Microstructure Characterizations of Thiol Functionalized Silica Pseudo-Nanospheres ($SH-SiO_2$) Nanostructured for Advanced Corrosion Protection Materials

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Abstract

In this study, the silica pseudo-nanospheres materials at ca. 500 nm were functionalized with thiol (SH) using non-surfactant surface modification method. Palm oil derived fatty alcohols (PODFA) was used as 'green' and sustainable surface modifier. The surface modification method successfully attached thiol functional groups in a 'surfactant-like'manner to produce thiol-silica ($SH-SiO_2$) pseudo-nanospheres. Thereafter, the resulting powder was turned into gel and spin-coated on mild carbon steel at several speeds for corrosion protection applications by exposing the surfaces to more than 36 months of exposure in ambient laboratory condition. Structural characterizations were done on the new surface and exposed surface. The surface microstructure after exposure exhibited less area coated with $SH-SiO_2$ pseudo-nanospheres particles compared with before exposure. Furthermore, elemental analyses results exhibited significant reduction of Si element over time of exposure at ca.70% while the X-ray diffraction analyses results exhibited no phase changes of the mild steel surfaces after 36 months of exposure. Visual inspection (VI) suggested that the coated mild steel surfaces were in good condition with no observable rust formation. Therefore, the results obtained in this study suggested that SiO_2 spheres functionalization with "green' and renewable surface modifier are promising candidates of low-cost coating alternatives for corrosion protection of commonly used mild steel.

Keywords: Thiol functionalization, corrosion protection, silica pseudo-nanospheres, non-surfactant, $SH-SiO_2$,

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Article Info

Received 7th May 2020
Accepted 1st September 2020
Published 1st December 2020
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ISSN: 1823-7010, eISSN: 2600-7444

Introduction

Coating is a well adopted technology to minimize the effect of corrosion of metallic materials. There are many types of coating materials such as ceramic coating, zinc coating, polymer based coating and chromate based coating. Chromate based coating has been the most effective types of coating materials for corrosion protection. However, the hexavalent chromium ions used in chromate based coating/produced by chromate based coating have a detrimental impact on the environmental and human health. Furthermore, the Registration, Evaluation, Authorisation, and Restriction of chemicals (REACH) has imposed legislation to prohibit the use of hexavalent chromium in almost all sectors except for aerospace industry [1]. Thus, there is a need to explore new alternatives for environmental friendly coating materials. One of the alternatives is surface functionalizations of coating materials. Surface functionalization process has wide applications such as corrosion inhibitor, coating protection, self – healing coating, and absorbent materials [2-5].

Parhizkar et.al reported on the corrosion inhibitive action of graphene oxide nanosheets modified with various organic/inorganic compounds where it was suggested that the interfacial adhesion and corrosion resistance were improved significantly using amino-functionalized graphene oxide nanosheet [6]. Meanwhile, Nayini *et.al* have successfully functionalized multiwall carbon nanotubes (MWCNTs) using oxidation of 1,3-dipolarcycloaddition,and silanization that improved the wettability effect [7] while Raza *et.al* developed silane-funtionalized graphene oxide (GO) coating on copper (Cu) metal and suggested that the corrosion resistance of Cu is enhanced by ca. 23 times compared to bare Cu metal. [8]. Furthermore, Bera *et.al.* suggested that by adding thiol group containing silane coupling agents coating to the reference coating solution, it has caused remarkable improvements in hydrophobic and corrosion resistance properties on Al-2024 substrate [2].

Many studies were done on the carbon functionalization with scarce reports on thiol (SH) based surface functionalization. Silica (SiO_2) was commonly used as a coating materials and added to heat resistant grade and stainless steels to improve the oxidation resistance [9-13]. In addition, the large surface area of silica nanomaterials is a huge advantage for surface functionalization to be successful. The oil soluble method usually contains the surfactant molecules that have weak attraction for the solvent environments and generally hydrophobic group. However, the conventional surfactant are harmful species to environment. Therefore, in this study, palm oil derived fatty alcohol (PODFA) bearing twelve carbon chains was used as a new alternative in the functionalization process [14] where it is a plant based molecules and and consider as a biomass. In this study SH-SiO_2 pseudo-nanospheres that were functionalized with thiol group (SH) using PODFA non-surfactant modifier has been developed using spin coating procedure onto mild steel materials and was kept for three years in common laboratory condition. After three years exposure in common laboratory condition, the SH-SiO_2 coating is still in good condition with no rust formed.

Materials and Methods

Materials

SiO_2 pseudo-nanospheres particles were synthesized using in-house procedure. The particle size distributions were varied centered at ca.100 nm, respectively. Fatty alcohol derived from palm oil (C12) was obtained from Malaysian Palm Oil Board (MPOB). Two-thiazoline-two-thiol ($C_3H_5NS_2$, 98%, Aldrich), phosphate buffer, ethanol (95%, Merck) were used in the as-received condition. Commercially available mild steel was used after polishing to mirrror-surface with raw diamond at ca. 3 micron.

Surface modification method of SiO_2 pseudo nanopheres

SiO_2 pseudo-nanospheres particles were functionalized with thiol groups (SH) using non-surfactant surface modification method employing palm oil derived fatty alcohols as surface modifier in phosphate buffer and ethanol. The process resulted in producing thiol-silica (SH-SiO2) pseudo-nanospheres where it was stirred and centrifuged before drying for 12 hours at the temperature of 60 °C.The resulting powder of SH-SiO_2 was sonicated to form liquid suspension for spin-coating process. Finally, the mixture of SH-SiO_2 pseudo-nanospheres was spin-coated on a mirror-surfaced polished mild steel materials at three different speed, which are at 2000 rpm, 2500 rpm and 3000 rpm.

Material characterizations

The morphology of the SH-SiO_2 was observed using field emission scanning electron microscopy (FESEM : HITACHI SU8020) at acceleration voltage of 15kV. The elemental analyses were conducted using Bruker X-Flash along wih FESEM machine at acceleration voltage of 15kV. X-ray diffraction analyses were performed using Shimadzu at 30 kV and 20 mA between the range of 2θ was at 15 – 70°.

Results and Discussion

Visual observation

The visual inspection for coated and uncoated samples are as shown in Fig 1 where in Fig 1a, the mild steel without coating was covered with corrosion after three years of while Fig 1b to Fig 1d shows results of the mild steel after 3 years of exposure with coating at different speed. No corrosion product were observed on the mild steel surface of coated samples.

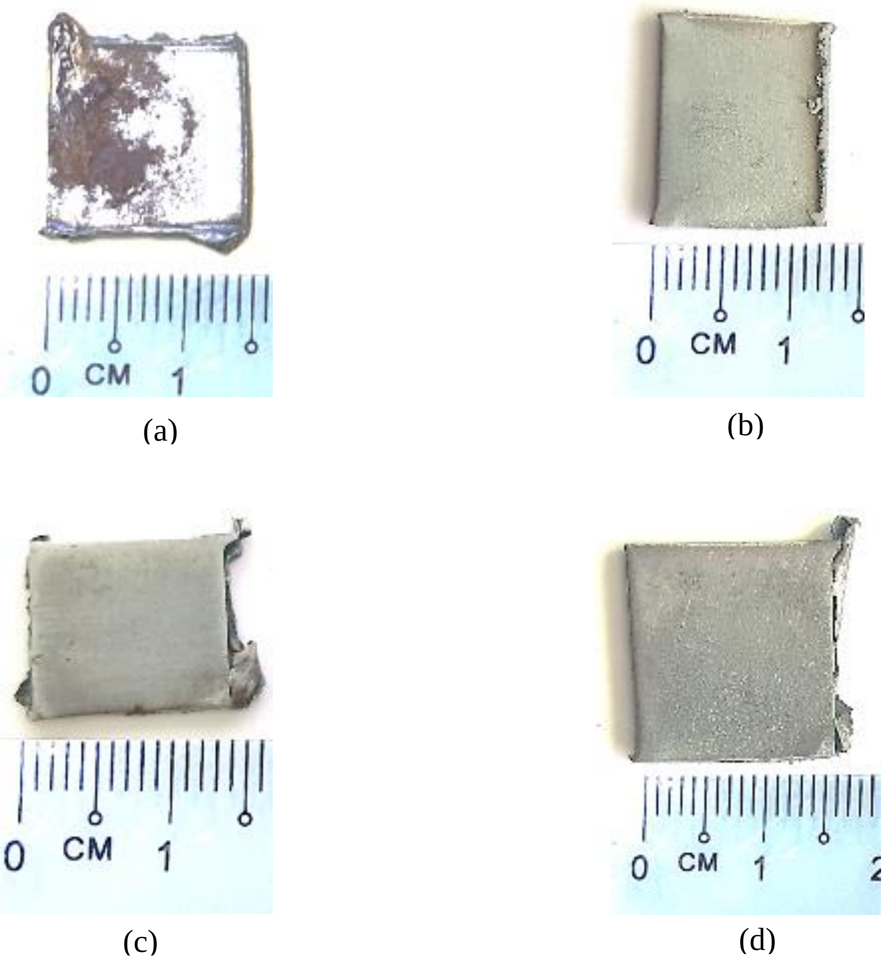

Figure 1, (a) Corrosion was observed at the surface of mild steel after three years of exposure without coating, Mild steel coated with SH-SiO2 after three years of exposure: (b) 2000 rpm, (c) 2500 rpm and (d) 3000 rpm

Morphology of SH-SiO$_2$

Fig. 2 shows SEM images of samples coated at different spin-coating condition. 2000 rpm showed less coverage of SH-SiO$_2$ coating as compared to 2500 rpm and 3000 rpm while 3000 rpm exhibited optimum coverage of SH-SiO$_2$ coating. The coverage of coating were deteriated over the time of exposure for all rpm. However, the spherical morphology of silica pseudo-nanospheres remain unchanged after three years of exposure. The percentage of coverage reduction ca. 47% for 2000 rpm, ca. 42% for 2500 rpm and ca. 47% for 3000 rpm. The calculation was processed using ImageJ software.

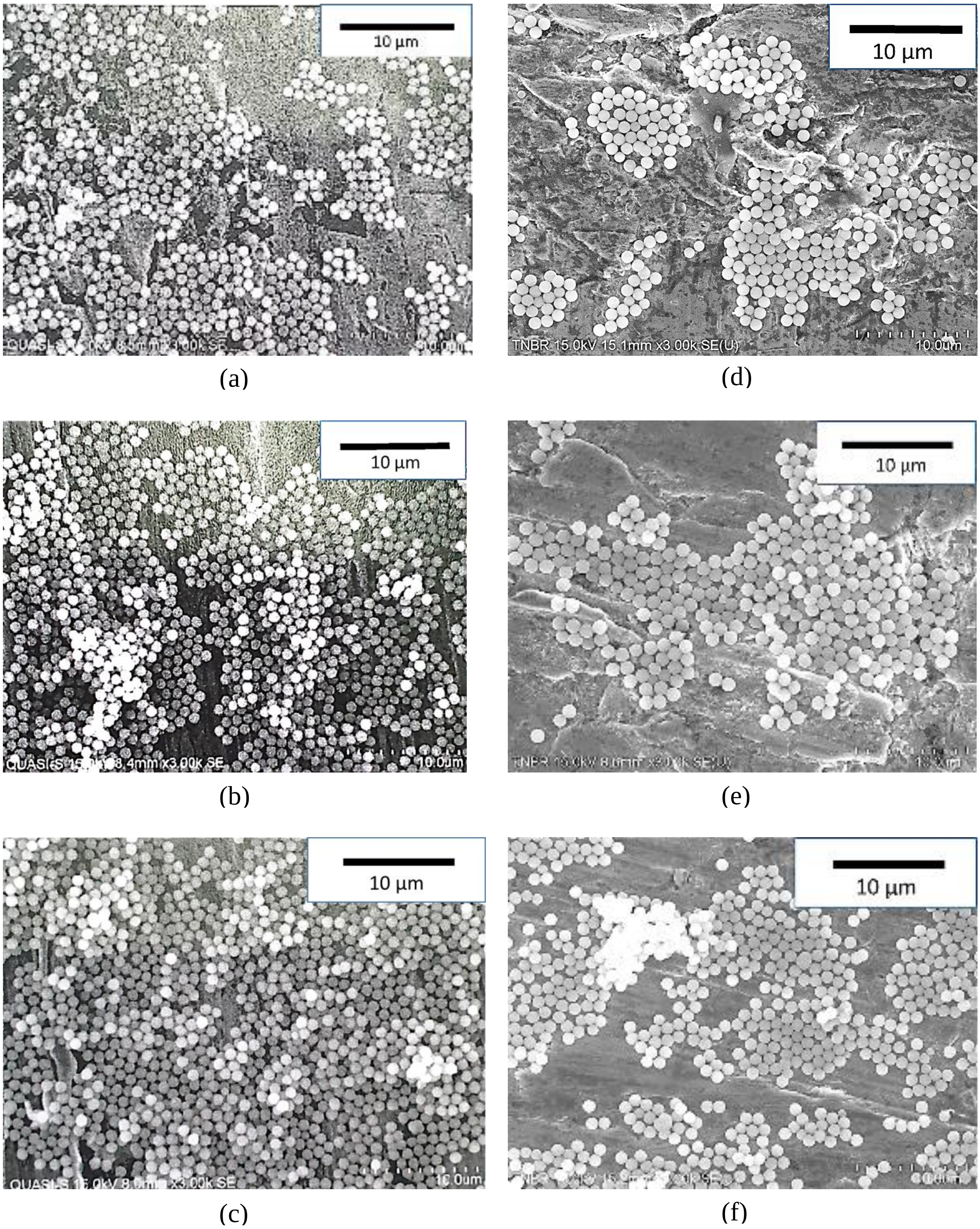

Figure 2, SH-SiO_2 coating morphology before exposure : (a) 2000 rpm, (b) 2500 rpm, (c) 3000 rpm; SH-SiO_2 coating morphology after 3 years exposure : (d) 2000 rpm, (e) 2500 rpm, (f) 3000 rpm.

Elemental analyses

The elemental analyses results for samples before and after three years of exposure with three different speeds are shown in Table 1 and the elemental mapping is shown in Figure 3. Table 1 suggested that, the silica pseudo nanospheres content was reduced to ca. 70 %, probably due to the reaction with humidity in the environment. The elemental mapping shows the coverage of silica pseudo nanospheres in purple.

Table 1. Elemental analysis results.

	Weight %					
	2000 rpm		2500 rpm		3000 rpm	
Element	0 year	3 years	0 year	3 years	0 year	3 years
C	2.26	6.09	2.67	3.16	1.96	2.33
O	36.92	8.36	40.46	12.20	46.57	15.5
Si	26.01	6.15	26.79	7.55	34.41	11.21
Fe	34.82	80.47	27.12	77.11	17.06	70.96

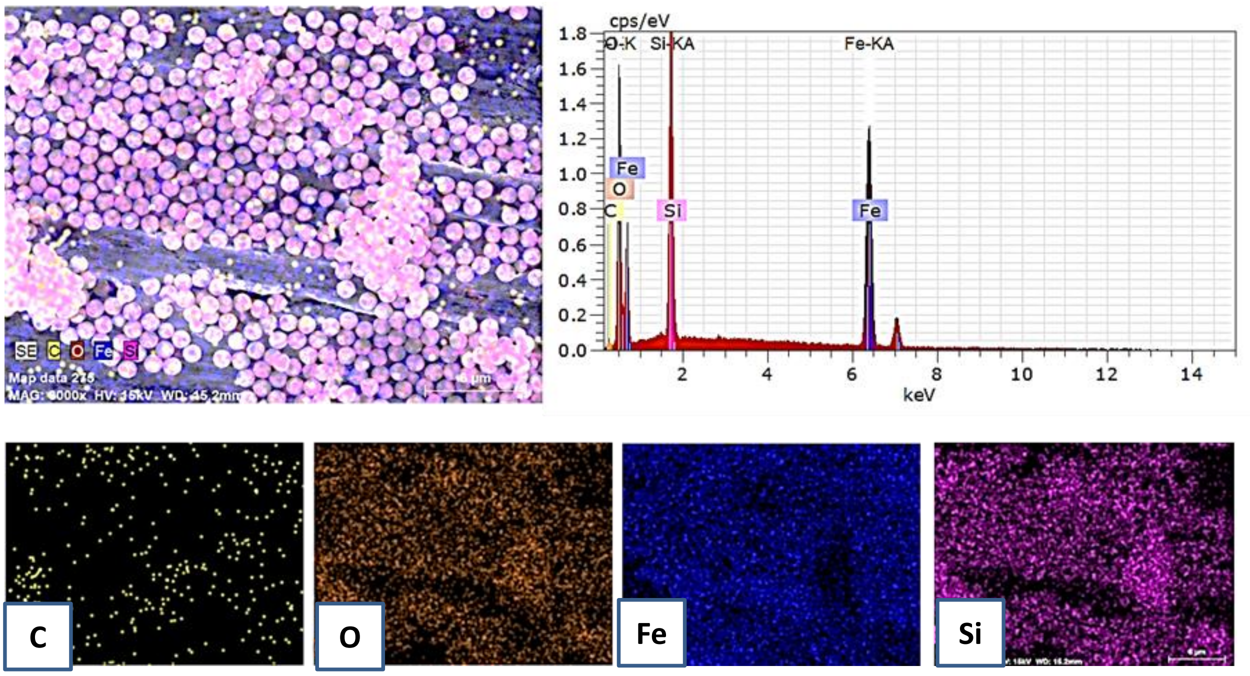

Figure 3 : Elemental mapping for sample prepared at 3000 rpm after 3 years of exposure.

X-ray diffraction (XRD) analyses

The XRD patterns of mild steel coated with SH-SiO_2 obtained in this study is as shown in Fig. 4 where the before and after exposure exhibited similar pattern for mild steel and SH-SiO_2 did not change the crystallinity of mild steel.

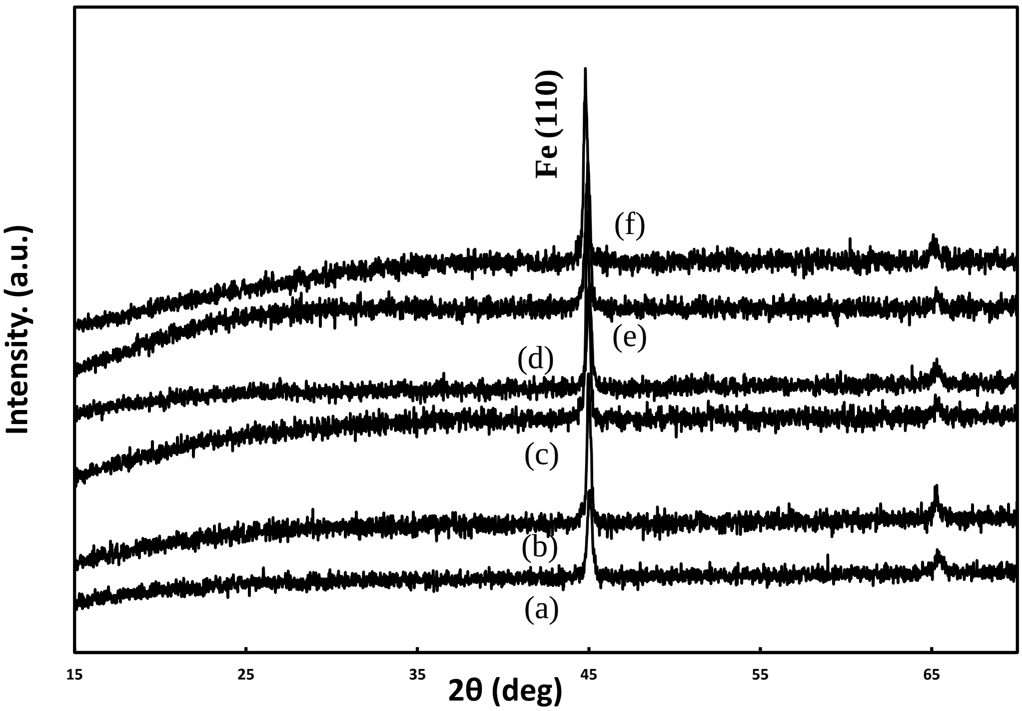

Figure 4 : XRD pattern of mild steel coated with SH-SiO_2, (a) after exposure for 2000 rpm, (b) before exposure for 2000 rpm, (c) before exposure for 2500 rpm, (d) after exposure for 2500 rpm, (e) before exposure for 3000 rpm, (f) after exposure for 3000 rpm

Conclusions

Functionalization process of SiO_2 with thiol group (SH) was introduced to develop new type of coating protection for mild steel materials. In addition, palm oil derived fatty alcohols (PODFA) successfully played the role of non-surfactant modifier in this study where it was found that all the SH-SiO_2 coating was in good condition after three years of exposure. Furthermore, this process is low-cost and environmental-friendly.

Acknowledgments

This work was supported by Universiti Tenaga Nasional under BOLD2025 grants. The authors thank TNB Research Sdn.Bhd for the FESEM images.

Author contributions

All authors contributed toward data analyses, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of conflict of interest

The authors have no disclosures to declare.

Compliance with ethical standards

The work is compliant with ethical standards.

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