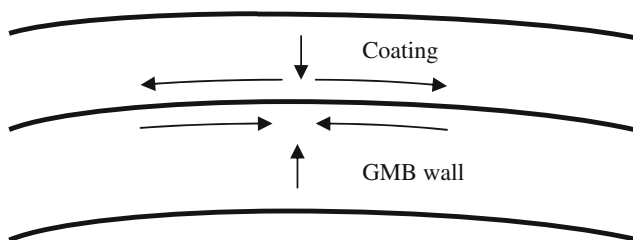
**Fig. 2** Polished cross sections of: (a) a titania-coated GMB showing a smooth ID and OD surface and a uniform wall thickness and (b) a cenosphere with a rougher ID and OD surface and more irregular wall thickness (SEM)



**Fig. 3** Surfaces of (a) titania-coated GMB showing a continuous coating with elongated depressions of open void and (b) titania-coated cenosphere showing continuous coating, but with agglomerated surface asperities (SEM)



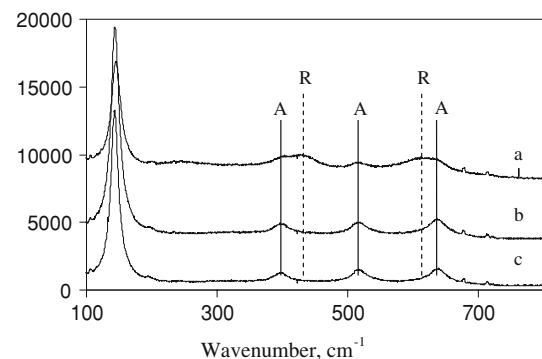
GMBs, but was not observed to be linked to microsphere diameter or other observable features. During sol–gel processing, the material undergoes a large decrease in volume due to coating consolidation, titania converting from an amorphous allotrope to the anatase phase [17]. There are also differences in coefficients of thermal expansion (CTE) between titania and GMBs and between titania and cenospheres. Although the porous structure of the titania films may vary from the fully dense material, the tetragonal anatase phase has a higher CTE than the borosilicate glass. Anatase titania has a CTE in air of  $8.57\text{--}8.71 \times 10^{-6} \text{ K}^{-1}$  depending on crystallographic orientation, whereas borosilicate glass has been measured at  $3.1\text{--}6.0 \times 10^{-6} \text{ K}^{-1}$  [18, 19]. This leads to tensile hoop stresses and a radial compressive stress in the coating and compressive hoop and radial stresses in the GMB wall [20]. The stress state of the coating and GMB wall in cross section are shown in Fig. 4. If the tensile stress exceeds the tensile strength of the gel or the fused titania particles, cracking will result. The initial stages of such cracking may originate at elongated depressions like those shown in Fig. 3a. Although roughening of the coated surface by porosity, agglomeration of titania particles, and cracking should aid photocatalytic reactivity by increasing the relative surface area and exposure to silica/titania interfaces, the same surface features would be expected to accelerate wear and/or spalling of the titania coatings by microsphere collision and abrasion.



**Fig. 4** Schematic cross section of coated GMB with arrows showing the anticipated stress states. Tensile hoop stresses are present in the consolidated coating with a component of radial compressive stress. Compressive hoop stress is expected in the GMB wall

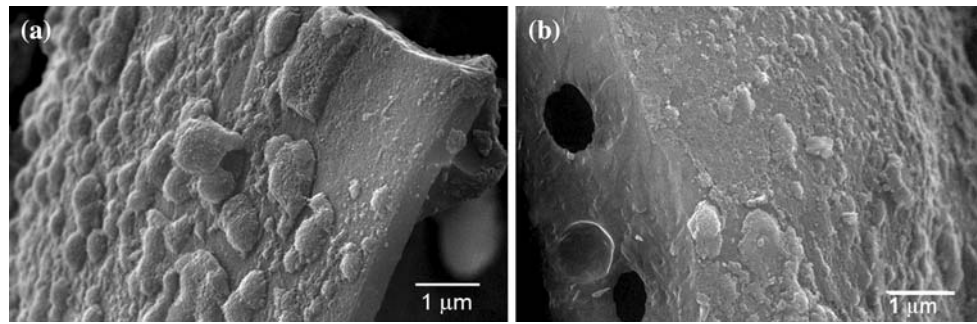
Raman analysis of samples formulated during development of the sol–gel coating process showed the presence of both the anatase and rutile phases of titania. Evidence of tensile stresses in titania was exhibited by a  $6\text{--}8 \text{ cm}^{-1}$  shift in wavenumber [21] of peaks relative to unconstrained titania, i.e., titania that was not part of a coating material and, consequently, was not subjected to the stresses of the coated GMBs. Raman analysis of spectra from GMBs and cenospheres from the current study showed the anatase phase for the GMBs and primarily anatase with some rutile phase for the cenospheres, Fig. 5.

The nature of the titania/silica interface in sol–gel titania coatings is not completely characterized, but several studies have presented evidence of chemical bonding [22–24]. The detection of Ti–O–Si bonding at the silica/titania interface was noted through the use of a range of analytical techniques. Chemical bonding would likely be significantly stronger than mechanical bonding, but was not investigated in the present work. Figure 2a, however, shows exposed GMB surface where a chip of titania coating was broken away, presumably during metallographic preparation. While some short-range interface failure is evident, the crack path has veered back through the titania coating, rather than continuing through the silica/titania interface.



**Fig. 5** Raman spectra with A representing peaks for anatase titania and R representing peaks for Rutile, from (a) cenosphere showing mixed rutile and anatase phases of titania, (b) cenosphere showing anatase titania, and (c) GMB showing anatase phase

**Fig. 6** (a) Broken titania-coated GMB showing retained coating and (b) broken cenosphere, also with retained titania coating (SEM)



**Table 1** Modulus and hardness measured by nanoindentation

Material	Young's modulus (GPa)		Hardness (GPa)	
	Mean	Dev.	Mean	Dev.
GMBs	57.7	2.1	3.0	0.2
Cenospheres	71.9	5.9	5.4	2.9
Titania	48.2	3.7	2.6	0.7

Additionally, samples of both titania-coated GMBs and cenospheres were intentionally fractured by lightly grinding between two aluminum stubs and prepared for SEM. The micrographs of Fig. 6 also show limited GMB and cenosphere exposed exterior surface, but also indicate strong interfacial bonding as evidenced by the retained titania coatings. There is evidence of silica diffusion into the titania coating creating a strong mechanical bond (Jones et al., unpublished research).

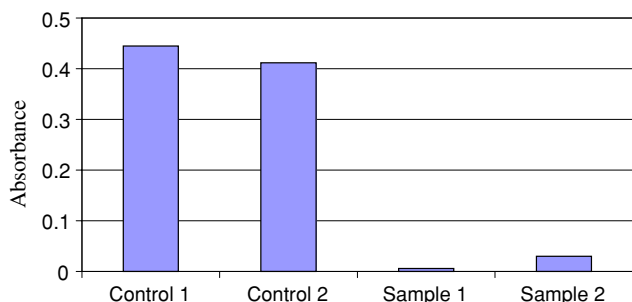
The values of modulus and hardness measurements presented in Table 1 were obtained from polished cross sections of intentionally broken materials by nanoindentation using a diamond Berkovich tip. Shallow depth plateaus between 20 and 200 nm were evident on some indentations using the continuous stiffness technique and were averaged to obtain the values given in Table 1. The value of Young's modulus for titania of 48.2 GPa is lower than that measured by other researchers who have reported values for sol-gel deposited titania films of 70–85 GPa [25, 26]. The lower value measured in the present work may be due to nano-scale porosity, evident in Fig. 2b. Although no data were found in the literature measuring the hardness or modulus of GMBs or cenospheres, values available for the bulk materials tend to be slightly higher than values for the thin-walled GMBs and cenospheres given in Table 1. Values reported for borosilicate glass and Duran<sup>®</sup> glass range from 60 to 70 GPa, compared to the measured value of 57.7 GPa [19, 27]. Matsunaga et al. [28] measured the volume fraction of crystalline phases in cenospheres of a comparable size to those in the present work to be 22–29% and estimated the modulus of precipitator fly ash to be between 82 and 126 GPa. The walls of GMBs and cenospheres are relatively thin, between 1 and 3 μm and it is

possible that values in Table 1 may have been influenced by the stress created by the indentations interacting with the interface between the microspheres and the mounting material, or by the mounting material itself.

### Photocatalytic reactivity

Industrial dyes are by design very stable compounds, and consequently represent difficult chemical compounds to breakdown. The presence of residual dyes in the wastewaters of textile industries causes toxicity in receiving waters, as well as undesirable esthetic effects. Numerous studies have investigated the break down of synthetic dyes by titania-assisted photocatalytic degradation with successful results, although these studies did not utilize hollow microspheres as a platform for the titania [11, 29, 30]. To verify the photocatalytic reactivity of the titania-coated GMBs and to gain an initial assessment of the material response to turbulent mixing, we examined the degradation of Procion Red dye using titania-coated GMBs as a photocatalyst. A control sample with no titania-coated GMBs was kept in darkness and three samples of dye solution were exposed to ambient UV solar radiation: a second control with no titania-coated GMBs, a beaker with titania-coated GMBs mixed by a magnetic stirrer and a beaker with titania-coated GMBs mixed with an aerator. Figure 7 shows the absorbance of light, as measured by a photometer, at 510 nm for the two control samples with no titania-coated GMBs and the two samples containing titania-coated GMBs. Note the dramatic decrease in the opacity of the dye solution for both samples that had titania-coated GMBs. Sample 1, which used a magnetic stirrer had the largest drop in absorbance showing nearly 0 absorbance as measured by the spectrophotometer after 3 h 40 min. Sample 2 also showed a profound drop in absorbance after 6 h 10 min of UV exposure.

After UV exposure, the two samples were allowed to rest undisturbed for at least 24 h, giving time for GMBs to float and debris to sediment before extraction of the solution for spectrophotometer measurements. It was noted that the sample that used the magnetic stirrer had a layer of clear water within approximately 1 cm of the surface, but



**Fig. 7** The measurement of the absorbance of light at 510 nm showed a dramatic decrease in the opacity of the Procion Red dye solution with the addition of titania-coated GMBs by both mixing methods. Control 1 had only dye solution with no GMBs and was kept in darkness. Control 2 also had only dye solution with no titania-coated GMBs, but received 3 h 40 min of UV exposure. Sample 1 had titania-coated GMBs mixed by magnetic stirring for 3 h 40 min of UV exposure, and Sample 2 had titania-coated GMBs mixed by aeration for 6 h 10 min of UV exposure

the remaining solution beneath that layer was cloudy. The sample that had used the aeration bubbler, however, was completely clear. It was hypothesized that submicrometer titania particles might have been fractured from the surfaces of the GMBs, since settling velocity is directly related to particle size and submicrometer particles are well known to readily stay in aqueous suspensions. A sample of floated GMB material from the magnetically stirred sample was imaged in an SEM, Fig. 8, and showed many GMBs with missing regions of titania coating. EDX analyses of regions with missing coating showed only trace or no presence of Ti, corroborating the apparent loss of the titania coating. In a study of the titania-assisted photo-degradation of de-icing agents, Krichevskaya et al. [8] observed higher photocatalytic reactivity of titania slurry compared to titania on hollow glass microspheres, but the microspheres were not mixed during UV exposure with the solution and the size of the particles in the slurry was not noted. The relationship between surface area and

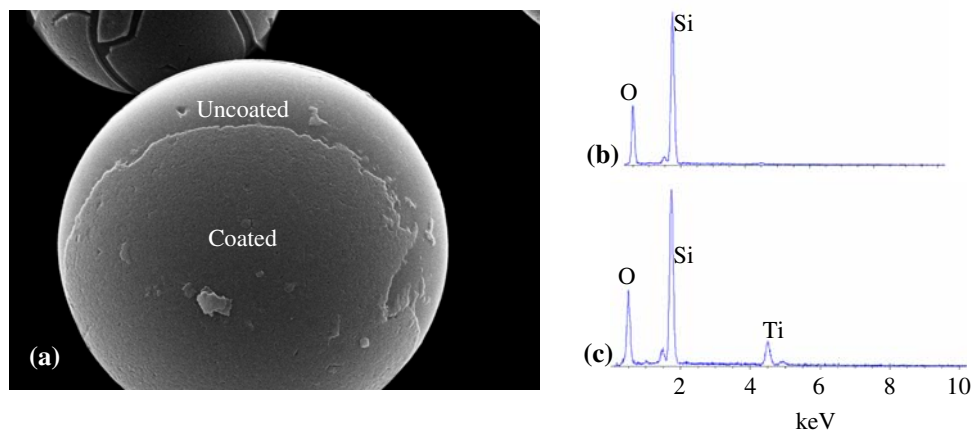
photocatalytic reaction rates in titania has been well documented [31–33], but it is necessary to employ flocculation and sedimentation techniques in order to remove submicrometer particles from suspension.

Although the sample that used aeration as a mixing method showed a lower reaction rate, it should be mentioned that a significant portion of the titania-coated GMBs was observed to be pushed up the sides of the beaker during the experiment, thus not making continuous contact with the solution. The titania-coated GMBs from the aeration mixing showed no discernible loss of coating, and the material studied here may have application in processes that do not require short processing times. Further experiments using larger volumes of solution and photocatalyst are needed and efforts to improve the reaction rates of the titania-coated GMB may also prove beneficial. Efforts to reduce the average diameter of the GMBs used and to increase the surface roughness of the coating could significantly increase the reaction rates beyond those observed in this study. Rougher surfaces have been seen to increase the reaction rate in sol–gel deposited titania [32] and smaller diameter GMBs will also increase the surface area to volume ratio.

## Conclusions

The titania-coated GMBs and cenospheres had good coating coverage and SEM analyses showed very limited cracking. The titania-coated cenospheres showed less uniform coatings with asperities of agglomerated titania particles. The titania coatings were observed to be rough at the microscopic level, increasing titania surface area. The titania coating/GMB interfaces in both commercially produced GMBs and in cenospheres were seen to have good toughness as evidenced by SEM analysis of broken GMBs. Hardness and modulus measurements were made on the

**Fig. 8** (a) A titania-coated GMB after 3 h 40 min of magnetic stirring, showing loss of titania coating and (b) EDX X-ray spectra of region exhibiting coating loss with no Ti, and (c) EDX X-ray spectra of coated region showing retained Ti (SEM)



titania coatings and both types of hollow microspheres by nanoindentation, which were slightly lower than those observed by other researchers on bulk materials. The photocatalytic activity of the titania-coated GMBs was verified by the degradation of a synthetic Procion dye by ambient solar UV radiation. In the photocatalytic experiments, magnetic stirring was observed to fracture the titania coating from the GMBs, but when the aeration bubbler was used the coatings were observed to remain relatively intact, indicating promise for practical applications.

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