Supplementary Information

Comprehensive Investigation of Structural and Photocatalytic Properties of Cobalt and Nickel co-doped Magnesium Oxide Nanoparticles

Shafaq Arif[a,*], Amna Sarwar[a], M.S. Anwar[b,*]

[a,*]Department of Physics, Lahore College for Women University, Lahore 54000, Pakistan
[b]Department of Engineering & Construction, School of Architecture, Computing & Engineering, University of East London, London E16 2RD, UK

S1. Crystallite Size and Strain Analysis Using XRD Models

Modified Scherrer's method applies a least-square approximation across all significant diffraction peaks. Comparatively, the Scherrer method does not consider the contribution of strain broadening. Thus, the modified Scherrer method offers a more comprehensive evaluation of nanocrystalline structure by simultaneously considering size and strain effects. In modified Scherrer's method the crystallite size can be calculated by taking natural logarithm on both side of equation 3 and plotting a graph between $\ln\beta$ and $\ln(1/\cos\theta)$ (see Fig. S1). The values of crystallite size and strain are calculated from the intercept and slope of linear fit of the data points, respectively (see Table 2). In addition, the slope of linear fit gives an indication of nature of strain. The negative slope is related to compressive strain, whereas, the positive slope attributed to tensile strain in the crystal lattice.

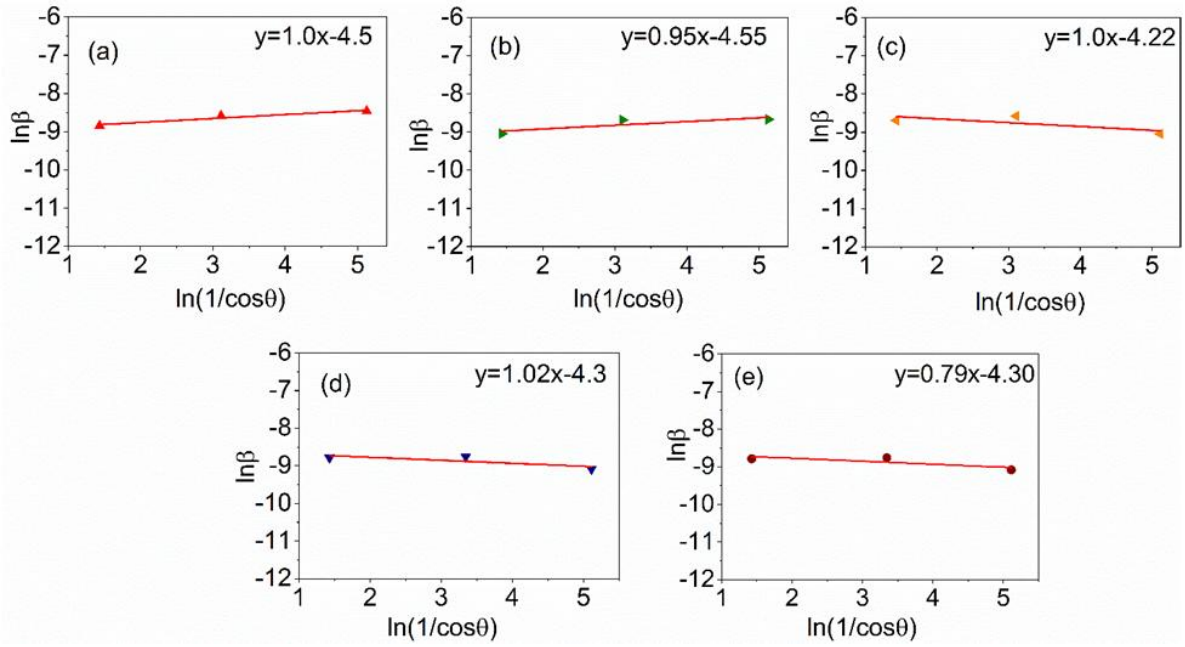


Figure S1: Determination of crystallite size and strain of $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles using Modified Scherer method

The Scherrer's method explains the effect of crystallite size on the XRD peak broadening and it does not consider the contribution of microstrain present in the lattice. In contrast, the Williamson-Hall (W-H) method considers the contribution of both crystallite size and lattice strain (ε) in peak broadening. Thus, the total broadening (β) of XRD peak can be expressed as [19-28]

$$\beta = \beta_{crystallite\ size} + \beta_{strain} \qquad \text{(S1)}$$

The intrinsic strain can be calculated by using the following relation

$$\beta_{strain} = 4\varepsilon \tan\theta \qquad \text{(S2)}$$

Substituting Eq. (3) and Eq. (S2) in Eq. (S1)

$$\beta = \frac{k\lambda}{D\ cos\theta} + 4\varepsilon tan\theta \qquad \text{(S3)}$$

Rearranging the Eq (S3),

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon Sin\theta \qquad \text{(S4)}$$

Eq. S4 shows W-H equation and also known as the uniform deformation model (UDM). By plotting a graph between $\beta\cos\theta$ versus $4\sin\theta$ and applying the linear fit, the vales of crystallite size and strain are determined (see Fig. S2). The slope of linear fit provides the strain while

crystallite size can be calculated from *y*-intercept of the linear fit. The results of crystallite size and strain are given in Table 2.

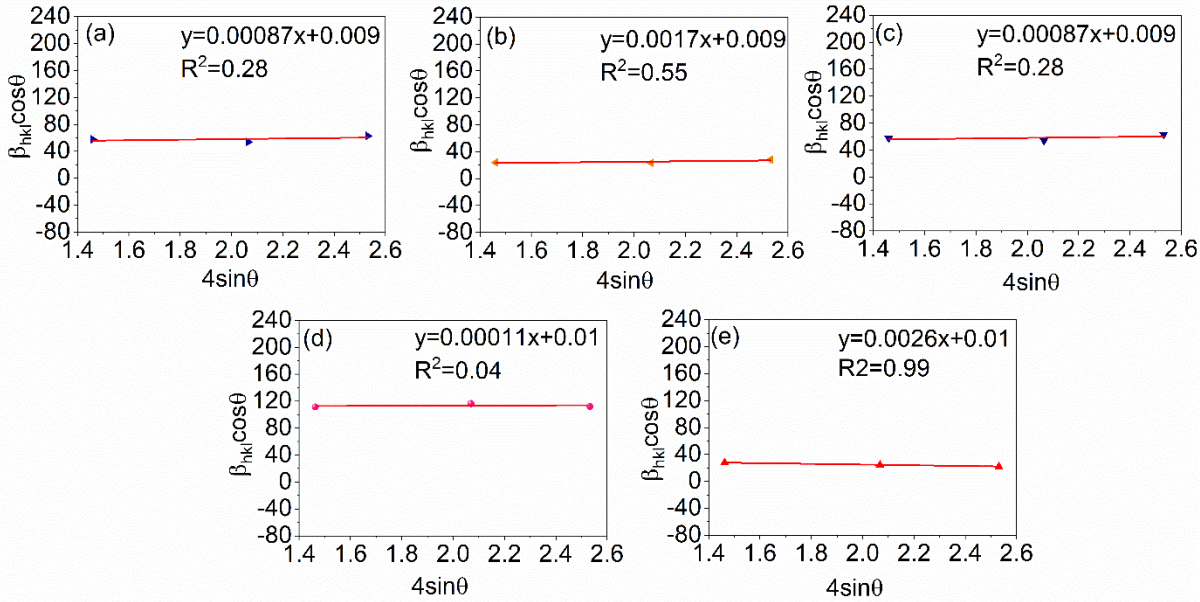


Figure S2: Determination of crystallite size and strain of $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles using uniform deformation model (UDM)

In UDM model, the strain is considered to be uniform in all directions in lattice. However, this assumption is not more accurate for all crystalline materials. An alternative XRD model, known as uniform stress deformation model (USDM), takes into account the uniform lattice strain by incorporating the effect of stress along all crystallographic directions within lattice. According to Hooke's law, the stress (σ) is directly proportional to strain of material and can be represented as $\sigma = \varepsilon Y$, where *Y* is the Young's modulus. By considering the contribution of uniform stress deformation, Eq. (S4) can be modified as [20]

$$\beta \cos\theta = \frac{k\lambda}{D} + \frac{4\sigma Sin\theta}{Y} \qquad (S5)$$

The uniform stress and crystallite size of NPs is investigated by plotting a graph between $\beta \cos\theta$ and $\frac{4\sin\theta}{Y}$ (see Fig. S3). Here, *Y* is calculated for cubic structure of doped MgO NPs by considering their elastic compliances S_{ij} (see Eq. S6) [17,22]

$$\frac{1}{Y} = S_{11} - 2[(S_{11} - S_{12}) - \frac{1}{2}S_{44}][\frac{h^2k^2+k^2l^2+l^2h^2}{(h^2+k^2+l^2)}] \qquad (S6)$$

where S_{11}, S_{12}, S_{44} are elastic compliances and can be calculated using the stiffness constant C_{11}, C_{12} and C_{44} (see Eqs. S7-S9)

$$S_{11} = \frac{C_{11}+C_{12}}{(C_{11}-C_{12})(C_{11}+2C_{12})} \qquad (S7)$$

$$S_{12} = \frac{-C_{12}}{(C_{11}-C_{12})(C_{11}+2C_{12})} \qquad \text{(S8)}$$

$$S_{44} = \frac{1}{C_{44}} \qquad \text{(S9)}$$

The values of C_{11}, C_{12} and C_{44} for cubic structure are 332, 96, and 136, respectively [21,24]. Using Eqs. S7-S9, the Young's modulus (Y) values are determined as 220.4, 197.9 and 68.31 MPa for the (111), (200), (220) planes, respectively. The average value of Y is calculated to be approximately 162.2 MPa. In USDM, the slope of the linear fit to data points relates to the value of stress, while the intercept gives the average crystallite size, as shown in Fig. S3 and Table 2.

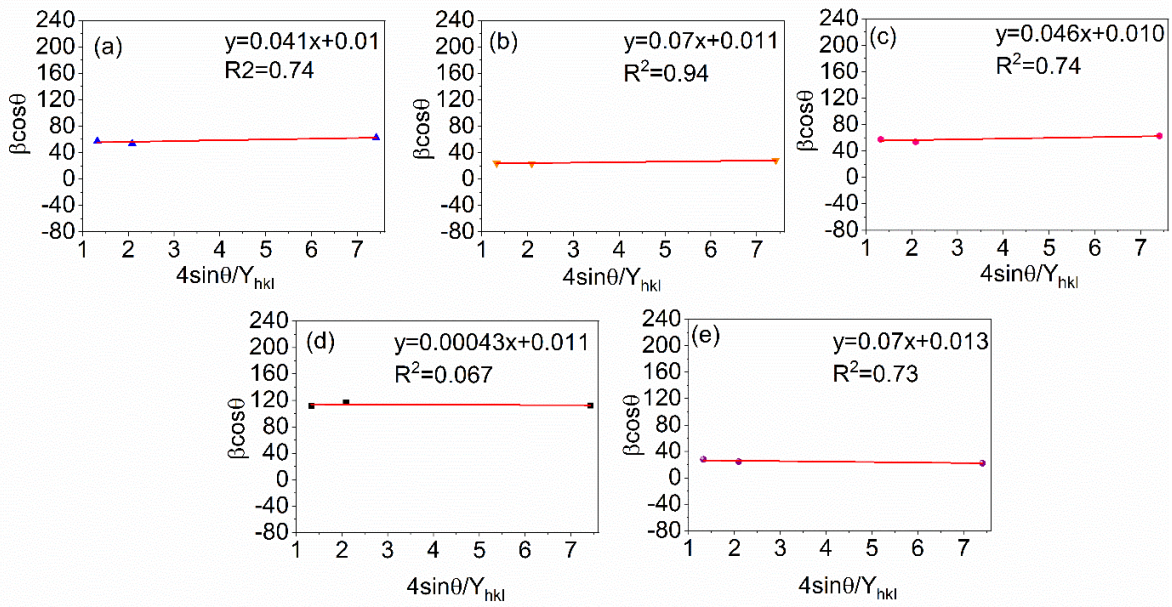


Figure S3: Determination of crystallite size and strain of $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles using uniform stress deformation model (USDM)

However, the assumption of homogeneity, isotropic nature and a linear relationship between stress and strain do not establish in all materials, particularly due to structural defects or presence of impurity agglomerates. In such cases, the uniform deformation energy density model (UDEDM) is used to estimate both the crystallite size and strain by considering the anisotropic nature of materials. This model uses the energy density defined as strain energy per unit volume. According to Hooke's law, the energy density (u) can be expressed as [16]

$$u = \varepsilon^2 \frac{Y}{2} \qquad \text{(S10)}$$

The relation between strain and energy density can be expressed as

$$\beta cos\theta = \frac{k\lambda}{D} + (4\sin\theta(\frac{2u}{Y})^{1/2}) \qquad \text{(S11)}$$

The deformation energy density is calculated by plotting a graph between $\beta\cos\theta$ and $4\sin\theta(\frac{2}{Y})^{1/2}$, as shown in Fig. S4. The slope of the linear fit to data points provides the strain energy, while the intercept is used to determine the crystallite size. The calculated values of crystallite size and lattice strain, obtained using Eq. S11, are given in Table 2.

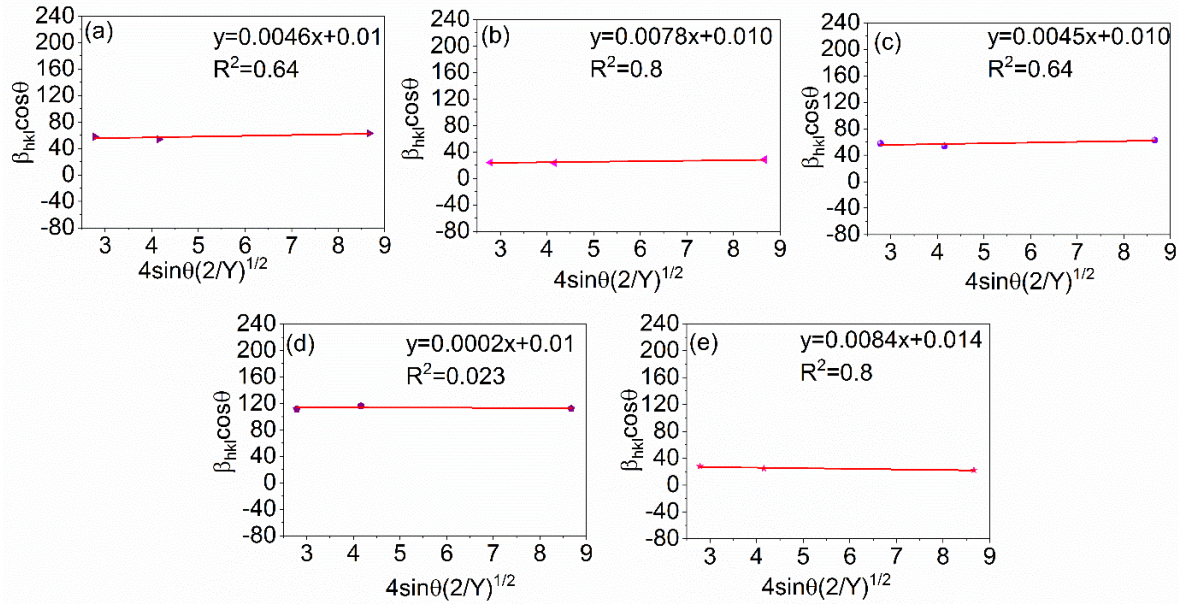


Figure S4: Determination of crystallite size and strain of $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles using uniform deformation energy density model (UDEDM)

The W-H plot confirms the broadening of diffraction peaks as a function of 2θ due to the contribution of both strain-induced and size-induced effects. Another method used to deconvolute these effects is known as Size-Strain Plot (SSP), which assumes that the XRD peak profile is a sum of Lorentzian and Gaussian functions [18]. Thus, the total peak broadening in the SSP models can be expressed as

$$\beta = \beta_G + \beta_L \qquad \text{(S12)}$$

where β_G and β_L are the Gaussian and Lorentz components of the peak broadening, respectively.

The SSP model emphasizes the low-angle reflections, thus it provides comparatively more accurate results for the materials exhibiting isotropic broadening [23]. According to SSP, the crystallite size and strain are determined using the following expression

$$(d\beta cos\theta)^2 = \frac{k\lambda}{D}(d^2\beta cos\theta) + \frac{\varepsilon^2}{4} \qquad \text{(S13)}$$

Figure S5 shows the plots of SSP model for $Co_{0.05}Ni_xMg_{0.95-x}O$ NPs. The slope of the linear fit provides the average crystallite size, while the intercept shows the lattice strain. The calculated results of crystallite size and strain are mentioned in Table 2.

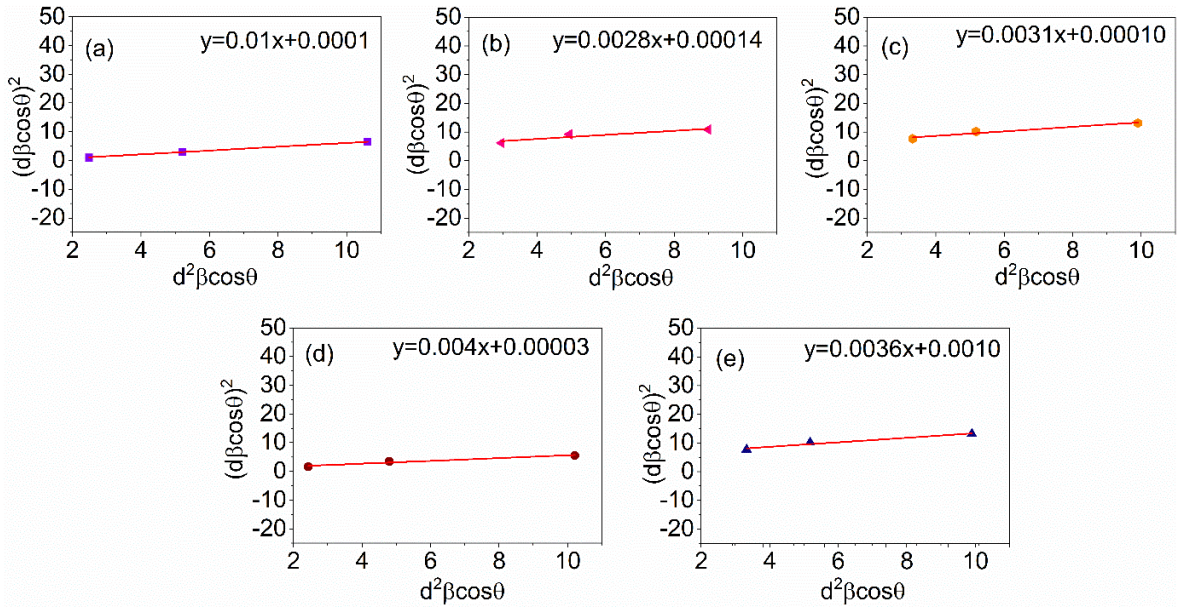


Figure S5: Determination of crystallite size and strain of $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles using Size Strain plot (SSP)

S2. FTIR Spectra of MgO Nanoparticles

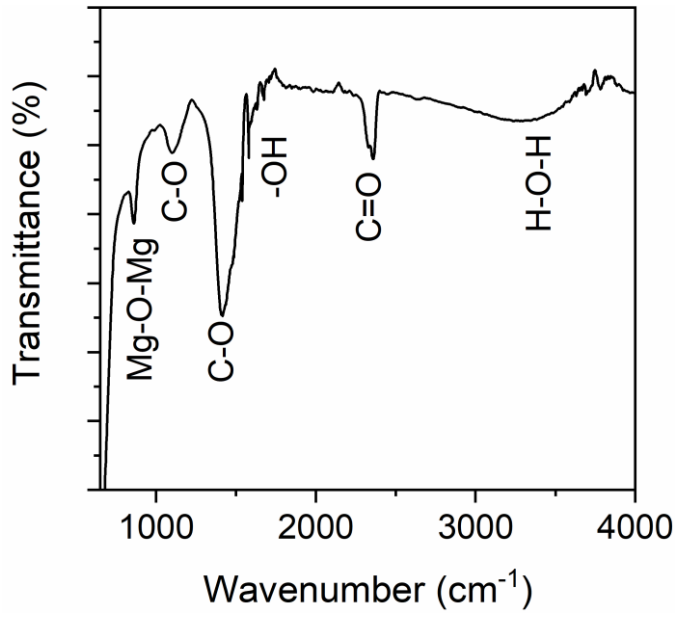


Figure S6: FTIR pattern of MgO nanoparticles

S3. Determination of Optical Bandgap Energies of $Co_{0.05}Ni_xMg_{0.95-x}O$ Nanoparticles

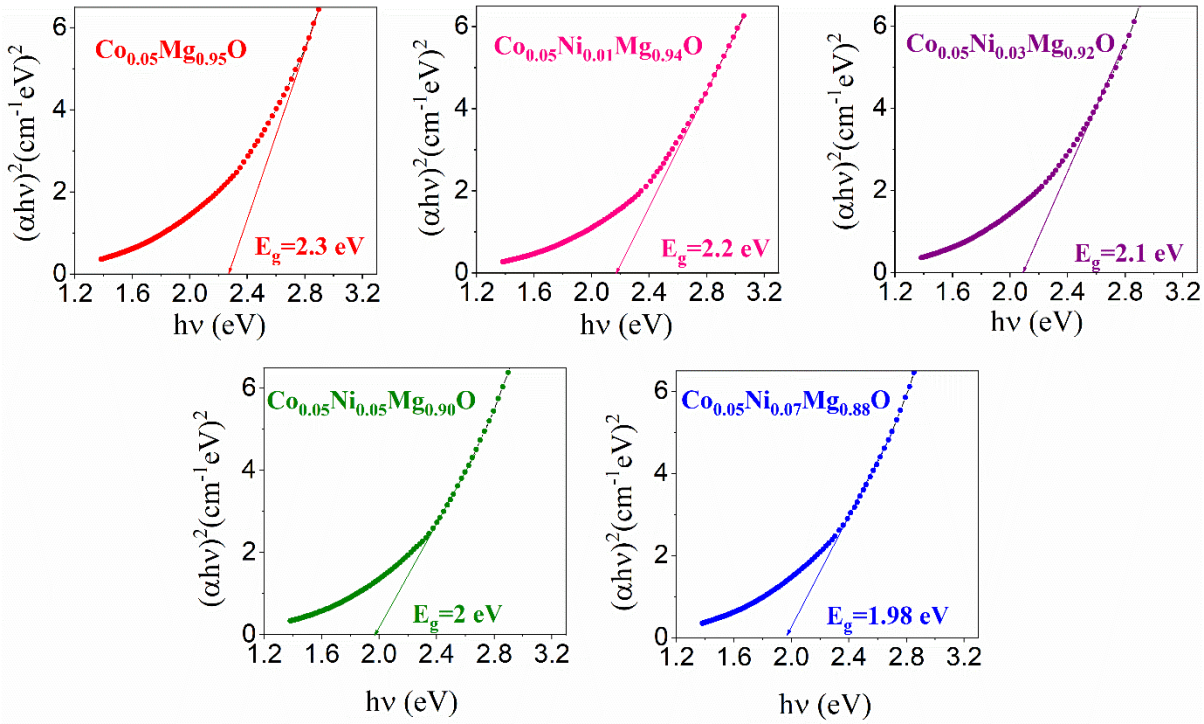


Figure S7: Determination of optical bandgap energy using Tauc relation for direct bandgap.

S4. Photocatalytic Activity and Degradation Efficiency Under Sunlight

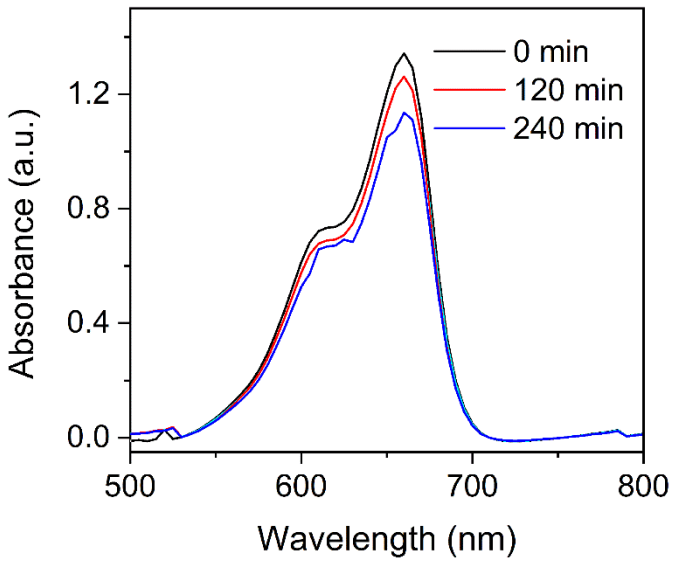


Figure S8: Optical absorbance of Methylene blue (MB) dye without $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles under the sunlight exposure of 0, 120 and 240 min. The optical absorbance spectrum at 0 min is regarded as reference sample. The MB dye show up to 15% degradation efficiency in the absence of $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles with sunlight exposure of 240 min.

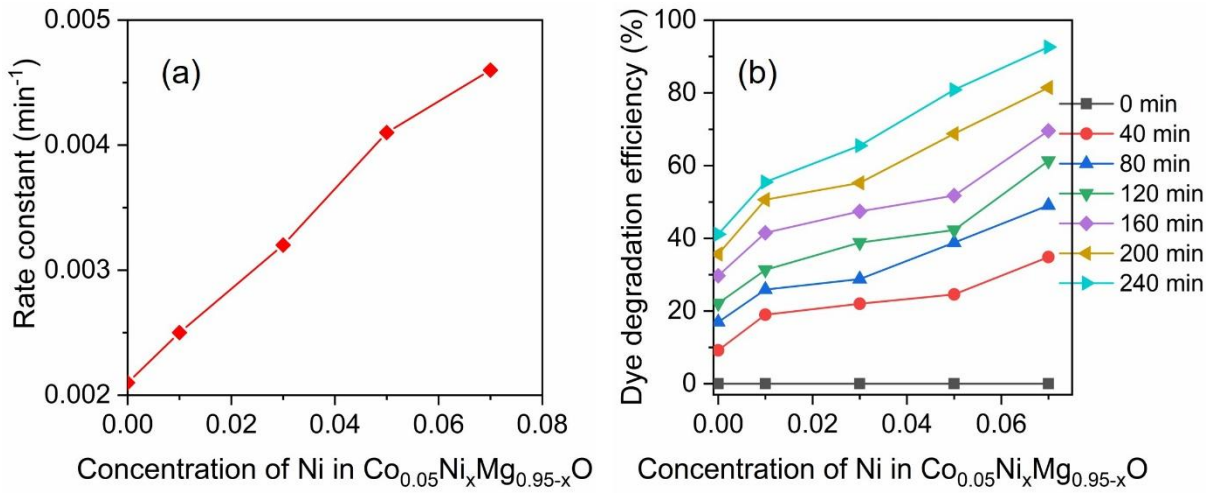


Figure S9: The variation in (a) rate constant and (b) dye degradation efficiency (%) of $Co_{0.05}Ni_xMg_{0.95-x}O$ nanoparticles under the sunlight exposure.