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Dual layer inorganic coating on magnesium for delaying the biodegradation for bone fixation implants

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ABSTRACT

In this study, a dual layer inorganic coating was formed on a pure magnesium metal using electrochemical methods to delay the biodegradation of the metal for potential bone fixation implant applications. Firstly, a layer of silicate-based coating was formed on the base metal using plasma electrolytic oxidation (PEO) method. A second layer of calcium phosphate (CaP) was formed on the PEO coating using electrodeposition method. In vitro electrochemical degradation testings showed that the double layer coating (PEO-CaP) has significantly improved the initial degradation resistance of the metal. Localized degradation was not evident on the PEO-CaP coated metal even after 72 h exposure to simulated body fluid (SBF).

Keywords: Magnesium; Biomaterials; Calcium phosphate; Plasma electrolytic oxidation; Degradation

1. Introduction

Inorganic phosphate-based and silicate-based coatings have been widely studied for reducing the degradation rate of magnesium and its alloys for their potential applications in bone fixation implants [1-7]. Plasma electrolytic oxidation (PEO) and electrodeposition methods are the two common techniques used for the inorganic coatings [1-3, 5-7].

In general, PEO technique produces a hard, thick and well adherent film on metallic materials [8]. Recent studies have shown that PEO coatings on magnesium and its alloys have improved their degradation resistance in simulated body fluid (SBF) [3,7]. However, due to the inherent porous nature of the PEO coatings, their performance for a relatively longer period of time in body fluid is questionable. In fact, Liang et al. [9] reported that a PEO coating on a magnesium alloy exhibited only short-term protection in chloride-containing solution. The aggressive chloride ions, present also in body fluid, penetrate through the pores and attack the inner compact layer, which is reported to be MgO [10]. A second coating layer to seal the PEO outer porous layer is necessary to produce implants with acceptable service life.

Calcium phosphate (CaP) has been widely used in biomedical applications due to its biocompatibility, osseointegration and low degradation [11]. Hence, this inorganic material could make a suitable sealing layer on the porous PEO coating. Recently, Liu et al. [4] carried out chemical deposition of CaP on PEO coated pure magnesium. They observed that the morphology of the CaP coating consisted of two regions, i.e., flake-like and porous structures, which indicate incomplete sealing of the PEO pores. This could be due to the relatively slow coating method on a degrading material. Although the authors reported improvement in the degradation resistance, the corrosion current density (i_{corr}) (calculated based on the cathodic curves) suggests that the improvement is not highly significant (PEO coated = $10 \mu\text{A}/\text{cm}^2$ and PEO-CaP coated $5 \mu\text{A}/\text{cm}^2$). An electrodeposition method could be

1 a more suitable technique to coat CaP on the PEO layer for achieving a complete coverage of
2 the pores. In electrodeposition method, the material is held at a cathodic potential and hence
3 there will be less dissolution of magnesium as compared to that of the chemical method,
4 during the coating process.
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9 In this work, a silicate-based layer was coated on pure magnesium using PEO method and
10 then CaP was coated using electrodeposition method. The in vitro degradation behaviour of
11 the dual layer (PEO-CaP) coated material was tested using electrochemical methods in
12 simulated body fluid.
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21 **2. Experimental procedure**

22 Pure magnesium (99.9 wt. %) was used as a base material in this study. PEO coating was
23 carried out in an electrolyte containing 2 g/l KOH and 7 g/l Na₂SiO₃. A pulsed constant-
24 current method, i.e., 30mA/cm², 2 ms/18 ms pulse on/off time, was applied for 20 min with a
25 final voltage of 483 ± 2V. An electrodeposition method, i.e., pulsed potential (-3V) with a
26 duty cycle of 35% [6] for 60 min, was used to coat CaP on the PEO coated metal. The CaP
27 coating solution consisted of 0.1 M Ca(NO₃)₂ and 0.06 M of NH₄H₂PO₄. The PEO and PEO-
28 CaP coatings were characterised using scanning electron microscopy (SEM) and Fourier
29 Transform Infrared (FTIR) Spectroscopy (PerkinElmer Spectrum 100). The coating thickness
30 was measured using a DualScope® coating thickness gauge.
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46 In vitro degradation studies were carried out in a simulated body fluid (SBF) maintained at a
47 physiological pH value of 7.4 and temperature of 37±0.5°C. The SBF composition and the
48 experimental set-up used in this study can be found elsewhere [12]. Electrochemical
49 impedance spectroscopy (EIS) tests were performed at the open circuit potential with AC
50 amplitude of 5 mV over the frequency range of 10⁵ Hz to 10⁻² Hz. Potentiodynamic
51 polarisation tests were performed at a scan rate of 0.5 mV/s.
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3. Results and discussion

The thickness of the PEO coating was measured to be $24\pm 3\mu\text{m}$. After the electrochemical deposition of CaP, the dual layer coating thickness was $37\pm 4\mu\text{m}$. The SEM micrographs of the PEO and PEO-CaP coatings are shown in Fig. 1 (a-d). The PEO coating exhibited a rough surface (Fig.1a). A higher magnification of the coating revealed porous structures (Fig.1b). However, the PEO-CaP coating showed a flat morphology with some CaP particles protruding outside the surface (Fig.1c). A higher magnification revealed aggregation of thin flat CaP particles (Fig.1d). There was no evidence of the underneath porous PEO layer, which suggests complete coverage by CaP coating. Fig. 2 shows the FTIR spectra of PEO and PEO-CaP coated samples. The PEO coating exhibited strong peaks at 970 and 870 cm^{-1} corresponding to silicate [13, 14], and the PEO-CaP coating showed strong peaks at 1130 , 1150 and 980 cm^{-1} corresponding to phosphate [15]. The absence of silicate peaks for the PEO-CaP coated samples further confirms the dense coating of CaP. Based on our previous work [2], it can be suggested that the CaP coated formed is dicalcium phosphate dihydrate ($\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$).

The Nyquist plots of the bare metal and the coated samples after 2 h exposure to SBF are shown in Fig.3a. As expected, the pure magnesium, which is prone to general and localized degradation, showed two capacitance loops (one at high frequency and another at a mid-frequency – suggesting partial protection) and an inductive loop at low frequency (indicating pitting corrosion) [16, 17]. Both the coated samples (PEO and PEO-CaP), however, exhibited a large single capacitive loop suggesting a better performance of the coatings in SBF. Importantly, there was no sign of inductive loop for both the coated samples indicating that the samples did not undergo localized degradation. The polarization resistance (R_p) of PEO-

1 CaP coated metal was found to be approximately two-order of magnitude higher as compared
2 to the pure magnesium and one-order of magnitude higher than the PEO coated metal.
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5 The potentiodynamic polarisation curves of the bare and the coated samples are shown in Fig.
6 3b and the corresponding electrochemical data are listed in Table 1. Interestingly, the E_{corr}
7 shifted by ~ 120 mV towards the active potential for PEO coated metal and the PEO-CaP
8 coated metal shifted by 140 mV toward the noble potential as compared to that of the pure
9 magnesium. However, the corrosion current density (i_{corr}) calculated based on the cathodic
10 curves showed $\sim 65\%$ reduction with the PEO coating, and $\sim 96\%$ reduction with the PEO-
11 CaP coating in comparison with that of the pure magnesium. Comparing the present study
12 (PEO + cathodic deposition of CaP) with Liu et al.'s [4] work (PEO + immersion coating of
13 CaP), both on pure magnesium, it is evident that cathodically deposited CaP performs better
14 than the CaP formed using immersion method. The corrosion current (i_{corr}) for PEO + CaP
15 (cathodically deposited) on magnesium ($i_{\text{corr}} = 0.85 \mu\text{A}/\text{cm}^2$) was lower as than that of PEO +
16 CaP (cathodically deposited) on magnesium ($i_{\text{corr}} = 5 \mu\text{A}/\text{cm}^2$). Liu et al. [4] observed $\sim 50\%$
17 decrease in the i_{corr} for PEO + CaP as compared to PEO only, whereas the current study
18 showed $\sim 90\%$ decrease for such comparison. This clearly suggested that cathodic deposition
19 of CaP is more effective than immersion coating of CaP.
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44 In order to understand the longevity of the coating, long-term EIS experiments were
45 conducted. The R_p values of the samples exposed to SBF for different time intervals are
46 shown in Fig. 4. For the pure magnesium, the R_p increased marginally from $510 \Omega \text{ cm}^2$ (2 h)
47 to $825 \Omega \text{ cm}^2$ (24h), which suggests partial passivation. But, the R_p remained relatively stable
48 with increase in exposure period ($1180 \Omega \text{ cm}^2 - 48$ h). Interestingly, the R_p of the PEO coated
49 metal dropped significantly after 24 h exposure, i.e., $4300 \Omega \cdot \text{cm}^2$ (2 h) to $780 \Omega \cdot \text{cm}^2$ (24 h). It
50 was noted that the R_p of the PEO coated metal after 24 h exposure was similar to that of the
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1 pure magnesium, which reveals the poor protective nature of the coating. On the other hand,
2 PEO-CaP coated metal showed significantly higher R_p as compared to the PEO coated metal,
3 after 24 h exposure. The R_p of the PEO-CaP coated metal was $2 \times 10^4 \Omega \text{ cm}^2$, i.e., 97% higher
4 than that of the PEO coated metal for same exposure time. Although the R_p of the PEO-CaP
5 coated metal decrease with increase in exposure period, the R_p recorded was more than one-
6 order of magnitude higher than the initial R_p of pure magnesium and two times higher than
7 that of the PEO coated metal, even after 72 h exposure to SBF.
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10 Fig. 5 shows the post-degradation SEM micrographs of the PEO and the PEO-CaP coated
11 samples. Interestingly, the PEO-coated metal, which exhibited similar R_p to the pure
12 magnesium, did not show any major degradation attack (Fig.5a), but only a few localized
13 attacks (Fig.5b). This suggests that the degradation was mainly underneath the PEO coating.
14 It can be expected that the PEO layer would exfoliate when exposed for a longer period of
15 time. However, the PEO-CaP coated metal did not show any sign of localized degradation
16 (Fig.5c,d). The porous nature of the underneath PEO coating was not evident even after 72 h
17 exposure, which confirms the protective nature of the CaP layer on the PEO layer. Hence, the
18 dual layer inorganic coating (PEO-CaP) could be a suitable method to delay the degradation
19 of the material.
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44 **4. Conclusions**

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46 The study suggests that the dual layer inorganic coating (PEO-CaP) is very effective in
47 delaying the general and localized degradation of the pure magnesium metal. The PEO-CaP
48 coating improved the polarization resistance (R_p) approximately two-order of magnitude and
49 reduced the corrosion current density (i_{corr}) by ~96% as compared to that of the pure
50 magnesium.
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Table 1

Electrochemical data for pure magnesium, PEO coated and PEO-CaP coated samples from potentiodynamic polarisation curves.

Sample	E_{corr} (V _(Ag/AgCl))	i_{corr} (μA/cm ²)
Pure Mg	-1.8±0.02	23.5±3.6
PEO	-1.92±0.02	8.3 ± 3
CaP-PEO	-1.66	0.85±0.07

LIST OF FIGURE CAPTIONS

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7 **Fig. 1.** SEM micrographs of the coatings on pure magnesium: (a, b) PEO coating, and (c, d)
8 PEO-CaP coating.
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12 **Fig. 2.** FTIR spectra of PEO and PEO-CaP coatings on pure magnesium.
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15 **Fig. 3.** Electrochemical result of pure magnesium, PEO coated and PEO-CaP coated
16 magnesium samples exposed to SBF: (a) Nyquist plots and (b) potentiodynamic polarisation
17 curves.
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23 **Fig. 4.** Polarization resistance (R_p) of pure magnesium, PEO coated and PEO-CaP coated
24 magnesium samples after different immersion intervals in SBF.
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29 **Fig. 5.** Post- degradation SEM micrographs of coated pure magnesium: (a, b) PEO coated,
30 and (c, d) PEO-CaP coated.
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Fig.1
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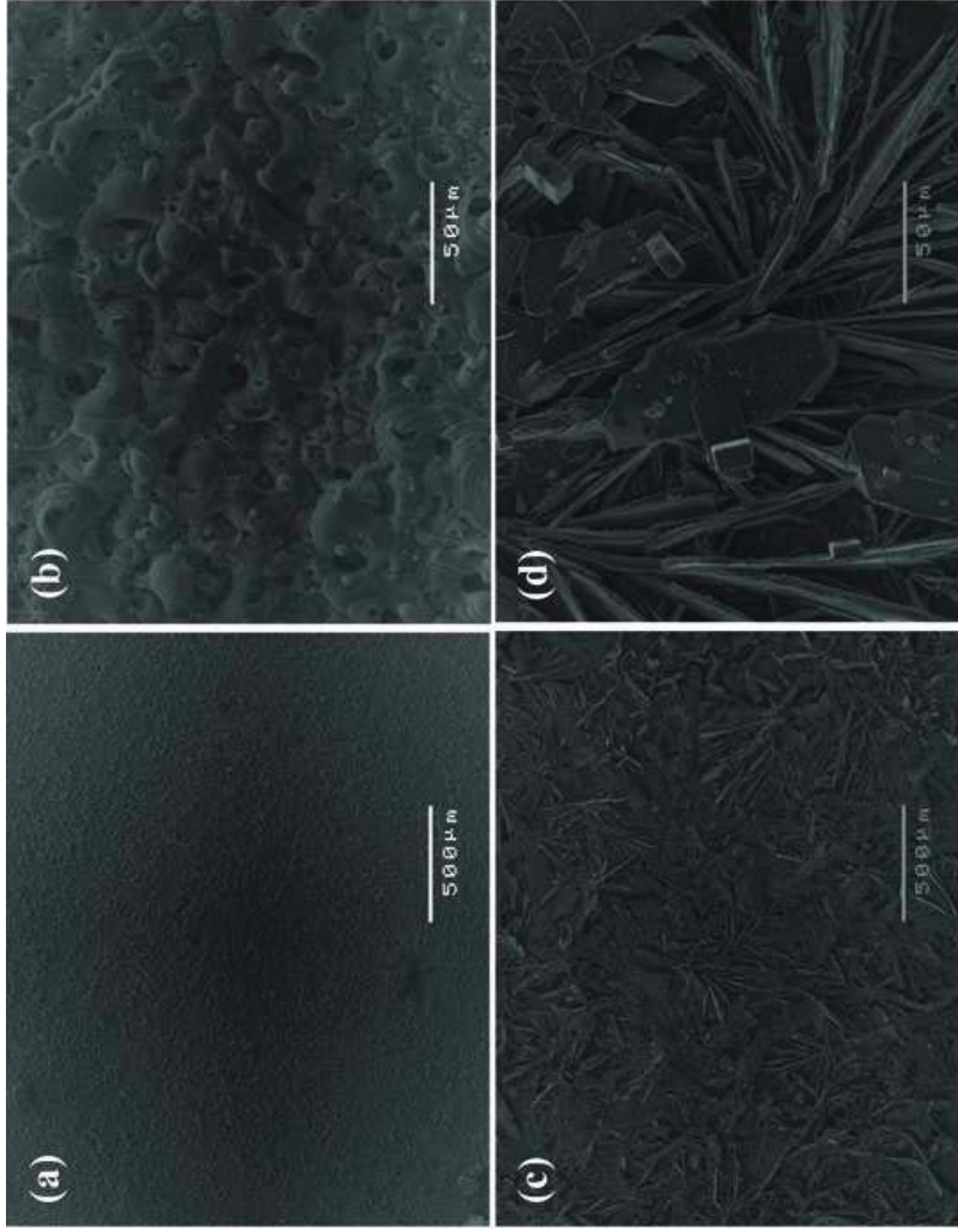


Fig.2
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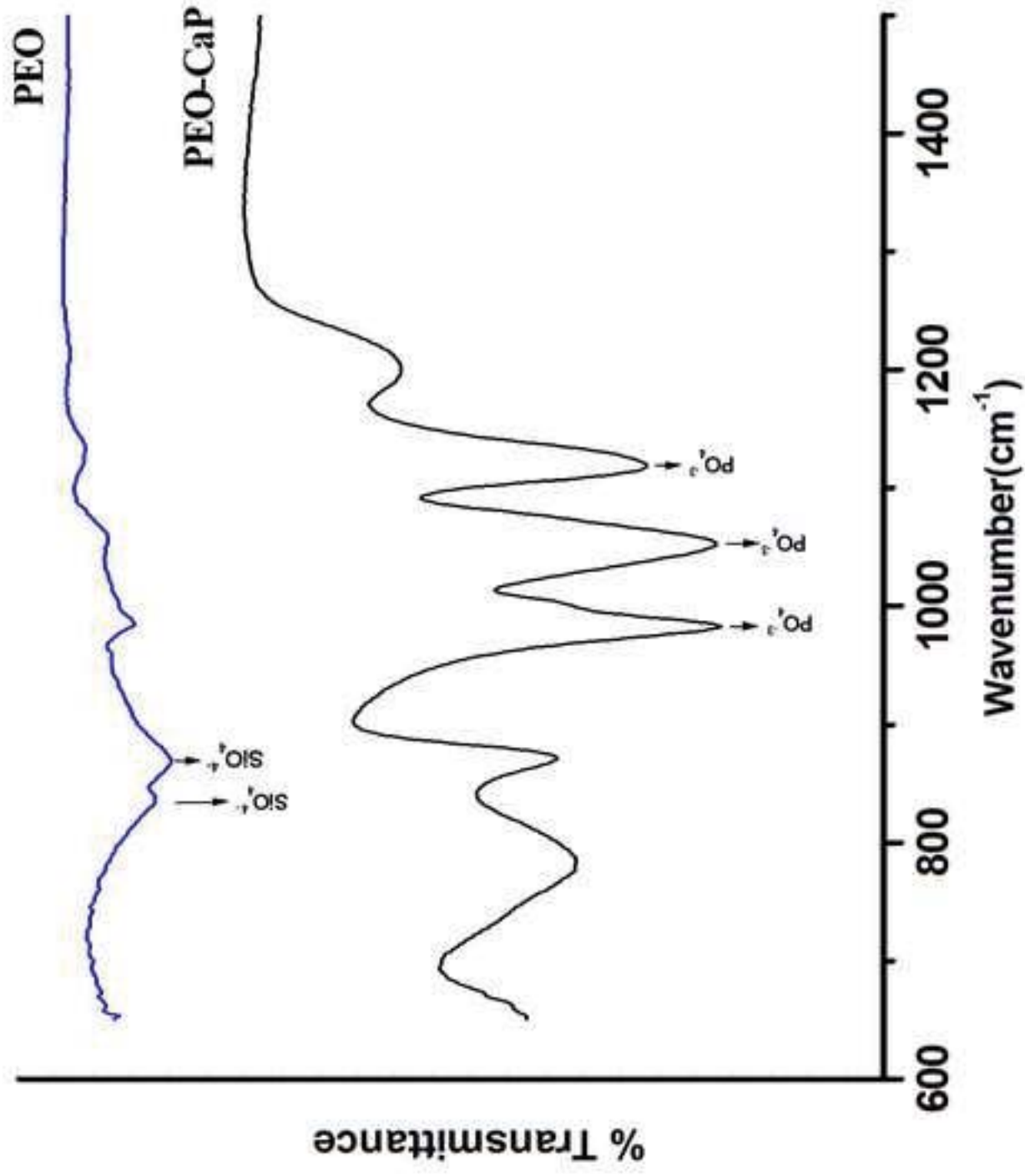


Fig.3a
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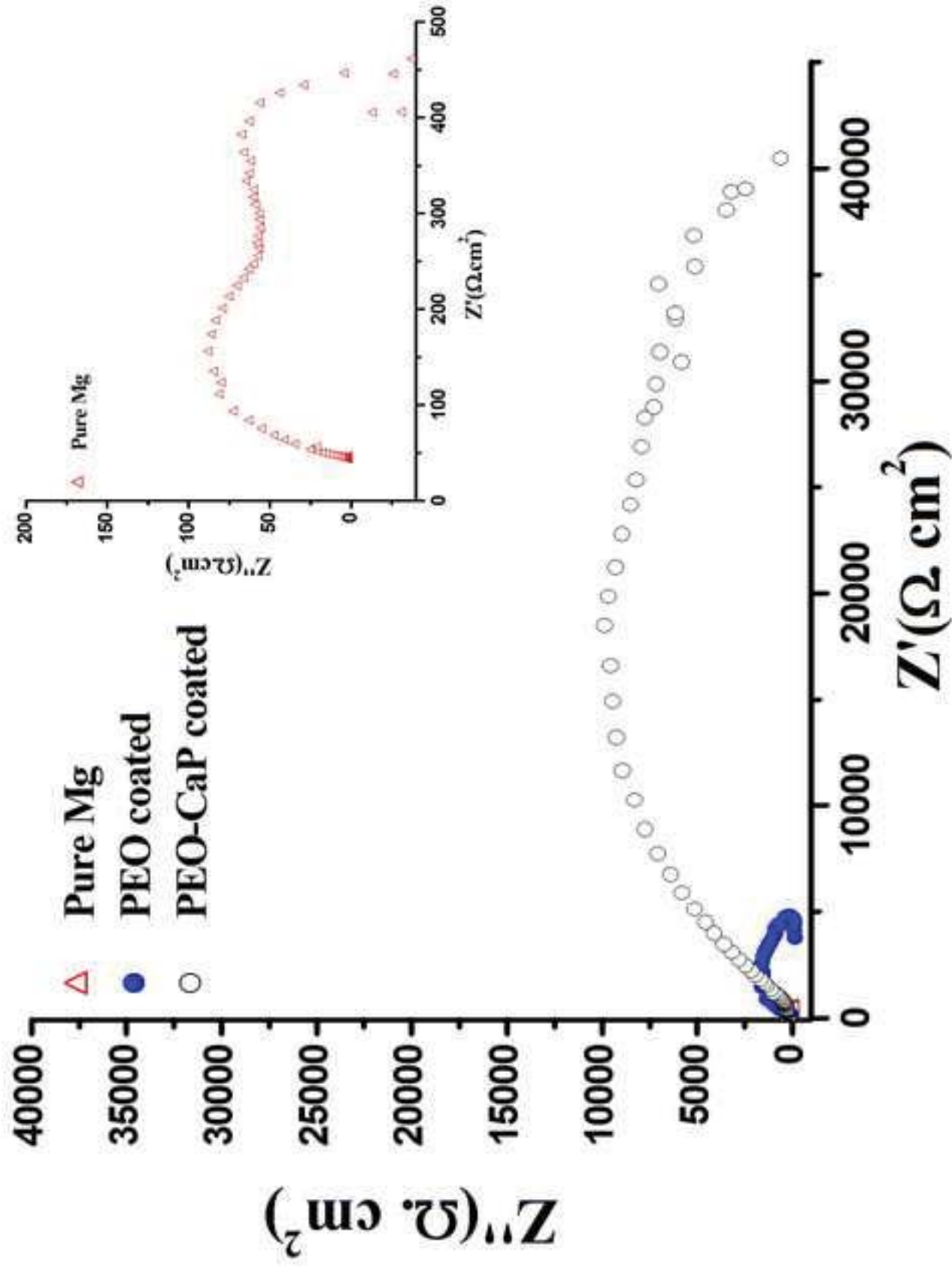


Fig.3b
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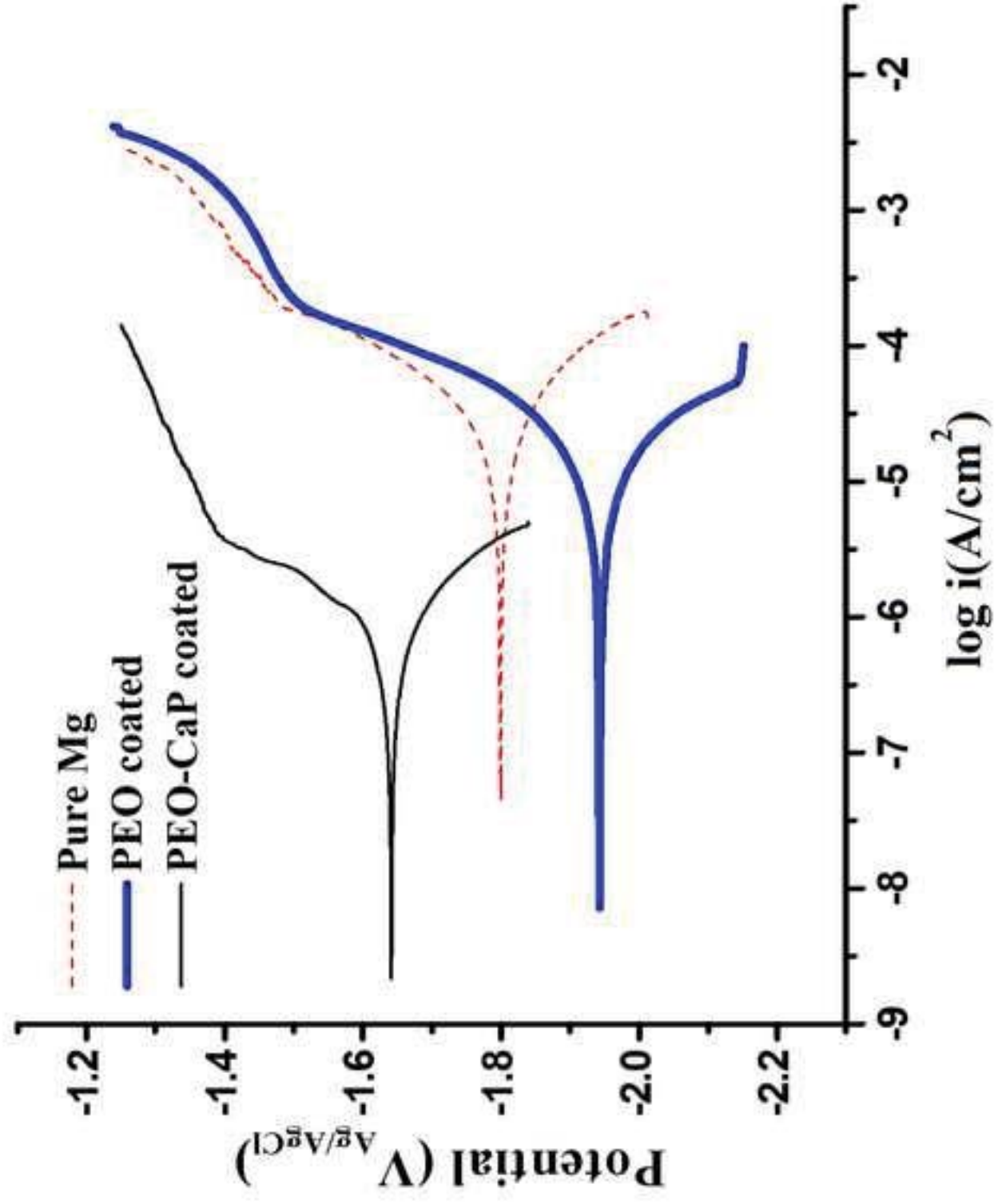


Fig.4
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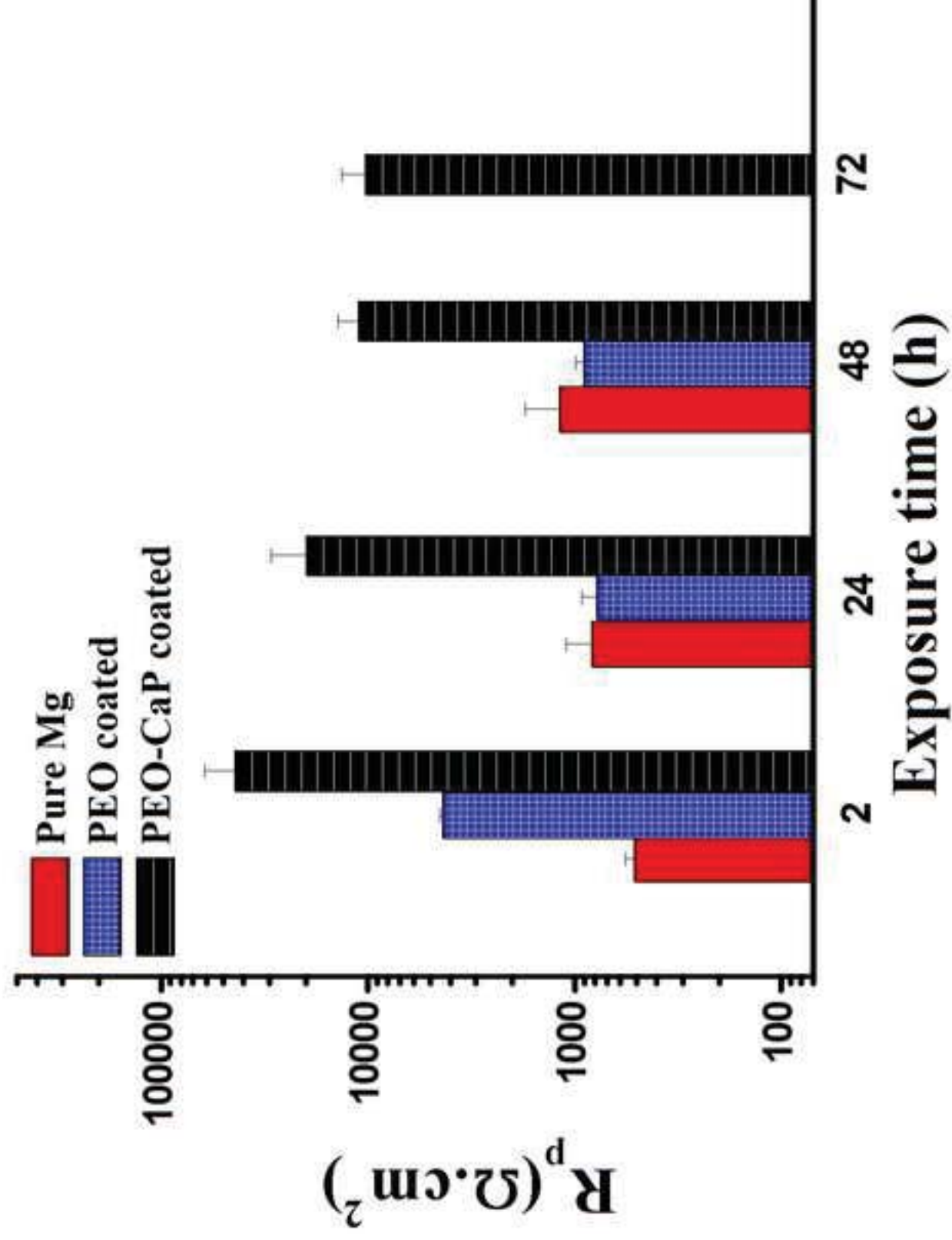


Fig.5
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